



reference electrode, a platinum wire as the auxiliary electrode and carbon paste electrode modified with zeolite as the working electrode were used.

Results and discussion:

In order to further clarify the electrochemical oxidation mechanism of ethanol on the electrode, the effect of ethanol concentrations on the cyclic voltammetric responses of this electrode was investigated (Fig.1A). As shown at Fig 1B, in low concentration of ethanol, there are two anodic peaks, Fig 1B shows that when ethanol concentration increases, the current density of the peak a₂ increases Significantly, while the peak a₁ decreases and even disappears.



Fig. 1-(A) Cyclic voltammograms of Ni/NiZSM-5/CPE in the presence of various concentrations of ethanol in 0.1 M NaOH solution at scan rate 20 mVs⁻¹. (B) Zoomed voltammograms of (b), (d), and (k) from main panel of (A).

Fig. 2, shows chronoamperogram of ethanol at Ni/NiZSM-5/CPE. We can simply calculate the value of rate constant for a given concentration of substrate from the slope of the I_C/I_L vs $t^{1/2}$ plot (Fig. 2A). The mean value for rate constant was found to be 1.4×10^5 cm³mol⁻¹s⁻¹.



Fig. 2- Chronoamperograms obtained at the Ni/NiZSM-5/CPE in the absence (a) and presence of (b) 0.003, (c) 0.008, (d) 0.06, and (e) 0.1 M OF ethanol in 0.1 M NaOH solution. Inset (A) dependence of I_C/I_L on $t^{1/2}$, derived from the data of chronoamperograms of (a) and (e) in the main panel.





Conclusion:

In this paper, Ni/NiZSM-5/CPE was prepared by immersion of a NiZSM-modified carbon paste electrode in 1 M Ni solution. Relatively, a good dependence of electrocatalytic current on ethanol concentration was observed. Finally, using chronoamperometric method, the catalytic rate constant for ethanol was estimated.

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Investigation of electrochemical properties of hetrodimeric nanoparticles (Fe₃O₄-Ag, Fe₂O₃-Ag and FeOOH-Ag) for determination of glucose

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Key words: Hetrodimeric nanoparticles, Modified electrode, Glucose.

Introduction:

Recently, it was found that a group of organic molecules having similar structures can be separated from each other according to their adsorption strengths onto the surfaces of metal oxides [1]. Iron oxides and iron hydroxides have ability to adsorb glucose in aqueous solution. It seems that glucose binds with mineral surfaces through hydrogen bonding [2]. Electrocatalytic oxidation of glucose has a crucial role in measuring blood sugar by blood glucose sensors. Metal electrodes (Cu, Co, Cd, Au, Ag, etc.) can be used as an electrocatalyst for oxidation of glucose. Ag electrodes have a high sensitivity in glucose oxidation [3]. Therefore, it seems that the modified electrodes containing Ag nanoparticles along with metal oxides might be more sensitive to glucose than the Ag electrodes.

Materials and methods:

In this study, iron oxides (Fe₃O₄, Fe₂O₃) nanoparticles were prepared by Co-precipitation from chloride salts of Fe (II) and Fe(III) in alkaline media. Iron hydroxides (FeOOH) nanoparticles were prepared from FeCl₃ solution at 60 °C for 24 hour. Then appropriate amount of Fe₃O₄, Fe₂O₃ or FeOOH together with oxalic acid and polyvinyl pyrolidone was dissolved in ethylene glycol. The reaction vessel was irradiated in microwave cavity for about 1 min. Iron oxides and iron hydroxide used as a substrate for deposition of silver nanoparticles. The synthesized heterodimeric nanoparticles (Fe₃O₄-Ag, Fe₂O₃-Ag and FeOOH-Ag) were used as modifier materials in preparation of the modified carbon paste electrodes. The prepared electrodes showed high affinity towards glucose. The hetrodimeric nanoparticles were physically characterized by UV-Vis spectrophotometry, scanning electron





microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis.

Results and discussions:

1-Electrochemical properties of the modified electrodes

Fig. 1 shows the cyclic voltammetries (CVs) of the bare carbon paste electrodes, modified carbon paste electrodes with Ag nanoparticles (Fig.1a) and heterodimeric nanoparticles (Fig. 1b) in the absence and presence of glucose. The cyclic voltammery was performed in NaOH electrolyte (0.1 M) in the potential range of -0.25 - +0.8 V (versus Ag/AgCl) and scan rate of 10 mVs⁻¹.



Figure 1.(a) The CVs of Ag modified electrode in the absence (-) and presence of 5mM glucose(...)(b) The CVs of heterodimeric modified electrode in 0.1M NaOH and 5mM glucose at a scan rate of 10mVs⁻¹.

In the potential sweep from -0.25 to +0.8 V on the surface of the Ag modified electrode, two peaks appear. The peaks relate to the oxidation of Ag to Ag₂O and Ag₂O to AgO, respectively. Similarly, during a reverse scan (+0.8 to -0.25), two peaks appear. The first peak relates to the reduction of AgO to Ag₂O and the second peak relates to the reduction of Ag₂O to Ag₂O to Ag. By adding glucose (5mM) to the solution, the second oxidation peak increased and two peaks in reverse scan was appeared in the range of +0.7 to +0.4 V(Fig. 1a). As shown in Fig.1b, in heterodimeric modified electrodes, Ag is an electroactive species and iron oxides or iron hydroxides nanoparticles, are as an adsorbent for glucose oxidation. Electrochemical behavior of hetrodimeric nanoparticles modified electrodes is similar to the Ag nanoparticles modified electrode, but in heterodimeric modified electrodes, the peak relates to conversion of Ag₂O to AgO contract with reduction peak of Fe³⁺ to Fe²⁺. Comparing to the Ag



nanoparticles modified electrode, in heterodimeric modified electrodes, the oxidation peak of glucose appears at lower concentration. Short electrode preparation steps and easy separation of Fe_3O_4 -Ag nanoparticles are advantages of the developed electrodes for optimization process and amperometric study. Investigating the effect of scan rate showed that by increasing the rate of scan, these two peaks merged in a single peak, confirming the low electron transfer in glucose oxidation. At higher scan rate, the capability of more oxidation of glucose intermediates was low. The glucose oxidation peak current (+0.63 V) in reverse scan was proportional to the second root of scan rate. By increasing the scan rate, the peak potential shifted positively, demonstrated that the glucose oxidation was a diffusion controlled irreversible process.

2-Amperometric determination of glucose using the Fe₃O₄-Ag nanoparticle modified electrode:

Determination of glucose by amperometric technique was performed using the Fe₃O₄-Ag nanoparticle modified electrode at potential of 0.63 V in NaOH electrolyte (Fig. 2). The linear response in the concentration range of 8.0×10^{-4} - 1.0×10^{-2} M glucose was obtained. The effect of some interfering species on the determination of glucose was examined and it was found that the developed procedure was suitable in determination of glucose in the human serum.



Figure.2 The amperometric determination of glucose using Fe_3O_4 -Ag modified electrode in 0.1M NaOH. Applied potential=0.63V. The concentration of glucose were added from 8.0×10^{-4} to 1.0×10^{-2} M

Conclusion:

In summary, we used iron oxide and hydroxides nanoparticles as a substrate for adsorption of glucose. Ag nanoparticles, as an electrocatalyst, were utilized for oxidation of glucose. The results





showed that the developed nonenzymatic sensors based on hetrodimeric modified electrodes are useful for glucose sensing. The electrode modified by Fe₃O₄-Ag nanoparticles by amperometric method was used for determination of glucose in the human serum.

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The use of chemically modified carbon paste electrode by deferiprone to determine trace amount of copper in water resources

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Key words: Copper, Chemically modified carbon paste electrode, Deferiprone

Introduction:

Copper is an important element in biological systems. It is an essential micronutrient present in at least thirty enzymes. On the other hand, it is toxic above a certain concentration. The World Health Organization (WHO) and the European Water Quality Directive recommends that the concentration in drinking water does not to exceed 2 mg/l[1]. Ordinary electrochemical solid electrodes have been developed for copper determination, such as modified carbon paste electrodes[2], modified conducting copolymer electrodes[3], selfassembled monolayer modified gold electrodes[4]. But the detection limits of those chemically modified electrodes were not low enough to detect trace level of copper in water samples[5]. Deferiprone is a small neutral water-soluble molecule with a molecular weight of 139 Da, that has a high affinity for iron ions, but also copper can form strong complexes with[6, 7]. On the basis of our knowledge, there isn't any report regarding the use of deferiprone in the electroanalysis of copper. Because, new alternative electrodes are highly desired to meet the growing demands of determination of copper in environmental monitoring and water research, the goal of this study was to develop a chemically modified carbon paste electrode with deferiprone to determine copper in water samples.

Materials and methods:

Unmodified carbon paste was prepared by hand mixing of 0.7 g of reagent-grade graphite powder and 0.3 g mineral oil with a mortar and pestle. Chemically modified carbon paste electrode (CMCPE) was prepared by thorough mixing different amount of deferiprone with





appropriate amount of graphite powder, and mineral oil. Both unmodified and modified pastes were packed into 1 ml polyethylene syringes (5 mm diameter). After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrochemical cell can be represented as follows: Ag, AgCl(s), KCl (3 M) || sample solution | carbon paste electrode

Cyclic voltammograms of standard solutions of copper 1mM were obtained in the potential window of -1.5 V to 1.5 V to optimize parameters like electrode composition, type of supporting electrolyte, pH, deposition potential, and deposition time. To determine copper quantitatively, differential pulse voltammetry was used at optimum condition. Calibration graph was drawn by plotting the current, I, versus the copper ion concentration. Method was validated regarding linearity, precision, accuracy, LOD, LOQ and selectivity. The developed method was applied for the analysis of real water samples of various sources. The results were compared with those obtained for the same samples analyzed with atomic absorption spectrometry.

Apparatus:

Voltammeter, Metrohm 757 VA Computrace (Herisau, Switzerland). The triple-electrode system consisted of a working electrode, modified carbon past electrode, a reference Ag/AgCl potassium chloride (3M) and auxiliary platinum electrode. pH meter, Metrohm (Herisau, Switzerland).

Results and discussion:

The best composition of working electrode was obtained to be 695mg graphite, 5 mg deferiprone and 300 mg mineral oil in potassium chloride 0.1 M as supporting electrolyte. Maximum electrode response was seen at pH 4, deposition time of 90 s, and deposition potential of -0.8 V. Differential pulse cathodic adsorptive voltammetry was used for quantitative analysis. Results showed that the method was linear in the concentration range of 50 to 400 ng/ml with the equation of Ip=3.15C+0.070 - (r=0.9995). RSD% of the repeated



measurements (n=3) were lower than 4.0 and 5.0% for interday and intraday precision, respectively. Error% of the method for the whole concentration range was less than 4.0%. LOD and LOQ of the method using SD of the 20 blank samples were calculated to be 80 and 90 ng/ml, respectively. The MCPE with MNCA was successfully applied for determination of copper in real samples of water from various sources.

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Copper determination in drinking water by differential pulse voltammetry at a modified carbon paste electrode with magnetic nanoparticles almond shell

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Key words: Copper, Modified carbon paste electrode, Magnetic nanoparticles, Almond shell

Introduction:

Copper (Cu) is an essential trace element, which is an integral part of many important enzymes involved in a number of varied vital biological processes. However in high levels, it becomes harmful, in particularly it is hepatotoxic. Water pollution by heavy metals is causing serious ecological problems[1] in the world, therefore, the determination of heavy metals such as copper in the environmental samples is needful today, and requires analytical techniques exhibiting with low detection limits for this toxic element[2]. Different methods have been used for the determination of copper, such as spectrophotometry[3], electrothermal atomic absorption spectrometry [4], flame atomic absorption spectrometry [5], inductively coupled plasma-mass spectrometry, and inductively coupled plasma optical emission spectrometry, microwave-induced plasma (MIP)[6]. Among these methods, electroanalytical methods are of great importance for the analysis of copper including very small amount of sample needed, no preliminary complex sample preparation methods, and inexpensive instrument for the analysis, selectivity and sensitivity of the voltammetric methods[7]. The main aim of this study was to develop a simple voltammetric method on the basis of a modified carbon paste electrode (MCPE) with magnetic nanoparticles coupled with carbon prepared from almond shell (MNCA).

Materials and methods:

Ferrous sulfate, ferric chloride, sodium hydroxide, copper chloride, potassium chloride, activated carbon, almond nutshell, copper wire used in this study was purchased from local





market made by Merck, Germany. Magnetic nanoparticles were prepared by chemical precipitation of mixed trivalent and divalent iron ions in alkaline medium at relatively high temperature (80°C)[8]. Carbon was prepared by ashing almond nutshell in an oven at 800 °C. The ash was milled in a mortar and mixed with MN to prepare MNCA. MCPE was prepared by mixing graphite, MNCA and mineral oil to obtain a paste and then was inserted into a syringe tip. A copper wire was immersed into the paste and was used as working electrode. Cyclic voltammograms of standard solutions of copper 1mM were obtained in the potential window of -1.5 V to 1.5 V to optimize parameters like electrode composition, type of supporting electrolyte, pH, deposition potential, and deposition time. To determine copper quantitatively, differential pulse voltammetry was used at optimum condition. Method was validated regarding linearity, precision, accuracy, LOD, LOQ and selectivity. The developed method was applied for the analysis of real water samples of various sources. The results were compared with those obtained for the same samples analyzed by atomic absorption spectrometry.

Apparatus:

Voltammeter, Metrohm 757 VA Computrace (Herisau, Switzerland). The triple-electrode system consisted of a working electrode, modified carbon past electrode, a reference Ag/AgCl potassium chloride (3M) and auxiliary platinum electrode. pH meter, Metrohm (Herisau, Switzerland).

Results and discussion:

The best composition of working electrode was obtained to be 695mg graphite, 5 mg MNCA and 300 mg mineral oil in potassium chloride 0.1 M as supporting electrolyte. Maximum electrode response was seen at pH 3, deposition time of 90 s, and deposition potential of -0.7 V. Differential pulse cathodic adsorptive voltammetry was used for quantitative analysis. Results showed that the method was linear in the concentration range of 50 to 300 ng/ml with the equation of Ip=33.92C-1.18 (r =0.996). RSD% of the repeated measurements (n=3) were lower than 4 and 6 % for inter-day and intra-day precision, respectively. Error% of the method for the whole concentration range was less than 5.5%. LOD and LOQ of the method using SD of the 20 blank samples were calculated to be 46 and 50 ng/ml, respectively. The





MCPE with MNCA was successfully applied for determination of copper in real samples of water from various sources.

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Nanostructure Construction of Au-MPA-Zr(IV)-[DTPA-Fe(III)] Based on Ex-Situ Method Characterized by CV, DPV and EIS

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Key words: Diethylenetriaminepentaacetic acid (DTPA), Zirconium(IV) ion glue, , Self-assembled monolayers, nanostructure.

Introduction:

Self-assembled monolayers (SAMs) that formed on gold surface, have high flexibility for modification at the single molecular levels and nanometer scale, In SAM formation, equilibrium processes that are highly kinetically limited exist between species bound to the surface and free adsorbates (in the solution phase, additional energetic factors such as the enthalpy and entropy of salvation play critical roles in the dynamics of adsorption) [1].

One of the most important of organic compounds that able to capture metal ion is aminopolycarboxylic acids (APCAs), from which diethylenetriaminepentaacetic acid (DTPA) is of special interest in this category in therapy and diagnosis of tumors. These metal complexes are stable and restrict the metal ions from playing their normal chemical role in solution, and thus, help to fix them on solid surfaces.

In this study, DTPA, as a chelating agents, is immobilized on gold thiol SAM via Zr(IV) ion glue by in-situ and ex-situ methods. The immobilization was assisted by using complexed form of DTPA with Fe(III) [Fe(III)-DTPA]. The results obtained by CV, DPV and EIS showed that Fe(III)-DTPA was immobilized successfully on gold electrode.

Materials and methods:

Diethylenetriaminepentaacetic acid (DTPA), 3-mercaptopropionic acid (MPA), ZrCl₄, Fe(NO₃)₃.9H₂O, was purchased from commercial (Merck, Fluka, Sigma-Aldrich) company and used without purification. The electrochemical measurements including cyclic and differential pulse voltammetry (CV and DPV), and electrochemical impedance spectroscopy





(EIS) were carried out on Potentiostat/Galvanostat Autolab 30. Electrochemical characterization was done by electrochemical probes like PBQ and $[Fe(CN)_6]^{3-}$ in two pHs.

Results and discussions:

This electrode can modify with two methods. Results that obtained from CV and DPV confirmed that in-situ modification cause one or more of these arms immobilize via covalance-coordinance bond on the top of the Au-MPA-Zr(IV).

To our the best knowledge, Fe-DTPA(III) is a coordinated complex using four acetate and three amines groups of DTPA, captured Fe(III) ion and the fifth carboxylic group, is left free [2], enables the complexed to be fixed via this group and forms specific nanostructure on the top of the Au-MPA-Zr(IV) electrode. This structure of immobilized DTPA via ex-situ method is very regular alignment and stable on the surface.



Fig. 1. Continuous DPV obtained from the Au-MPA-Zr(IV)-[DTPA-Fe (III)] prepared by in-situ and exsitu methods in absence of probe in acetate solution pH 3.0, scan rate 100 mV/s.

Furthermore, the measurements allowed determining a surface pK_a of 6.1±0.1, which in turn, recognizes the charge state of the surface at any pH. The electrochemical data that extracted from the voltammetry and EIS measurements are presented and discussed from which the new nanostructure is characterized.

Conclusion:

In this work, Au-MPA-Zr(IV) electrode is modified with [DTPA-Fe(III)] by ex-situ method, that first complexation of iron with DTPA is done in two pHs and then this complex is





immobilized on surface of Au-MPA-Zr(IV) electrode. We observed two different behaviors. The effect of scan rate and solution pH is investigated by electrochemical methods.

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Application of novel voltammetric nano-sensor based on carbon nanotubes paste electrode determination of hydroxylamine

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Key words: Voltammetry, Electrochemical investigation, Hydroxylamine, Phenol, Carbon nanotubes, p-Chloranil

Introduction:

The quantitative determination of hydroxylamine is very important both in studies of biological processes and for industrial purposes. It has been confirmed that hydroxylamine is produced during the reduction of nitrates by E. coli and Torula yeast [1].

Phenol is one of the environmental pollutants. Phenol and its vapors are corrosive to the eyes, the skin, and the respiratory tract [2]. Therefore, determination of this compound is very important.

Carbon nanotubes (CNTs) are currently in the forefront of materials research. They are recognized as a new class of materials that have had a profound impact on a wide range of applications [3].

As yet, based on our knowledge, no paper has been reported on the simultaneous determination of HX pulse PL using electrochemical methods. In the present work, we describe preparation of a new electrode composed of multiwall carbon nanotubes paste electrode modified with p-chloranil and investigate its performance for the electrocatalytic determination of HX in aqueous solutions. We also evaluate the analytical performance of the modified electrode for simultaneous determination of HX and PL.

Materials and methods:

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. Cyclic





voltammetry (CV), impedance spectroscopy, and square wave voltammetry were performed in an analytical system, Autolab with PGSTAT 302N (Eco Chemie, the Netherlands). The system was run on a PC using GPES and FRA 4.9 software.

Results and discussion:

Results show, the anodic peak potential for HX oxidation at p-CAMCNTPE and at p-CAMCPE was about 110 mV, while at CNTPE, the peak potential was about 1050 mV. At the unmodified CPE, the peak potential of HX was about 1100 mV. From these results, it was concluded that the best electrocatalytic effect for HX oxidation was observed at p-CAMCNTPE. For example, the results show that the peak potential of HX oxidation at p-CAMCNTPE shifted by about 990 and 940 mV toward less positive values when compared with CNTPE and unmodified CPE, respectively. However, p-CAMCNTPE shows bigger anodic peak current for the oxidation of HX compared to p-CAMCPE, indicating that the combination of MWCNTs and the mediator (p-chloranil) has significantly improved the performance of the electrode toward HX oxidation.

Conclusion:

In the present study, carbon-paste electrode modified with *p*-chloranil and CNTs was used for the determination of HX. The CV, EIS and SWV investigations showed effective electrocatalytic activity of the modified electrode in lowering the anodic over potential for the oxidation of HX.

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Influence of sodium dodecyl sulfate micelles on the Palladium Nanoparticle formation on GNS for oxygen reduction reaction

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Key words: Pd deposition, SDS, graphene, ORR

Introduction:

Graphene (G) is a two-dimensional single-layer sheet of graphite with p-electrons fully delocalized on the graphitic plane. It is highly conductive and mechanically strong and has been found for molecular electronic device, energy storage, fuel cell and catalytic applications. It has been shown in the Pt (or Pd)-based nanoparticle (NP) catalysts grown on G for electrocatalytic reactions and in the activation of Co_3O_4 and MoS_2 NPs by G for oxygen reduction reaction (ORR) in alkaline media and for hydrogen evolution in H₂SO₄ solution. In these studies, the catalyst NPs were grown directly on the G surface to maximize G–NP contact and to achieve the desired catalysis enhancement. The objective of our work is to use the electrodeposition method to disperse small palladium particles on graphene sheets, which was previously electrosynthesised on a glassy carbon electrode from an aqueous acid solution[1-3].

Material and methods:

Electrochemical reduction of graphene was performed on a GC electrode or carbon paper by CV technique at 50 mVs⁻¹ for 100 cycles in mixture containing graphite (Merck) (5mg/ml), SDS and water .Pd particles were electrodeposited on the surface of GC or graphene electrodes from 6mM Pd⁺²and different concentration of SDS solution with cyclic potential polarization (-0.25-0.65 V) at 50 mVs⁻¹ for 25 cycles[4].

Result and Discussion:

The effect of surfactant concentration on the loading and size of the palladium nanoparticles was studied by employing constant potentials and was studied on the graphen preparation.





When we use anionic emulsifier such as sodium dodecyl sulfate (SDS) then the interface is negatively charged. The metal cations of their salts will be preferentially located close to this interface, whereas the hydrophilic co-reactants prefer to be located in a region away from the interface. This can lead to the separation of reactants within the larger microdroplet. This separation factor can depress or inhibit the rate of reaction.

Conclusion:

In this work, a green and fast electrochemical approach (CV in high negative potential) to the synthesis of graphene nanosheets is reported using graphite powder in 14mM SDS surfactant as precursors. Graphene is successfully characterized by employing SEM and CVs techniques.then Pd particles is deposited on the graphene surface in before and after CMC of SDS solutions. Finally ORR is studied by LSV, CV, chronoamperomettry and SEM characterization.

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The effects of electrodeposition methods on the pseudocapacitive properties of nanostructured Manganese dioxide

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Key words: Nanostructure, Electrodeposition, Manganese dioxide, Pseudocapacitor

Introduction:

Pseudocapacitors are electrochemical energy storage device with higher power density than batteries and higher energy density than ordinary capacitors, which utilize a faradaic process [1]. So far, several materials have been studied as the pseudocapacitor electrodes. Amongst all these materials, manganese oxide has been conceived as a promising supercapacitive material because of its low cost, high electrochemical activity and more friendly environmental nature [2]. It is well known that the pseudo-capacitive reaction of MnO_2 is a surface reaction, only the surface or a very thin surface layer of the oxide can participate in this pseudo-capacitive reaction. Along with different methods for making manganese oxide, electrochemical methods have several advantages like the better attachment to the electrode surface, simplicity, having a low cost and so on. The source of MnO_2 in the most reports is a salt of Mn^{+2} and a few reports exist for electrodeposition of MnO_2 from KMnO₄. In this study, we prepared nanostructured manganese oxide by potentiostatic, galvanostatic and potentiodynamic electrodeposition.

Materials and methods:

KMnO₄, Na₂SO₄ purchased from Merck Company and all solutions prepared using deionized water. Electrodeposition took place on the surface of a piece of commercial stainless steel from a solution of 0.2M KMnO₄, Only for galvanostatic case cetyltrimethylamonium bromide, CTAB, as a cationic surfactant with different concentrations was added to the electrodeposition bath. The applied potential in potentiostatic method was 0.2V vs. Ag/AgCl, the applied current density was -0.001 Acm⁻² in galvanostatic electrodeposition and potential





range was between 1.1V and -0.1V vs. Ag/AgCl and different scan rates applied for potentiodynamic method. The morphology of deposited materials was studied by Atomic Force Microscopy, AFM. The capacitive behaviors of as-deposited materials were investigated in a solution of 0.1M Na₂SO₄ using cyclic voltammetry, glavanostatic charge/discharge curves and electrochemical impedance spectroscopy.

Apparatus:

All electrochemical experiments were carried out via a standard three electrodes cell containing of an Ag/AgCl electrode, a platinum grid and a MnO₂-coated stainless steel as reference, auxiliary and working electrodes, respectively and using a Solartron Electrochemical interface SI1287 and Solartron Phase Gain Analyzer SI 1260. Surface morphological studies were carried out with scanning probe micrographs, obtained with a Dual Scope SPM (DME, Denmark).

Results and discussion:

Our studies showed that as-deposited MnO_2 is amorphous and has a nanostructured morphology which is depend to electrodeposition conditions. Although using CTAB in galvanostatic electrodeposition bath causes increasing the surface area of deposited materials but it decreases the capacity of nanostructured MnO_2 due to increasing in the film resistance. The same behavior was observed for increasing in scan rate during potentiodynamic method.

Conclusion:

Our studies depicted that nanostructured MnO_2 has a capacitance around 125 F/g in a weak electrolyte like Na_2SO_4 with a low concentration prepared by potentiodynamic method at a potential scan rate of 50 mV/s. Also, the galvanostatic deposited nano-materials showed a capacity around 120F/g without CTAB as an additive emphasizing on the effect of electrodeposition method on the capacitive behavior of deposited materials.

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Preparation of modified electrodes using multiwall carbon nanotubes and isoprenaline mediator for cysteamine analysis by voltammetric method

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Key words: Cysteamine, Multiwall carbon nanotubes, Voltammetry, Isoprenaline.

Introduction:

Cysteamine is an aminothiol compound used as a drug for the treatment of cystinosis [1]. The deficiency of a cystine carrier in the lysosomal membrane leads to cystine accumulation within the lysosomes, ultimately crystallizing in vital organs such as the liver, kidney, spleen, intestines, and cornea [2]. With this goal in mind, a rapid but specific and sufficiently sensitive analytical method was required for total cysteamine determination in biological and pharmaceutical samples. Numerous methods have been reported for the determination of CA. However, Long response time, expensive instruments, complicated procedure, and low detection capability are the shortcomings associated with most such methods reported. Carbon nanotubes (CNTs) are presently in the forefront of materials research. They are recognized as a new class of materials that have had a profound impact on a wide range of applications. One of the areas in which carbon nanotubes have confirmed their advantages is electrochemistry, for applications such as energy storage devices and sensors.

Materials and methods:

Spectrally pure graphite powder (particle size $<50 \ \mu\text{m}$) from Merck and multiwall carbon nanotubes (>90% MWCNTs basis, d × l = (110–70 nm) × (5–9 μ m) from Fluka were used as the substrate for the preparation of the carbon paste electrode.





Results and discussion:

The voltammetric behavior of the ISPT in the buffer solution (pH 4.0) is shown in Figure. The cyclic voltammetric responses for the electrochemical oxidation of 300 μ M of CA at MWCNTPE (curve c), and at the carbon paste electrode (curve b), in the presence of mediator, curves d and e are as c, b respectively, without ISPT. As can be seen, the anodic peak potentials for the oxidation of CA at MWCNTPE in the presence of mediator (curve c) is about 536, while at the MWCNTPE (without mediator) (curve d), the peak potential was about 705 mV. Potential is at 546 mV when using carbon paste electrode with ISPT (curve b), Whereas this at the unmodified CPE and without mediator, the peak potential was about 720 mV of CA (curve e). Similarly, when we compared the oxidation of CA at the surface of MWCNTPE (curve c) and carbon paste electrode with mediator (curve b), it was observed that a dramatic enhancement of the anodic peak current occurred at MWCNTPE vs. the value obtained with carbon paste electrode. In other words, the data obtained clearly show that the combination of MWCNTPE and the mediator (ISPT) definitely improve the characteristics of the electrode for the oxidation of CA.



Figure: Cyclic voltammograms of 200 μ M ISPT at the surface of MWCNTPE in 0.04 M universal buffer (pH 4.0) at a scan rate of 10 mV s⁻¹ in the absence and in the presence of 300 μ M AC.

Conclusion:

This work demonstrates the construction of a chemically modified carbon paste electrode by incorporating of multiwall carbon nanotube as a suitable electrochemical sensor in the presence of ISPT as a mediator for CA determination at trace level. The proposed method is a selective, simple and precise method for voltammetric determination of CA in real samples such as drug and urine, as low as $0.09 \ \mu M$ CA.





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Performance Prediction of Palladium Nanoparticles on Anode of Solid Oxide Fuel Cells

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Keywords: Nanostructure, Solid Oxide Fuel Cells, polarization, Pd, Nanoparticle.

Introduction:

Solid Oxide Fuel cells (SOFCs) have great potentials to produce clean energy in the form of electrical energy from chemical fuels with nearly zero pollution emission. SOFCs also offer high levels of energy conversion efficiency. In this paper, a modeling approach of nanostructured anode of SOFCs has been employed to calculate the effects of nanoparticles on the SOFCs' electrodes performance.

Materials and methods:

Nanostructured electrodes of the SOFCs prepared by wet impregnation or infiltration have attracted increasing attention as the most effective way to make highly active and advanced structures in the electrodes [1]. The effects of infiltrated Pd-Nanoparticles on the performance of Nickel/ Gadolinium doped Ceria (Ni/GDC) anode of SOFC have been investigated and it is reported that a small amount of Pd catalyst has a significant decreasing effect on the overpotential of anodes [2]. One-dimensional analysis has been carried out using a suitable geometry to calculate the effective polarization resistance by assuming the ionic conductor phase (GDC) as columns, and the Pd phase mounted on these columns [3].

Results and discussion:

The results of modeling were calculated and compared with the experimental data as a function of temperature. For this model, following assumptions has been made porosity of





anode: 32 %Vol.; average nanoparticle radius: 18 nm, number of particle: 2.26 x 10^{12} , and charge transfer surface resistance: 4.5 Ω .cm². Standard error of prediction (SEP) of modelling is calculated around 7.7%. Therefore, Predicted results show good agreement with experimental data.

Conclusion:

The Pd nanoparticles can improve the anode SOFC performance significantly. This modeling shows a high decrease about 0.35 Ω .cm² in polarization resistance vs. temperature from 700 to 900 °C. These results were compared with experimental results with standard error of prediction (SEP) around 7.7% and shown good agreement.

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Application of Au Nano Particles Modified Carbon Paste Electrode for Simultaneous Determination of Tryptophan, Uric Acid and Ascorbic Acid

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Keywords: Au nano particles, Tryptophan, uric acid, ascorbic acid, voltammetry methods

Introduction:

Chemical modification of the electrode surface is a strategy for improving the analytical performance of conventional electrodes for various applications especially sensors. Metal nanoparticles such as gold nanoparticles, owing to their small dimensional size, good conductivity and excellent catalytic activity have been demonstrated to be very appropriate for the development of modified electrodes [1,2].

Tryptophan (Trp) is an essential amino acid that humans cannot live without consuming [3]. Uric acid (UA), the principal final product of purine metabolism, is present in blood and urine [4].

Ascorbic acid (AA) is a water soluble vitamin present in many biological systems and in multivitamin preparations [5]. It is essential to exploit simple and rapid methods for determination of these biological molecules in routine analysis. In present study, Au nanoparticles modified carbon paste electrode (AuNPs/CPE), was constructed and used for simultaneous determination of Trp, UA and AA. The detection of Trp, UA and AA in human serum was finally demonstrated as real sample applications.

Materials and methods:

All chemicals were of analytical reagent grade from Merck except UA that was purchased from Aldrich and used without further purification. All electrochemical experiments were carried out using an Autolab potentiostat/galvanostat PGSTAT 30 (Eco Chemie, The Netherlands) controlled with General Purpose Electrochemical System (GPES) software.





Result and discussion:

One of the main objectives of this study was the development of a modified electrode capable of the electrocatalytic oxidation of Trp and separation of the electrochemical responses of Trp, UA and AA. As shown in Fig. 1, the peak currents of Trp in the presence of 100 μ M AA and 50 μ M UA is positively proportional to its concentrations in the range of 6.0 to 200.0 μ M with two linear segments with different slopes and the detection limit of 0.65 μ M (S/N = 3).



Fig. 1 Differential pulse voltammograms of the AuNPs/CPE in 0.2 M B-R buffer solution (pH=3.0) containing 100 μ M AA, 50 μ M UA and different concentrations of Trp; a to j correspond to 0, 6, 10, 20, 40, 60, 100, 140, 180, and 200 μ M. Inset B: plot of the electrocatalytic peak current as a function of Trp concentration (scan rate: 60 mV s⁻¹).

The results confirm that the electro-oxidation peaks for Trp, UA and AA at the surface of AuNPs/CPE are well-separated from each other when they co-exist in B-R buffer solution of pH 3.0.

Conclusion:

This work demonstrates the preparation of AuNps/CPE and its application in simultaneous determination of Trp, UA and AA. The Au nanoparticle modified carbon paste electrode (AuNPs/CPE) showed very efficient electrocatalytic activity for anodic oxidation of Trp, UA, and AA. Moreover the proposed electrode was used for determination of Trp and UA in human serum, and AA in vitamin C tablet, without the necessity for sample pretreatment or any time-consuming extraction or evaporation steps prior to the analysis, with satisfactory recovery.

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Differential pulse voltammetry and cyclic voltammetry detection of furan on platinum Electrode in aprotic solvent

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Key words: Furan, Differential pulse voltammetry, Platinum electrode, Acetonitrile, Cyclic Voltammetry.

Introduction:

Furan, a volatile oxygen heterocyclic compound, is classified as a possible human carcinogen by International Agency for Research on Cancer (IARC, 1995). The liver is the primary target organ of furan toxicity, after oral application. For this reason, the United States Environmental Protection Agency (US EPA) relates the limit of 1×10^{-3} mg/kg a day as Reference Dose for Chronic Oral Exposure. Numerous studies on the anodic oxidation of furan [1, 2] have been carried out in acetonitrile in order to produce polymeric coatings on electrodes. Pons and Scott-Hinman [2] reported that the anodic oxidation of 2-methylfuran leads to the formation of soluble oligomers and an insulating polymer layer at a platinum electrode. However, no systematic electrochemical study on the anodic oxidation of crmethyl-substituted furans has been reported [3, 4].

We were interested in study the electrochemical behaviour of furan in acetonitrile containing tetra-n-butylammonium perchlorate as the supporting electrolyte on a platinum electrode. This study was carried out using cyclic voltammetry and Differential pulse voltammetry.

Materials and methods:

Furan (Aldrich, \geq 99%) and acetonitrile (Sigma-Aldrich, HPLC grade) were used as received. Sample solutions were constituted by 20 or 40 mL acetonitrile and 0.1 M tetrabutylammonium perchlorate (TBAP, Fluka, \geq 99.0%) was used as supporting electrolyte.



0.1 M furan stock solution (standard mother solution) in acetonitrile was prepared by weight on an analytical balance, while 0.01 M and 0.001 M stock standard solutions were prepared by dilution of the mother one. Consecutive additions of 10 or 20 μ L standard solutions to the sample were made by Kartell automatic pipettes.

Apparatus:

Electroanalytical determinations were performed using a conventional three electrode cell with platinum based electrodes, saturated calomel electrode (SCE) and platinum foil as working, reference and counter electrodes, respectively.

The voltammetric curves were registered using an μ Autolab III (EcoChemie B.V., The Netherlands) potentiostat/galvanostat, equipped with NOVA software for the results analysis.

Result and discussion:

A rapid, precise and accurate electroanalytical methodology for the determination of furan, a possible human carcinogen, is proposed. The method is based on the use of cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) on a platinum disk Electrode, performed in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte. The oxidation peak height or area present good linear relationship with the furan concentration in the range $5 \times 10^{-5} - 1 \times 10^{-3}$ M, ensuring a detection limit of $5-6 \times 10^{-5}$ M (50 - 60 ppm). The DPV parameters, concentration effect, scan rate effect are also discussed. The application in a complex matrix is performed. Under the CV measurements, the reaction followed a Cottrellian behavior and the diffusion coefficient of furan was found to be 2×10^{-6} cm²s⁻¹.

Conclusion:

The Aniline adsorption was due to immobilized ligand- aniline interactions. The mesopores also present the advantage of high adsorption capacity, good reusability and high chemical stability. The sorption/desorption of aniline takes place in moderate time, making the analytical procedure reasonably fast.





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Screen Printed Carbon Electrode Modified by Ionic Liquid/ Ag Nanoparticles for Determination of Metronidazole in Biological Samples

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Keywords: Screen Printed Electrode, Metronidazole, Differential Pulse Voltammetry, Ionic Liquid, Ag Nanoparticles

Introduction:

Metallic nanoparticles can be used to increase electrochemical activities as they offer higher catalytic efficiency than the bulk materials because of their large surface-to-volume ratios. Electrodes modified with metallic nanoparticles reveal good performances, and enhance the electrochemical reaction rates on these electrodes. Compared with other metal nanoparticles, the silver (Ag) nanoparticles have attracted much interest in biosensing applications. In this study, a new home-made disposable screen-printed carbon electrode (SPCE) consisted of graphite and cellulose acetate printing ink modified with ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM]PF₆) and Ag nanoparticles, respectively, for electrochemical determination of metronidazole (MTZ) is introduced.

Materials and methods:

All the chemicals were of the analytical grade and the solutions were prepared in double distilled water. Stock solution (0.005 mol L^{-1}) of MTZ was prepared by dissolving appropriate amount of powder in deionized water. Graphite powder, silver nitrate and ionic liquid [OMIM]PF₆ were purchased from Merck. Cellulose acetate (CA) and poly vinyl chloride (PVC) were provided from Fluka. A 0.04M Britton-Robinson buffer solution consisted of *o*-boric acid, *o*-phosphoric acid and acetic acid was used for adjustment of pH.

A conducting pad was firstly printed on the PVC substrate using home-made silver ink. Afterwards, the working electrode layer was then printed over the conducting pad using a home-made carbon ink prepared by mixing PVC, graphite powder and plasticizer. Then, a





layer of an insulator was placed onto the printed electrode, so that a defined circle shape (diameter 3.5mm) left at the surface of electrode as working area. Then twenty SPCEs were produced on the home-made printing machine.

Apparatus:

A Metrohm model 746 VA Trace Analyzer processor and 747 VA stand equipped with Ag/AgCl/3M KCl reference electrode and platinum counter electrodes were employed. The modified SPCEs were used as the working electrode for electrochemical measurements. The pH measurements were carried out using a Corning pH meter 125 equipped with a combined glass electrode. Ultrasonic agitating of inks was performed to disperse of particles in solvent by a 1510R MTH Branson sonicator.

Result and discussion:

Performance of the SPCE with different plasticizers having different dielectric constants, namely, DOP, BA, DBS, as well as combination of ionic liquid (IL) with the selected plasticizer were examined. The plasticizer content within the carbon ink is an important factor that affects the viscosity of the printing ink, thickness, adhesion and the ohmic resistance of the printed electrodes. The Ag nanoparticles were electrodeposited on the modified substrate using a two-step potentiostatic method. The surface morphology of the nanoparticles was characterized by SEM technique (Fig. 1). The CV voltammograms revealed that the Ag nanoparticles decorated SPCE under optimum conditions compared to bare SPCE had high electrocatalytic effect towards MTZ reduction. In the electrochemical depositions, various parameters such as deposition time, potential and concentration of silver ions in the deposition solution were optimized. The electroanalytical performance of the modified SPCE for reduction of MTZ based on the differential pulse voltammetry was intensively evaluated. The results indicated that the developed SPCE exhibited well linear behavior in the MTZ concentration range from 0.1 to 1200.0 µM with a detection limit of $0.036 \mu M$ (S/N = 3). In addition, the developed electrode was applied for the determination of MTZ in pharmaceutical and human urine samples.







Fig 1. SEM of modified SPCE with Ag nanoparticles

Conclusion:

The screen-printed carbon electrode is a promising tool for direct MTZ determination and can be used for direct applications in real samples without any pretreatment. A good analytical performance has been demonstrated. In comparison with the bare SPCE, the modified SPCE with Ag nanoparticles and ionic-liquid provided high sensitivity towards MTZ. It was possible to determine the MTZ contained in urine samples following the standard addition method using the same screen-printed electrode.

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Preparation and Investigation of Hydrogen Storage Properties of Pd-Ni Nano-alloys for Fuel Cells

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Keywords: Nano-alloy, Hydrogen Storage, Fuel Cell

Introduction :

Hydrogen is proposed as a clean and efficient energy carrier, which can be an alternative to fossil fuels [1]. Hydrogen is a highly reactive element and is known to form hydrides with several metals and alloys [2]. Palladium has been intensively studied because of its high hydrogen storage capacity, but unfortunately it has a high cost for application in industrial scale. Therefore, there are several trends to find new materials for this intend.

Materials and methods:

The chemical substances used in the experiments were: Nickel(II) sulfate(NiSO4(H2O)6), Palladium(II) acetate(Pd(OAc)2), Ammonia(NH₃)

Hydrochloric acid (HCl) and Lithium hydroxide (LioH). A well-polished stainless steel (SS) with a with dimensions of 1cm×6cm was used as a work electrode. The electrochemically stored hydrogen amount into the electrodeposited palladium and Ni-Pd was studied in 0.1 M LiOH solution via cyclic voltammetry and electrochemical impedance spectroscopy

Apparatus:

The electrochemical measurements were carried out using a Solartron SI 1260 Frequency Response Analyzer, and a Solartron 1287 electrochemical interface. The AFM model DME-1180 was used for morphology studies of both palladium and Ni-Pd nano-alloys.

Result and discussion:

In this study, nanostructured palladium and Pd-Ni nanoalloyes have been prepared by different electrodeposition method containing of potentiostatic, galvanosstatic and




potentiodynamic methods on the surface of commercial stainless steel. XRD pattern nanlysis shows the electrodeposited materials are amorphous. The AFM studies illustrated nanostructured morphology for both palladium and Ni-Pd nano-alloys. A typical AFM analysis has been shown in Figure 1. The amount of electrodeposited materials was measured by dissolving them in an acidic solution and atomic adsorption spectroscopy.

Conclusion:

The experimental results showed that the potentiostatic deposited palladium is able to store more hydrogen compared to galvanostatic and potentiodynamic electrodeposited ones and in nano-alloy cases by increasing in nickel amount hydrogen storage capacity decreased.



Fig. 1: A typical AFM results for electrodeposited Ni-Pd nanoalloy.

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Simultaneous determination of norepinephrine and acetaminophen using modified room temperature ionic liquid/multiwall carbon nanotubes paste electrode

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Keywords: Norepinephrine; Acetaminophen; Ionic liquid; Multiwall carbon nanotubes; Voltammetry

Introduction:

Drug analysis plays important roles in drug quality control, and has a great impact on public health. Therefore, a simple, sensitive and accurate method for the determination of active ingredient is very important.

Norepinephrine (NE) is a drug belonging to the stimulants that are on the World Anti-Doping Agency's 2005 Prohibited List.[1,2].

Acetaminophen (AC) is a widely used anti-pyretic and analgesic drug with actions similar to aspirin. Its ready access has resulted in its increased use in attempted suicide [3]. Therefore, simultaneous determination of NE and AC is very important.

We used a novel multiwall carbon nanotubes modified carbon ionic liquid paste electrode as a binder. The results showed the superiority of MWCNTs/CILE to the other electrodes in terms of both provision of better reversibility and higher sensitivity.

Materials and methods:

Spectrally pure graphite powder (particle size<50 μ m) from Merck and multiwall carbon nanotubes (>90% MWNT basis, $d \times l = (100 - 80 \text{ nm}) \times (5 - 9 \mu\text{m})$ from Fluka were used as the substrate for the preparation of the electrodes.

Apparatus:

Cyclic voltammetry (CV), impedance spectroscopy, and differential pulse voltammetry (DPV) were performed in an analytical system, Autolab with PGSTAT 302N (Eco Chemie, the Netherlands). The system was run on a PC using GPES and FRA 4.9 software.





Results and discussion:

To obtain the best condition in the preparation of modified electrode, the ratio of MWCNTs to ionic liquid in MWCNTs/CILE was optimized. Figure 1 compared the morphological features of MWCNTs/CILE and CPE using SEM. From the resulting slope and Cottrell equation the mean value of the D was found to be 4.4×10^{-5} cm²/s.

DPV method was used to prepare the calibration plot. The detection limit (3σ) of NE was found to be 0.09μ M.



Fig. 1. SEM images of CPE (a) and MWCNTs/CILE (b).

Conclusion:

The main object of this study was to detect NE and AC simultaneously using MWCNTs/CILE. This was performed by simultaneously changing the concentrations of NE and AC, and recording the DPVs. The voltammetric results showed well defined anodic peaks at potentials of 200 and 430 mV, corresponding to the oxidation of NE and AC, respectively.

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Tetrazolic derivatives as effective inhibitors for the corrosion of steel in 0.5 M H2SO4 solution

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Key words: tetrazole, inhibitor, steel, corrosion, polarization.

Introduction:

The corrosion of steel and its alloys is of industrial concernthat has received a considerable amount of attention. The corrosion of steel in sulphuric acid is important in the context of pickling, acid cleaning, acid descaling, etc. Becauseof the general aggressiveness of acid solutions, the useof inhibitors to control the destructive attack of acid environmentfinds widespread application in many industries. Avariety of organic compounds with functional groups containingheteroatom which can donate electron pairs are found to be useful as inhibitors in various media [1-5].

Materials and methods:

The synthesized CMT,TTM tested as corrosion inhibitors was purified and characterised by NMR and IR spectroscopies and element analysis before use.Gravimetric measurements are carried out in a doublewalled glass cell equipped with a thermostat-cooling condenser.The solution volume is 50 cm3. The steel specimensused have a rectangular form (1 cm×1 cm×1m).Electrochemicalexperiments are recorded using a potentiostatmodelAoltalab GZ100. Aplatinum counter electrodeand a saturated calomel electrode (SCE) are used. The workingelectrode (WE) in the form of a disc cut from steel, isembedded in polytetrafluoroethylene (PTFE). Gas pebbling is maintained through the experiments. TheWEis then inserted and prepolarised at–800mV(SCE) for 10 min in order to remove the oxide film from theelectrode and *E*corr is monitored until stationary. The scanrate is 20mVmn–1.





Results and discussion:

The effect of addition of CMT,TTMcompounds tested atdifferent concentrations on corrosion of steel in deaerated0.5MH2SO4 solution is studied by weight loss at 298K after6 h of immersion. Inhibition efficiency (*E*w, %) is calculatedas follow:

 $E(\%) = 100 \times (1 - W/W_0)$ (1)

W and *W*o are the corrosion rates of steel with and without organic compound. Current–potential characteristics resulting from cathodicand anodic polarisation curves of steel in 0.5M H2SO4in the absence and presence of CMT,TTM at various concentrationsare (E %) = $[1 - (Icorr / I 0 corr)] \times 100$ (2)

where I0corr and Icorr are the corrosion current density values without and with the inhibitor.

Conclusions:

The two tetrazolic compounds studied are good inhibitors for steel in 0.5 MH2SO4.The inhibition efficiency increases with the inhibitors concentration, but decrease slightly with the temperature.TTM,CMT acts as a mixed-type inhibitor.

The results obtained from weight loss, potentiodynamic polarisation are in good agreement.

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Voltammetric determination of L-cysteine using modified electrode with multi-wall carbon nanotubes and 3,4-dihydroxycinnamic acid

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Key words: L-Cysteine, Multiwall carbon nanotubes, Voltammetry, 3,4-Dihydroxycinnamic acid.

Introduction:

Two of these are sulfur-containing amino acids; cysteine and methionine. The only trait differentiating cysteine from serine is the sulfur of its thiol replacing the oxygen of the alcohol. Cysteine plays an important role in stabilizing extracellular proteins. It can also react with itself to form an oxidized dimer by forming a disulfide bond. The thiol residue of cysteine is readily oxidized in electrochemical reactions at the surface of various thiol-sensitive electrodes [1]. Different methods have been reported for the determination of L-cysteine in different samples. However, Long response time, expensive instruments, complicated procedure, and low detection capability are the shortcomings associated with most such methods reported.

Carbon nanotubes (CNT) are an important nano structural that used building blocks of nanotechnology. CNTs have generated great interest for future applications based on their field emission and electronic transport properties, their high mechanical strength and high conductivity [2]. The modification of electrode substrates with CNTs for use in analytical sensing has been documented to result in low detection limits, high sensitivities, reduction of over-potentials, and resistance to surface fouling.

Preparation of the electrode:

Graphite powder (0.900 g) was dissolved in diethyl ether and hand mixed with 0.100 g carbon nanotubes in a mortar and pestle. The solvent was evaporated by stirring. A syringe





was used to add paraffin to the mixture, which was mixed well for 40 min until a uniformly wetted paste, was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

Results and discussion:

The electrochemical behavior of the 3,4-DHCA was characterized by cyclic voltammetry at MWCNTPE in the PBS (pH 6.0) at various scan rates. The experimental results showed well defined and reproducible anodic and cathodic peaks related to 3,4-DHCA_(red)/ 3,4-DHCA_(ox) redox couple with a quasi reversible behavior and with a peak separation potential of $\Delta E_p(E_{pa}-E_{pc})=95$ mV. These cyclic voltammograms were used to examine the variation of the peak currents vs. the square root of potential scan rates. The plot of the anodic peak current was linearly dependent on v^{1/2} with a correlation coefficient of 0.9938 at all scan rates.

Conclusion:

The electrochemical behavior of the 3,4-DHCA and MWCNTPE as a new electrochemical sensor for l-cysteine determination has been studied by cyclic voltammetry and chronoamperometry. It has been found that with cyclic voltammetry, the oxidation of acetylcysteine occurred at a potential about 320 mV less positive that than unmodified carbon nanotubes paste electrode. The proposed method is sensitive to detect cysteine as low as 0.5 μ mol L⁻¹. The proposed method was also used as a selective, simple and precise new sensor for voltammetric determination of l-cysteine in real sample such as urine.

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Chemical Kinetics





A Comprehensive Study on the Mechanism of Diallyl Disulfide (All₂S₂) Thermal Decomposition in the Gas Phase

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Keywords: Radical mechanism; Diallyl disulfide; DFT; Thermal decomposition

Introduction:

Organic disulfides are less stable than the corresponding sulfides and therefore readily undergo diverse transformations and react with organic compounds under the liquid and gas phase thermolysis conditions. The existence of an equilibrium at the room temperature between these compounds and thiosulfoxides, which formed by facile [2,3]-sigmatropic process have been proved [1]. In addition to [2,3]-sigmatropic rearrangement, a second parallel process accompany with All₂S₂ homolytic bond cleavage. Since it has not been reported any mechanistic study on the gas phase pyrolysis reaction of diallyl disulfide so far, a comprehensive study with the aim of elucidation the molecular mechanism associated with this pyrolysis process is done in order to have a precise idea of the reaction pathway.

Computational Methods:

Gaussian 09 computational package [2] with the DFT method was applied for all of the calculations. In this procedure optimized geometries of the stationary points on the potential energy surface (PES) were performed using the B3LYP and 6-311++G(d,p)/6-31G(d) basis sets. The synchronous transit-guided quasi-Newton method was used to locate the TS for the concerted mechanism. Activation parameters were also determined in the temperature range of the pyrolysis reaction of 603K. The activation energy, Ea, and the Arrhenious factor were computed using the transition state theory. The natural bond orbital (NBO) analysis was applied to determine the charge changes through the reaction.





Results and Discussion:



[2,3]- sigmatropic process, intermolecular sulfurization-desulfurization, and free-radical reaction are the main mechanisms of DADS thermal decomposition (Scheme 1). The first is started by thiosulfoxide formation due to facile [2,3]-signatropic process follows by a direct unimolecular splitting through six-center TS. The concerted mechanism is initiated with the H–C bond formation and C–S bond cleavage yielding propene and thioacrolein S-sulfide. The comparison of the calculated with the our experimental one shows that the first one for concerted mechanism is much less than the second one. Therefore the concerted mechanism is rejected. This brought our attention to the latter mechanism and the radical mechanism was fully investigated. For radical mechanism three paths were proposed. Since the allylic $C-S_n$ bonds are common in vulcanized rubber, homolytic cleavage of C-S bonds may represent an important role of initiation for the thermal degradation of these materials, which competes with S-S bond cleavage. Bond dissociation energy for the C-S bond and S-S bonds have been calculated. Bond dissociation energies are 46 and 62 kcal.mol⁻¹ for D(allyl-SS-allyl) and D(allyl-S-S-allyl), respectively. These results show that the allylic C-S bond is weaker than the S–S bond by 16 kcal.mol⁻¹, hence this difference should be decisive for the mode of thermal dissociation. Calculated parameters for the radical mechanism are in good agreement with the experimental one [3] which confirmed that the pyrolysis reaction of All_2S_2 proceeds through a radical mechanism introducing the C-S bond cleavage at the TS. Analyses of natural charges on the reactant and radicals confirmed the feasibility of C-S bond cleavage at the radical TS.





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5th Physical Chemistry Conference





Quantum Study of the Gas Phase Unimolecular Elimination Kinetics of 5-Substituted Groups of Allyl Sulfides

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Keywords: Elimination; Concerted mechanism; Gas-phase kinetics; G3MP2; DFT

Introduction:

Gas phase pyrolysis of organo-sulfur compounds has a special place among the great variety of chemical reactions, because of the generation of labile sulfur containing intermediates, which are difficult to obtain alternatively. The most important molecular mechanisms that are involved in the gas phase pyrolysis of organosulfur compounds include the radical and concerted mechanisms. The kind of molecular mechanism depends on different factors. The most important factors are; temperature, C–S bond strength, electron donating and electron withdrawing properties of the substituents and intramolecular parameters. The aim of this research is the study of electron-withdrawing and electron-donating groups on the kinetics of alkyl allyl sulfides pyrolysis.

Computational Methods:

Upon pyrolysis reaction, alkyl allyl sulfides eliminate propene and corresponding thiocarbonyl compounds via an intramolecular γ -hydrogen transfer. The structures corresponding to the reactant, transition state and products for the studied reaction were optimized using the GAUSSIAN 09 computational package [1] with DFT method. The corresponding TSs were calculated using the synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel et al (Figure 1). [2].



Fig. 1. Optimized structures for the reactants and the TSs at the B3L YP/6-31G(d) level.





Results and Discussion:

The most important feature of the transition structures is that the X substitution leads to the sizable changes in the geometry. For the TSs, changes in the calculated H1–C2 and C4–S5 bond lengths are important; the electron donating substituent (X= CH3) makes the H1–C2 distance 0.12 A ° shorter, but C4–S5 distance 0.17 longer than unsubstituted (X=H) molecule, while the electron with-drawing substituents (X=F, Cl) significantly reduce H1–C2 bond length at the TSs relative to the same one in the reactant. Since the H1–C2 bond formation can be considered as a driving force for the concerted pathway, the electron with-drawing groups (X=F, Cl) noticeably affect the calculated barrier height. Activation energies, free energies and entropies for the pyrolysis reactions at the G3MP2 level of the theory were computed. Calculated potential energy barriers for the reactions are around (average) 154 kJ molK⁻¹, the usual range for the experimental activation energies of alkyl allyl sulfides. TS3 (X=F) is more stable than TS4 (X=Cl) by 3.89 kJ molK⁻¹, TS4 is more stable than TS1 (X=H) by 5.39 kJ molK⁻¹ and TS1 is more stable than TS2 (X=CH3) by 13.2 kJ molK⁻¹, according to acidic character of H1 atom. The overall reactivity for the alkyl allyl sulfides is found to decrease in the order of R3>R4>R1>R2.

Negative values for the activation entropy confirmed the concerted mechanism for the studied reactions. The reactivity of alkyl allyl sulfides can be explained in terms of the acidic character of the H1 atom and HOMO– LUMO energy difference. Charge distribution on the atoms for the reactants and the TSs was calculated using the Merz–Kollman–Singh (MKS) electrostatic properties at the B3LYP/6-31G(d) level. Computed data show that the positive charge on C6 and H1 atoms increases from X=CH3- to-F. This positive character shows that acidic character for H1 atom increases from X=CH3-to-F according to activation energy depletion and reactivity order.

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Solvent Effects on Protonation and Complexation of Aspartic Acids with Molybdenum(VI) in Different Aqueous Solutions of Methanol

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Keywords: Solvent effect- Solvent polarity- Protonation Constant- Complexation Constant.

Introduction:

Chemists are usually interested to understand solvent effects on overall solution capabilities that depend on all possible intermolecular interactions between solute and solvent molecules. Solvent effects on transition metal complexes are reviewed and more attention has been paid to binary solvent mixtures in this field. Solute-solvent interactions are much more complex in mixed solvent systems than in pure solvent due to the possibility of preferential solvation by any of the solvent present in the mixtures. Moreover, the solvent-solvent interactions produced in solvent mixtures can affect the solute-solvent interactions and therefore they can also affect preferential solvations.

Methods:

The formation constants of the species formed in the systems $H^++Mo(VI)$ + aspartic acid and aspartic acids have been determined in different aqueous solutions of methanol (0-40 % v/v), using a combination of spectrophotometric and potentiometric techniques.For each experiment two solutions of Mo(VI) + asp have been prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate and that of the second with sodium hydroxide, both with the same mole fraction of methanol. In all solutions the total concentration of the amino acid and the metal ion were kept constant, $[MoO_4^{2^-}]$ + [amino acid] = 2.0×10^{-3} mol dm⁻³. The first solution was then titrated with the second one.The procedure was repeated with different solutions of Mo(VI) and the amino acid with varying the mole fraction of Mo(VI) in the range 0-1 in constant of the total concentration of Mo(VI) and each ligand in different aqueous solutions of methanol.



Results and discussion:

The protonation constant of the amino, K_3 , and the side chain carboxylic acid, K_2 , groups of the amino acids decreased as the solvent became enriched in the organic component, but the protonation constant of the other carboxylic acid group, K_1 , increased as methanol increased in the mixtures. The correlation between log K_3 and log K_2 with the reciprocal of the dielectric constant of methanol-water mixtures are linear, with correlation coefficients more than 0.99. The solvent polarity has been introduced by Kamlet, Abboud, and Taft (KAT).¹⁻² The multiparametric equation, eq 2, has been proposed for use in so-called Linear Solvation Energy Relationship. $\log K = A_0 + a\alpha + b\beta + p\pi^*$ (2)

We used the Gauss-Newton non-linear least-squares method in the computer program to refine the log *K* by minimizing the error squares sum from eq 3. Single-parameter correlations of log K_1 , log K_2 and log K_3 in terms of individually with α , β or π^* did not give a good results in all cases. So, we thought it interesting to correlate log *K* versus a multi-parametric equation involving α , β and π^* . However, the result presented from eq 2, multi-parametric equation, indicates significant improvement with regard to the single-parameter models.

 $\log K_1 = 0.95 + 1.26\alpha + 3.87\beta - 2.01\pi^* (5a) \qquad \log K_2 = 0.83 + 0.34\alpha + 0.51\beta + 2.54\pi^* (5b)$ $\log K_3 = 4.85 + 0.65\alpha + 1.52\beta + 3.07\pi^* (5c)$

methanol %	$\alpha^{(a)}$	$\beta^{(a)}$	$\pi^{*(a)}$	$\mathcal{E}_{r}^{(a)}$
0.0	1.17	0.47	1.09	78.36
10	1.17	0.49	1.07	73.50
10	1.13	0.49	0.00	60.22
20	1.13	0.51	0.99	69.22
30	1.11	0.53	0.94	64.65
40	1.09	0.55	0.89	60.08

The calculated values of solvatochromic parameters are listed in Table 1.

Complexation Constant.

In this stage we again used the Gauss-Newton non-linear least-squares method in the computer program to refine the log K_S by minimizing the error squares sum from eq 2. The result presented in eq 5, multi-parametric equation, indicates significant improvement with regard to the single-parameter models. $\log K_S = 20.68 + 1.23 \alpha + 3.46\beta - 5.70 \pi^*$



Table 2. The	e Percentage C	Contribution	of Kamlet and	d Taft's Parame	ters on the	e Effect of	Different	Media on
]	Protonation ar	d Complexatio	n.			

species	α	β	π^*
$\log K_1(asp)$	17.6	54.2	28.2
$\log K_2(asp)$	10.0	15.0	75.0
$\log K_3(asp)$	12.4	29.0	58.6
$\log K_{\rm S}({\rm asp})$	11.8	33.3	54.9

Conclusion:

The polarity parameter power of the solvent is the most important, the hydrogen-bond acceptor basicity parameter plays a relatively small role, and finally the hydrogen-bond donor acidity parameter nearly has no significant in changing the formation constants of Mo(VI) + asp systems in the proposed various aqueous solutions of methanol.

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Photocatalytic activity of Cu-doped ZnS prepared by ultrasonic method

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Keywords: Photocatalysis, Reaction kinetics, Degradation, Nanoparticles.

Introduction

Many industries are widely using dyes and pigments for various purposes and their effluents can cause environmental pollution. Traditional techniques such as adsorption and coagulation are non-destructive and simply transfer the contaminant from water to another phase [1]. Photocatalysis, an advanced oxidation technology employing semiconductors as photocatalysts, is a promising method for the treatment of contaminated water [2]. This method is clean, low temperature and non-energy intensive approach for treatment of pollutants. Most of photocatalysts are not highly efficient under visible light irradiation [3], therefore, there is a need to look for other photocatalysts that absorb in the visible range [4]. In the present paper, ultrasonic method was applied for preparation nanoparticles of Cudoped ZnS in water and influence of ultrasonic irradiation time, catalyst weight, calcinations temperature, concentration of methylene blue (MB) and pH of solution on photodegradation reaction of MB has been studied to achieve maximum degradation efficiency.

Materials and methods

Zinc acetate, cupper acetate, thioacetamide and absolute ethanol were obtained from Merck, and employed without further purification. Similar to our previous papers [4], photocatalysis experiments were performed in a cylindrical pyrex reactor. A tungsten lamp with 500 W was used as visible light source.

Results and discussion

To obtain maximum degradation efficiency of MB on $Zn_{0.985}Cu_{0.015}S$ nanoparticles, the reaction variables were optimized and the results described. The results demonstrate that ultrasonic irradiation time has not remarkable effect on the photodegradation reaction. A series of experiments were carried out to find the optimum catalyst amount by varying weight



of the Zn_{0.985}Cu_{0.015}S nanoparticles between 0.01 and 0.15 g prepared by 15 minutes ultrasonic irradiation. The photodegradation rate constant increases with increasing weight of the photocatalyst and then decreases. Indeed, maximum value was achieved at 0.05 g of the photocatalyst. The degradation rate constant on the nanoparticles without calcinations and the catalysts calcined at 200, 300 and 400 °C are 8.44×10^{-3} , 6.48×10^{-3} , 5.49×10^{-3} and 2.33×10^{-3} min⁻¹, respectively. Then, the photodegradation rate constant decreases with calcinations temperature. Decreasing the rate constant for photocatalytic degradation of MB may be due to aggregation of the nanoparticles. Moreover, the rate constant of the degradation reaction suddenly increases with increasing in pH and then decreases. These results were described by electrostatic interactions and solution of the nanoparticles. In order to know reusability of the photocatalyst, the photodegradation experiments were carried out on the Zn_{0.985}Cu_{0.015}S nanoparticles in optimized conditions (catalyst weight=0.05 g, without calcinations, *[MB]* =2.55×10⁻⁵ M and pH=5.5). In the experiments, the photocatalyst was recycled after washing and drying at 60 °C for 24 h. The degradation percent decreases to 62 % after five runs, indicating that the photocatalytic activity has a better repeatability.

Conclusions

Photocatalytic activity of the nanoparticles towards photodegradation of MB was evaluated under visible light irradiation. The photocatalytic activity of Cu-doped ZnS nanoparticles is higher than that of pure ZnS. To achieve maximum degradation efficiency, the influence of various operational parameters such as ultrasonic irradiation time, catalyst weight, calcinations temperature, concentration of MB and pH of solution on the photodegradation reaction was studied and the results were discussed.

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Effect of ultrasound on 3-chlorophenol degradation, comparison with Fenton's reagent effect

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Key words: 3-chlorophenol, Ultrasound, catalyst, Fenton's reagent, degradation.

Introduction:

The study of chemical effects of ultrasound on organic systems is of interest because of the widespread universal tries for water purifying[1]. It's chemical effects revealed because of generated cavities during acoustic wave transmitting the solution which collapsed and lead to chemical damage that called sonolysis[2-4]. In brief sonolysis is due to high local instantaneous temperature and pressure that made in solution after cavitation[5]. It has been proposed that ultrasound-induced reactions in aqueous solutions involve free-radical mechanisms due to the formation of hydroxyl radicals[6].

The kinetic study of ultrasonic and Fenton's reagent assisted degradation of 3-chlorophenol in water was performed to compare them. Fenton's reagent consist of FeSO₄ and H₂O₂ that produces OH in water medium[7]. Apparent kinetic rate constants were studied. Comparative analysis revealed that ultrasound irradiation using compared with catalytic case increased rate constant from 0.0016 min⁻¹ to 0.0051 min⁻¹ that showed about 3-times higher degradation rate. In combination method the rate constant reached to 0.0072 min⁻¹ that is more than one of others. The more OH radicals produced in combination method caused the larger rate constant was observed. The observed degradation seem to be related OH radical attacks to phenol ring that ring made be transient and break it[8].

Materials and methods:

3-chlorophenol, hydrogen peroxide(30%), iron(II) sulfate were purchased from Merck and used without further purification. The samples of 2-chlorophenol solution spotted 100 μ M and prepared using de-ionized water. Ultrasonic waves were emitted from a tip immersed into





solution at a 100 ml beaker. Temperature increased to 340 K during the sonication that measured with an electronic thermometer. We carried out the classic experiments in a 100 ml beaker that shake 150 rpm with an magnetic stirrer.

Apparatus:

The ultrasonic irradiation was carried out with equipment operating at 20 kHz (sonicator XL 2020). Ultrasonic waves were emitted from the standard tip which immersed into the solution. The degraded 3-chlorophenol was measured by a HPLC Waters 600E. Detection was made at 220 nm. The eluent was a mixture of water–methanol (60/40 v/v).

Result and discussion:

Experiments on 50 ml of the pollutant were carried out under three different conditions at its natural pH. The first one only transactioned in presence of 0.01 Formal FeSO₄ and 0.005 Molar H_2O_2 . In the experiment we pour 50 ml of the pollutant in a 100 ml beaker and shake 150 rpm with a magnetic stirrer for one hundred ten minutes. Every 15 to 20 minutes we pick up a sample and injected to HPLC. The second carried out in presence 20 kHz ultrasonic irradiation, and third of them was carried when Fenton's reagent and ultrasonic irradiation were both present. We identify the mechanism of meta chlorophenol degradation pseudo-first order.



In the figure below we comparison the results of the experiments.

The rate constant of the classic experiment is 0.0016 min⁻¹ that is the lowest rate constant, in presence of ultrasonic waves the rate constant increased to 0.0051 min⁻¹ that about 3 times





larger than the classic one and finally in the third we observed the largest rate constant that relevant in it more OH radicals rather than two former produced.

Conclusion:

The below mechanism proposed for the observed break up in experiments, that sure related to OH radical attacks to Phenol ring[9]. We may consider to proposed mechanism that the more OH radical caused increased degradation of 3-chlorophenol.



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A Theoretical Study on the Thermal Unimolecular Reactions of *cis*-1,2-Dimethylcyclopropane and *trans*-1,2-Dimethylcyclopropane

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Keywords: Dimethylcyclopropane, Unimolecular Reactions, RRKM theory, Ab initio

Introduction:

The isomerization of cyclopropane into propylene is the first true elementary unimolecular gas reaction [1]. In the thermal processes such as combustion, partial oxidation and cracking, cyclic hydrocarbons, particularly cycloalkanes, represent an important class of compounds. In this research, the unimolecular reactions of two simple branched cyclopropanes are theoretically studied.

Method:

In order to compute accurate energies, the high-level composite methods CBS-QB3, G3//B3LYP were employed. These methods are combinations of many single point energy calculations on the geometries optimized by B3LYP/CBSB7 and B3LYP/6-31+G(d) methods, respectively. G3//B3LYP is a variation of Gaussian-3 (G3) theory in which the geometries and zero-point energies are obtained from B3LYP method instead of geometries from MP2 method and zero-point energies from Hartree-Fock method. A modified strong collision/RRKM model [2] is employed to calculate the thermal rate coefficients for the formation of major products as a function of temperature and pressure. The computed rate constants are compared with the available experimental data.

Results and Discussions:

The different reaction channels for unimolecular reactions of the title compounds proceed via the opening of the cyclopropane rings. Following the ring opening, a hydrogen atom shifts to



give the corresponding alkene. Both title compounds rearrange to yield 2-methyl-2-butane, *trans*-2-pentane, *cis*-2-pentane and 2-methyl-1-butane. *Cis*-1,2-dimethylcyclopropane also rearranges to yield more stable *trans*-1,2-dimethylcyclopropane. The isomerization barriers of *cis*-1,2-dimethylcyclopropane to 2-methyl-2-butane (R1), *trans*-2-pentane (R2), *cis*-2pentane (R3) and 2-methyl-1-butane (R4), computed at the CBS-QB3 level are 280.9, 271.3, 281.0 and 265.6 kJ mol⁻¹ respectively. By using the barrier height at the CBS-QB3 level, the high-pressure Arrhenius expressions for latter reaction channels were found to be: $k_1 = 3.8 \times 10^{13} \times exp(-288.7 \text{ kJ mol}^{-1}/\text{ RT}) \text{ s}^{-1}$ $k_2 = 7.2 \times 10^{13} \times exp(-279.1 \text{ kJ mol}^{-1}/\text{ RT}) \text{ s}^{-1}$

 $k_3 = 7.7 \times 10^{13} \times exp (-289.1 \text{ kJ mol}^{-1} / \text{ RT}) \text{ s}^{-1}$

 $k_4 = 3.2 \times 10^{13} \times exp (-273.4 \text{ kJ mol}^{-1} / \text{RT}) \text{ s}^{-1}$

Conclusion:

A number of important results emerge from this study. (1) A biradical mechanism for ring opening, following a hydrogen shift, is envisaged for two branched cyclopropanes. (2) A modified strong collision/RRKM model predicts well the thermal rate coefficients and the overall rate coefficient computed in the temperature range of 600-2500 K are in accordance with the available experimental data.

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Kinetic study of electron detachment reaction for CI by using of ion mobility spectrometry

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Keyword: Ion Mobility, Electron Detachment, Kinetic Study, Rate Constant

Introduction:

Ion mobility spectrometry (IMS) is basically an ion separation technique at atmospheric pressure. In this technique, ions are separated according to their individual velocities as they drift through an inert gas, driven by an electric field. It is a simple, inexpensive, and sensitive analytical method for the detection of organic trace compounds. Recently researchers are interested to investigate the kinetic of electron attachment reaction, dissociation reaction and proton transfer reaction by this method [1-5]. In the present study, we describe the use of ion mobility spectrometry for determination of thermal electron detachment (TED) reaction for the chloride ions Cl⁻ over atmospheric pressure and a temperature range from 30 to 150 °C.

Experimental Section:

The IMS apparatus with the continuous corona discharge as ionization source has been used in this study. Corona discharge source is constructed from a stainless steel needle and an aluminum ring in front of it. The IMS cell has been made from 16 aluminum rings that were separated from each other by non-conductive Teflon sheets. The aluminum rings are connected to each other by a series of resistors in order to form a uniform electric field. The system has an oven with ability to elevate temperature to 220°C. The system works at atmospheric pressure. Carrier gas and drift gas in this experiment was He. The electric field in drift region was about 250 V.cm⁻¹. We used syringe pump for introducing the sample





vapor to the IMS cell. Mono chloro benzene was used in this study as sample. The follow rates of carrier and drift gas were 300 and 600 ml/min respectively.

Result and Discussion:

Rate constants, k_{TED} , and their temperature dependence for the thermal electron detachment reaction of the Cl⁻ anion (Cl⁻ \rightarrow Cl + e) have been determined by ion mobility spectrometry. By this method, Cl⁻ ions that are produced in ionization region are periodically introduced to the drift tube containing He gas. The drift tube contains a counter flowing current of drift gas that prevents the penetration of sample vapor into the drift region. In the drift tube, all ions and electrons are transported to a Faraday detection plate at rates determined by their respective mobilities and the applied electric field. Some of the Cl⁻ ions are expected to undergo thermal electron detachment during the Cl drift period, and this is expected to cause the apparent baseline between t = 1 and 3 ms as a tail of electron signal. This tail should be due to the thermally detached electrons that are produced as the Cl⁻ packet passes through the drift tube. This is a first-order reaction [2, 3]. Because the mobility of electrons is several orders of magnitude greater than that of all negative ions, the occurrence of a thermal detachment event by Cl⁻ anywhere along the drift tube is expected to result in the near-instantaneous arrival of that detached electron at the Faraday plate. Figure 1 shows the Cl⁻ peak and electron peak with tail that is related to the electrons produced from electron detachment reaction of Cl⁻. At all temperatures, the decay of the elevated baseline observed for electron signal is expected to be given by equation $\ln I = -k_{\text{TED}} t + C$, where I is the intensity of electron tail signal, t is the drift time of them, and C is constant. As it was shown in figure 2 a plot of ln I versus t is thereby expected to provide a straight line of slope equal to - k_{TED} . This is expected to provide a means of determining k_{TED} under different temperature conditions. The activation energy of electron detachment reaction was obtained from rate constant data at different temperatures based on Arrhenius equation. Figure 3 shows $\ln k$ versus I/T is thereby expected to provide a straight line with the slope equal to $-E_a/R$.





Conclusion:

We have shown here that the IMS method can be successfully applied for studying of gas phase ionic reactions at atmospheric pressures such as TED reactions. Rate constants were determined here for TED of the Cl⁻ anion at different temperatures. We can also obtain the activation energy from rate constant data at different temperatures. It would seem likely that the results identified here for the TED reaction of Cl⁻ might also be operative for other ion–molecule reaction systems.





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Quantum Chemical and Theoretical Kinetics Studies on the H + CO₂ Reaction

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Keywords: Quantum Chemical, Kinetics study, RRKM theory, Carbon dioxide.

Introduction:

The $H + CO_2$ reaction is of great importance in atmospheric and combustion chemistry. Although its reverse reaction, OH + CO, has an extensive literature [1], no theoretical study is performed on kinetics and mechanism of the title reaction.

Method:

The potential energy surface for the reaction of $H + CO_2$ is explored by using various quantum chemical methods including W1BD, CBS-QB3, G4, G3B3, CCSD(T), QCISD(T), M06-2X, B2PLYPD, mPW2PLYPD, ω -B97XD and BB1K. Transition state theory and a modified strong collision/RRKM model [2] are employed to calculate the thermal rate coefficients for the formation of major products as a function of temperature and pressure. The computed rate constants and branching ratios are compared with the available experimental data.

Results and Discussions:

The relative energies of the stationary points located on the doublet ground-state potential energy surface of the reaction calculated by W1BD method are illustrated in Figure 1. Figure 2 shows the Arrhenius plot for the reaction channel R1 in comparison with the available experimental data. By using the barrier heights at the W1BD level, the non-Arrhenius expressions for the reaction channels R1 were found to be $k_1 = 7.0 \times 10^9 \times (T/298)^{1.3} \times exp(-11000 \text{ K/T}) \text{ L mol}^{-1} \text{ s}^{-1}$.



Conclusion:

A number of important results emerge from this study. The major product channel is OH + CO. A modified strong collision/RRKM model predicts well the thermal rate coefficients and the overall rate coefficient computed in the temperature range of 600-2500 K are in accordance with the available experimental data.

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High efficiency photoreduction of Nitrobenzene to Aniline over CdS-TiO₂/based photocatalysts modified with Amino acid under visible light

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Key words : CdS-TiO₂, Amino acid, Microemulsion, Nitrobenzene

Abstract:

Nanosized CdS coupled TiO₂ nanocrystals were prepared by a microemulsion-mediated solvothermal method at relatively low temperatures. Nanocomposite modificated with different types of Amino acid (AA) such as Tyrosine, Phenyl alanine, Glysine and Glutamate .The prepared samples were characterized by DRS ,SEM-EDX ,XRD ,BET and FTIR analysis methods. The results showed that Tyrosine induces more enhance in photoreduction rate of Nitrobenzene (NB) to aniline, under visible light irradiation. Highly dispersed nanocrystals ,a homogenous and mesoporous structure of nanocomposite can be the advantages of microemulsion method.

Introduction :

Nitrobenzene (NB) is considered to be a highly toxic aromatic compound which is widely used in different productions. Due to the electron-deficient, the oxidation of nitroaromatic compounds is very difficult to achieve .Nanosized particles of titanium dioxide (TiO₂) have excellent photocatalytic properties and have found applications in environmental remediation[1,2]. Lots of efforts have been made to modify titania in order to develop photocatalytic performance.CdS–TiO₂ is an excellent candidate for Photo decomposition of pollutants due to its intrinsic energy band gap[3,4]. In CdS-nanocomposite CdS which is a narrow band gap semiconductor was added to TiO₂ to improve the response of TiO₂ to visible light and also TiO₂ prevents the photocorrision of CdS .





Experimental (Methods and materials):

Titanium tetraisopropoxide (TTIP) was used as a titanium precursors $,Cd(NO_3)_2$ and $(NH_4)_2S$ were used as precursors of CdS obtained from Merck. A typical synthesis of sample involved the use of cyclohexane as oil phase, Triton X-100 as surfactant and 1-hexanol as cosurfactant. The resulted microemulsion was placed in a Teflon-lined stainless steel autoclave which is initially bubbled with N₂ gas and then solvothermally treated. The yellow slurry obtained was centrifuged and washed with ethanol and water. Finally modified CdS- TiO₂ catalyst was achieved by soaking the prepared TiO₂ for 24 h in ethanol solution of (AA) at room temperature. Photocatalytic activities of the samples were evaluated by investigation of (NB) photoreduction in aqueous solution under visible light irradiation.

Results and Discussions:

XRD analysis shows distinctive TiO_2 and CdS peaks that are corresponded to the anatase and cubic phase respectively. It was not appeared new diffraction peaks in the pattern of photocatalysts contained (AA) .SEM images reveal that the distribution of the surface particles is homogenous with average size 45nm of nanoparticles. The BET data demonstrate that modifying CdS-TiO₂ (AA) increases the surface area. The effect of surface modification on the adsorption capability and photoreduction efficiency, pH on the photoactivity and amount of loaded (AA) was investigated. The results indicated that the highest photoreduction efficiency and adsorption is obtained with Tyrosine modification. Tyrosine with a phenol ring has a compatible structure with NB .

Conclusion:

The effects of surface modification of CdS- TiO_2 with (AA) on selective photoreduction of (NB) to aniline were investigated. Due to the strong electron-donatin properties, they act as a hole trap to prevent electron/hole recombination and provide stable surface layer with reduction pathway. Furthermore, the modification enhanced the adsorption capability and the absorption properties of CdS-TiO₂ in visible light range and reduced the band gap.

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investigation of dye- surfactant ion pair formation in aqueous solution

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Keywords: Conductometry, Anionic dye, Cationic surfactant, Thermodynamics

Introduction:

The interaction between dyes and surfactants are subjects of numerous investigations [1]. If a surfactant is added to a dye solution at submicellar concentrations, the surfactant monomers and dye aggregates can interact. The formation of ion association complexes between ionic surfactants and dyes with opposite charge, at surfactant concentrations below the critical micelle concentration (CMC), is supported by most published data.

In this paper, conductometric studies of the interactions between anionic dye Acid Greeen 25 (AG25) and cetylpyridinium chloride (CPC), is described. To understand the importance of different types of interactions for the formation of a dye- surfactant ion pair, a series of conductance measurement was performed at five different temperatures. A theoretical method was used to calculate the equilibrium constant and other thermodynamic functions for the formation of the dye- surfactant ion pair.

Methods:

The conductance measurements of solutions were performed with Metrohm 712 digital conductometer using a dip type cell of cell constant 0.99 cm⁻¹. The specific conductivity of deionized water was measured before the each series of measurement at each temperature. Then the specific conductivity of an exact volume and known concentration of AG solution (10^{-4} M) was measured. Binary mixtures of dye/surfactant were prepared by keeping the dye concentration constant but by increasing the surfactant concentration. Then the specific conductivity of each solution was measured. Measurements were made at 25.0, 30.0, 35.0, 40.0, and 45.0 °C. The temperature of solutions was kept within the range of ± 0.1 °C.





Results and discussion:

The results of experimental data show that, the measured conductances of the AG25-CPC mixtures are lower than the sum of the specific conductivities of the individual AG25 and of the individual surfactant molecules. If there were no interaction between AG25 and surfactant in the solution, the experimentally measured conductance of the mixed solution should be the sum of the conductivities of the individual AG25 ions and surfactant ions in the solution [2-5]. The decrease in the measured values can be explained by the formation of a non-conducting or a less-conducting specie in the solution. The increase in temperature from 25 to 45°C caused an decrease in the formation of non-conducting or less-conducting species for the studied system. The equilibrium constants were calculated by using a theoretical model based on the deviation from linear behavior. This model is based on the comparison between the measured conductivity of the dye-surfactant mixture and a theoretical straight line that represents the sum of the specific conductivities of the dye and the surfactant. The values of equilibrium constant, K, standard free energy changes, ΔG^{o} , the standard enthalpy changes, ΔH^{o} and the standard entropy changes, ΔS^{o} , for the reaction of complex formation were given in Table 1. Results revealed that an increase in temperature caused a decrease in equilibrium constant and the negative ΔG° values as seen from table 1. It is clear that as the temperature increases, the tendency to form dye- surfactant complex decreases. The similar trends were reported in the literature [2-5]. The negative values of ΔH° indicate that complex formation processes of dye- surfactant system is exothermic and the positive ΔS° values means that the binding of AG to the surfactant causes a decrease in the order of the process.

Т	K	$\Delta \mathbf{G^o}$	ΔH°	ΔS ^o
(⁰ C)	(M ⁻²)	(kJ.mol ⁻¹)	(kJ.mol ⁻¹)	(J.mol ⁻¹ .K ⁻¹)
25	9.91×10 ⁷	-45.62		152.97
30	8.04×10^{7}	-45.85		151.22
35	6.65×10^7	-46.12	-31.47	149.65
40	5.25×10^{7}	-46.26		147.69
45	4.52×10^{7}	-46.6		146.44

Table 1: The values of K, ΔG° , ΔH° and ΔS° for AG25- CPC complex formations.

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Adsorption kinetics of congo red on cellulose

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Keywords: Adsorption Kinetics, dye, isotherm.

Introduction:

The removal of color from aquatic systems caused by presence of synthetic dyes that usually contains azo-aromatic groups is extremely important from the environmental viewpoint because most of these dyes are toxic,mutagenic,and carcinogenic.Congo red (CR) is an anionic dye widely used in textile,rubber,paper,and plastic industries,and as a pH indicator (Figure 1).Using kinetic models,we can investigate the mechanism of adsorption.The study of adsorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid-liquid interface [1-4].



Materials and Methods:

In adsorption kinetic experiments, 20 ml of CR aqueous solution in the concentration range of 2×10^{-5} - 2×10^{-4} M was transferred to a series of glass stoppered bottles, each containing 0.1 g of chromatography paper sample. At predetermined times, the content of CR in the solutions was determined by UV spectrometry at λ_{max} = 499nm.These experiments were conducted by batch procedure and constant shaking (148 rpm) at 308, 318 and 328 K in a thermostated shaker.





In this work , kinetics of adsorption rate of CR on cellulose were studied. Kinetics of adsorption process was evaluated by the lagergern , pseudo- second- order , avrami ,tobin Elovich and pore-diffusion equations.

Results and discussion:

Figs. 2 a-c show adsorption amounts of CR on cellulose. Results show that the that equilibrium CR uptake, q_e , values decrease with increasing temperature. Effects of time



variations on extent of adsorption can be divided into three different regions, They are (1) linear increase in adsorption with time, (2) transition region where the rate of adsorption levels off, and (3) a plateau region. The range over which the regions extend varies with the bulk concentration, presence of salt, nature of solid surface and so on [3].

Figure 2 Variation of adsorption capacity, q_t , with time at (a) 308 ,(b) 318 and (c) 328 K.The initial concentrations of CR are 0.02, \Box 0.045, Δ 0.07, x 0.2, \blacksquare 0.45 and \diamond 0.7 m M.

Conclusion:

Kinetic data were modeled using the pseudo-second-order equation. It is obtaind from the Elovich equation that initial adsorption rate of adsorption is first-order in CR and diffusion of the CR molecules into the filter paper is the main rate-limiting step of the process.

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Thermal degradation behavior of Polyvinyl alcohol/Starch/Carboxymethyl cellulose biocomposites

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Keywords: Thermal degradation; Thermal stability; Biocomposite; PVA/S/CMC blend; Thermogravimetry

Introduction:

Biodegradable polymers have recently attracted much public and industrial interest because of the increasing waste disposal problem. Besides solutions such as incineration, recycling or re-use, biodegradable polymers can be entirely converted by microbial activity in a biologically active environment to biomass and biological by-products. Nowadays, the use of biodegradable polymers as replacement of commodities for large scale applications is quite small, as their cost is still not competitive. One economically and ecologically attractive approach to overcome these limitations is to incorporate natural polymers into biodegradable polymers to obtain environmentally friendly composite materials called biocomposites, with the advantage of being completely biodegradable. Several articles in the literature were devoted to the study of the thermal decomposition of biomass derived materials, and mixtures of vinyl polymers and lignocellulosic materials. The analysis of the thermal behavior of mixtures of biodegradable/synthetic polymers is important not only from the recycling but also from the processing point of view. The understanding of their thermal stability and degradation has importance in processing and recycling. The main goal of this paper is to evaluate the effect CMC on the PVA/S blends thermal degradation or study of thermal degradation of PVA/S/CMC blends. Thermal analysis of the mixtures was performed by TG/DTG under dynamic conditions. The calculation of apparent activation energies was based on the application the kinetic models proposed by the Van Krevelen, Broido, and Ozawa.





Methods: Films were obtained by the casting method. The kinetics of thermal degradation of PVA/S/CMC blends were investigated by thermogravimetry (TGA) and derivative thermogravimetry (DTG). Experiments under non-isothermal conditions were carried out for samples in nitrogen at heating rates of 7.5, 10 and 15^oC/min.

Results and discussion:

The TGA and DTG curves for PVA/S/CMC blends at heating rate 10° C min⁻¹ are shown in Figure 1. The DTG curves show the degradation rate of the samples. It can be seen that PVA/S/CMC blends exhibited a four-step degradation pattern. The thermal degradation rate depends on conversion (α). For different reactions, the degradation rate given as a function of conversion is different and must be determined from experimental data. In these cases, we used the model free kinetic methods such as the Van krevelen, Broido and Ozawa equations to study the complex degradations of PVA/S/CMC blends. By using Equation Ozawa, the activation energy of degradation can be obtained from the plot of log[β] vs. 1/T. The results were plotted in Figure 2.



Conclusions:

The thermal degradation of PVA/S and PVA/S/CMC blends was divided into four stages. The third stage was the principal degradation process. The calculation of the activation energy of degradation was based on this stage. For PVA/S and PVA/S/CMC, the activation energy of degradation obtained by the Van Krevelen, Broido and Ozawa methods. Obviously, the activation energy obtained by Van Krevelen and Broido was close to that by Ozawa, which meant that these three methods were suitable to describe the thermal degradation of PVA/S and PVA/S/CMC blends. The results obtained from the methods chosen in this study suggested that the addition of CMC improved the thermal stability of PVA/S films. With





considering these results, it seems that the PVA/S/CMC biocomposite films show better thermal properties than PVA/S films and can be potentially replaced of PVA/S films.

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Mechanochemical activation of carboxy methyl cellulose and its thermoplastic polyvinyl alcohol/starch biocomposites with enhanced physicochemical properties

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Keywords: Starch; Polyvinyl alcohol; Carboxy methyl cellulose; Biocomposites; Physical properties.

Introduction:

Naturally renewable biopolymers, such as polysaccharides can form into either coating or stand-alone films. Biopolymer films have been the focus of worldwide attention for the past few decades because they offer favorable environmental advantages. In order to solve the problems generated by plastic waste, many efforts have been done to obtain an environmental friendly material. Most of the researches are focused on substitution of the petro-based plastics by biodegradable materials with similar properties and low in cost [1-2]. PVA, carboxy methyl cellulose (CMC) and starch are polar polymers; thus a composite of PVA, CMC and starch is likely to produce a material having excellent mechanical properties [3]. This study reports on the effect of CMC content, on the properties of PVA/starch films, such as mechanical, thermal and morphological parameters. These studies were carried out to assess their potential uses as packaging films.

Methods: Films were obtained by the casting method [4]. Ultimate tensile strength and strain to break of the films were determined using a tensile tester according to ASTM standard method D882-91[5]. Solubility in water was defined as the percentage of the dry matter of film which is solubilized after 24 h immersion in water. Infrared spectra with a resolution of 4 cm⁻¹ of the samples as KBr pellets were recorded by Shimadzu FT-IR RF50





spectrometer. The morphology of the surface of the films was investigated using a scanning electronic microscope.

Results and discussion:

The curves reported in Fig. 1 show an improvement of the mechanical strength with the increase of CMC content. FTIR spectra of thermoplastic PVA/S/CMC composite showed a number or variants in H-bonding between starch chains, PVA and CMC during casting processing. Fig. 2 shows the morphology of PVA/S/CMC films with different contents of starch and CMC. The addition of CMC significantly changes the morphology of PVA/S/CMC composite. Blends PVA/S and PVA/S/CMC had a uniform morphology, with no evidence of phase separation.



Conclusions:

The present study shows the role of CMC on the physicmechanical properties of PVA/S films. Solubility of the films increased from 27.14% to 46.27%. The addition of CMC to PVA/S blends improved the mechanical properties of the resulted starch based composites. In addition, by increasing of CMC content, outward properties of the composite films improved appreciably. The Scanning electron microscopy indicates morphological structure of the PVA/S films in the different percent of CMC.





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Intramolecular hydrogen bonding in enol form of α-substitution of (Z) -4, 6-dioxo-6-phenylhex-2-enoic acid [ZDPEA]

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Key word: Intramolecular hydrogen bonding, β -Dicarbonyl, α -substitution, (Z) -4, 6-dioxo-6-phenylhex-2-enoic acid

Introduction:

The cis-enol forms of β -diketones are stabilized by a strong intramolecular hydrogen bond. This hydrogen bond formation lead to an enhancement of the resonance conjugation of the π electrons, which causes a marked tendency for equalization of the bond order of the valence bonds in the resulting six-member chelated ring. Therefore, it seems that any parameter that effects the electron density of the chelated ring will change the hydrogen bond strength. It is well known that substitution in α - or β -position drastically changes the hydrogen bond strength and the equilibrium between keto and enol tautomers.

Methods:

The GAUSSIAN 98w program suite was used for all quantum chemical calculations. The full geometry optimization was performed at B3LYP level with 6-311G** basis sets.

Result and discussion:

According to our calculation, the energy values of 1, 2, 3, 4: -764.4163103, -856.6738484, -1254.8666362 and -1101.544 3214(hartree) respectively, therefore the following trend in stability has been obtained: 1 < 2 < 4 < 3

The intramolecular H bond stabilizes the cis– enol Form of ZDPEA by14.34381183 kcal/mol. Calculations indicate that the strength of such a bridge decreases when an electron-withdrawing group replaces the H in position α (position 3 in Fig. 1). The CN, CF₃ and SCN





functional groups have different substitution effects such as electron withdrawing, steric and mesomeric effects .The full-optimized geometries of ZDPEA, CN, CF₃ and SCN are summarized in Table 1 and the geometry of ZDPEA and the numbering of the atoms is given in Fig. 1. The effect of the CN, SCN and CF₃ groups on the π -delocalization in the chelated ring could also be explained in terms of the Gilli's symmetry coordinates q₁, q₂, Q, λ (see Table 1). By comparing these coordinates for the most stable molecules respectively 4, 3, 2 one can deduce that there is less bond equalization, or π -delocalization, in SCN, CF₃ and CN substituted ZDPEA than in ZDPEA itself.

Conclusion:

The results of theoretical calculations show that the, SCN, CN, CF₃, substitution in α -Position of ZDPEA caused that the conjugation in the chelate ring is decreased. Geometrical analysis indicates that SCN, CN, CF₃ substitution in α - position decreases the hydrogen bond strength. All theoretical calculations reveal weaker intramolecular H-bond by CN, SCN and CF₃ substitution in the α -position of ZDPEA than that in ZDPEA.



Fig.1.The geometry of ZDPEA (X=H) X=H (1), CN (2), SCN (3), CF₃ (4)





Table 1

Geometrical parameters of the enol ring of the1, 2, 3, 4 molecules, calculated at B3LYP/6-311G**

Bond lengths (A°)	1(X=H)	2(X=CN)	3(X=SCN)	4(X=CF ₃)	
С=О	1.260	1.262	1.263	1.262	
C-C	1.420	1.450	1.450	1.450	
С=С	1.380	1.400	1.400	1.400	
C-0	1.320	1.310	1.310	1.310	
00	2.520	2.470	2.467	2.460	
О-Н	1.002	1.009	1.007	1.006	
Bond angles(degrees)					
C-C=0	121.070	119.652	119.112	119.514	
C=C-C	121.360	120.000	119.980	118.920	
C=C-O	120.730	119.900	120.550	120.530	
С-О-Н	107.160	107.740	107.520	107.660	
^a Gilli's Parameters		X			
q ₁	0.040	0.050	0.050	0.050	
q ₂	0.06	0.048	0.047	0.048	
Q	0.1	0.098	0.097	0.098	
λ	0.34375	0.346875	0.348438	0.498469	
E _{HB} (kcal/mol)	14.34381183	13.79693687	13.01888722	12.29712522	

^a $q_1 = (d C-C)-(d C=C), q_2 = (d C-O)-(d C=O), Q = q_1+q_2, \lambda = (1 - Q/0.32)/2$

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Kinetic study of Pb²⁺ adsorption on the polypyrole/HMS nanocomposite

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Key words: nanocomposite · polypyrole · sol-gel method ·

Introduction

Water pollution by heavy metals remains an important environmental issue associated negatively with the health and ecosystem [1] and removal of them from aqueous streams is an important problem in the waste water treatment plants. Various treatment processes have been introduced for the removal of metal ions [2]. Current treatment processes include precipitation, oxidation/reduction, membrane filtration/ osmosis, ion exchange and adsorption. In this paper a new nanocomposite including polypyrole conductive polymer supported on hexagonal mesoporous silicate (HMS) was synthesized. The kinetic study of adsorption of Pb cations on the composite was investigated.

Method

The HMS materials were synthesized by sol–gel method similar to Pinnavaia and coworkers [3], used TEOS as the silica source and dodecylamine as the surfactant. Coating of polymer on HMS was performed by pyrole as the monomer, KIO₃ as an initiator in 100 cc of sulfuric acid (1M). The adsorption experiments were done for the study the effect of experimental conditions on Pb²⁺ adsorption and determining the conditions that achieve the maximum amount of removal. Isotherm, kinetic and thermodynamic evaluations were also conducted in this study.





Results and discussion

Our results showed that the synthesized nanocomposite of polypyrole/HMS had a high efficiency for removal of Pb cations from water. Maximum efficiency was 100% for solution having the concentration of lower than 100 ppm and 99% for upper than 100 ppm.



Figure 1. Pseudo-second-order diagram for 100 ppm solution of Pb^{2+} at pH=5 and 0.05 gr nanocomposite Analysis of kinetic study showed that all experiments were performed as the pseudo-secondorder reactions.

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Kinetic study of DPPH scavenging in the presence of Taxol as an anti cancer , Ascorbic Acid as an antioxidant and mixture of them

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Key words: Chemical Kinetics, Antioxidant, Paclitaxel (Taxol), DPPH, UV-Vis spectroscopy

Introduction

Antioxidant compounds in food play an important role as a healthprotecting factor. Scientific evidence suggests that antioxidants reduce the risk for chronic diseases including cancer and heart disease. Antioxidants are substances that can prevent or delay oxidative damage of lipids, proteins and nucleic acids by reactive oxygen species, which include reactive free radicals such as superoxide, hydroxyl, peroxyl, alkoxyl and non- radicals such as hydrogen peroxide, hypochlorous, etc. They scavenge radicals by inhibiting initiation and breaking chain propagation or suppressing formation of free radicals by binding to the metal ions, reducing hydrogen peroxide, and quenching superoxide and singlet oxygen . These analytical methods measure the radicalscavenging activity of antioxidants against free radicals like the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical, the superoxide anion radical (O2), the hydroxyl radical (OH), or the peroxyl radical (ROO). Paclitaxel is a mitotic inhibitor used in cancer chemotherapy. It was discovered in a U.S. National Cancer Institute program at the Research Triangle Institute in 1967 .Taxus brevifolia and named it taxol. Paclitaxel is now used to treat patients with lung, ovarian, breast cancer, head and neck cancer [1-3].

It is the aim of this paper to investigate the free radical-scavenging and antioxidant activities of Ascorbic Acid (vitamin C), Paclitaxel(Taxol) and mixture of them





Materials and methods:

Taxol was obtained from Biolyse Pharmacopee (Port-Danial, quebec) and recrystallized from methanol [3]. .2,2-diphenyl-1-picrylhydrazyl (DPPH) was obtained from Sigma Aldrich Co., St. Louis, USA . Vitamin C was purchased from Sigma–Aldrich. Acetonitrile solvent (CH3CN) was purchased from Merck[4]. The H-transfer reactions from an antioxidant and drug to DPPH were monitored using UV-Vis spectrophotometer. The temperature in the cell was kept at 25°C by using circulator. The Kinetic parameters such as rate constant and activation energy in experimental conditions were calculated.

Apparatus:

UV- Vis spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory which model is Perkin Elmer Lamda 25. Circulator is usually a three port ferro-magnetic device .

Result and discussion:

In this study, the antioxditve activity of the Vitamin C and Taxol were measured using DPPH free radical scavenging activity. The DPPH method is based on the ability to scavenge the free radical DPPH in the presence of the non radical from DPPH-H. The rate constants of the H atom abstraction by DPPH (k) were determined by plotting $\ln(A_t - A_{\infty})/(A_0 - A_{\infty})$ versus time, in the presence of Vitamin C, Taxol and mixture of them were obtained 0.1671, 0.0271, 0.0918 (s⁻¹) under pseudo-first-order conditions at 25° C. The activation energy for DPPH scavenging in the presence of Taxol, Vitamin C and mixture of them was calculated from the angular coefficient of the plot of ln (k) versus 1/T. The value of activation energy for binary system is $E_a = -23.15$ kJ.mol⁻¹, $E_a = -4.868$ kJ.mol⁻¹ for Vitamin C and $E_a = -21.676$ kJ.mol⁻¹ for Taxol. In the presence of Taxol, Vitamin C and mixture of them capable of donating an H atom its free radical nature is lost hence the reduction in DPPH radical was determined by the decrease in its absorbance at a wavelength of 515-522 nm [5].





Conclusion:

The present study shows that the antioxidant activity of taxol and antioxidant activity of vitamin C, will aid in the interpretation of clinical results obtained as various food products are tested in biological models for chronic disease. It is reasonable to expect that high antioxidant of vitamin c has greater potential to reduce free radicals in the body than do mixture of vitamin C and taxol.

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Kinetic and Thermodynamic study of Molecule 6-Amino-3-Hydroxy-3,4-Dimethyl-1-Phenyl-2,3- Dihydropyrano[3,4-C]Pyrrole-7-Carbonitrile in the gas phase

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Key words: Kinetics, Potential Energy Surface, Barrier Energy, Thermodynamic.

Introduction:

In the present work, the reaction of 6-amino-3-hydroxy-3,4-dimethyl-1-phenyl-2,3dihydropyrano[3,4-c]pyrrole-7-carbonitrile are studied in gas phase.



There are two possible pathways for the reaction which could either lead to the generation 6amino-4-methyl-3-methylene-1-phenyl-2,3-dihydropyrano[3,4-c]pyrrole-7-carbonitrile (pathway 1) or 6-amino-3-methyl-4-methylene-1-phenyl-2,4-dihydropyrano [3,4-c]pyrrole-7-carbonitrile (pathway 2) as reaction products. Therefore, the theoretical method was used to estimate the activation energy of each reaction step through construction of transition state. Comparison of the calculated activation energies of reaction steps can be used to get information about more favorable pathway and major product. All calculations are studied at MPWBIK^[1]/6-31+G(d,p)level of theory. Potential energy surface (PES), energy barrier and Gibbs free energy are obtained for possible channels.

Materials and methods:





All the geometries of the molecules at gas phase are fully optimized at MPWB1k/6-31+G(d,p) level of theory using the Gaussian03 programs. The potential energy Surface (PES) for each pathway are plotted. Frequency calculations were carried out in order to confirm the structures ground states and saddle points and to obtain zero-point vibration energy corrections ^[2].

Result and discussion:

Two possible reaction pathways were investigated carefully. The geometries of all compounds at gas phase were fully optimized (scheme 2). Relative energies of reaction have reported in figure 1.



the stationary points at of MPWb1K/6-31+G(d,p) level.

Figure 1: Comparison The potential energy reaction pathway 1 and 2.

In this reaction oxygen atom number 27 abstract hydrogen atom number 7 to generated product 1 via transition state 1.the activation energy for this pathway is 289.23 kJ/mol. In other hand oxygen atom number 27 abstract hydrogen atom number 12 to generated product 2 via transition state 2. the activation energy for this path 205.58 kJ/mol. This result indicates that activation energy of R2 is 83.65kJ/mol less than this value for R1. The product 2 is also 61.91kj/mol more stable than product 1. Δ G, Ea and Δ H are reported in table1.

	Ea	$\Delta \mathbf{H}$	$\Delta \mathbf{G}$
R 1	289.23	81.49	32.51
R 2	205.58	0.01	-29.60

Table 1. Activation Energy(E_a), enthalpy (Δ H), Gibbs free energy (Δ G) in (kJ/mol) at the MPWBIK/6-31+G(d,p) level. All value are corrected byZero Point Energy





Conclusion:

Kinetics and thermodynamic parameters achieved in this study showed that P2 is a significant product.

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Kinetic study of reaction of -nitro-1H-benzo[d]imidazole to produce6-nitro-1Hbenzo[d]imidazole

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Key words: Kinetics, potential energy surface, Rate Constant, Tautomerization.

Introduction:

In this investigation, reaction of 5-nitro-1H-benzo[d]imidazole to produce 6-nitro-1H-benzo[d]imidazole is studied in the gas phase at the MPWblK/6-31+G(d,p) level of theory.



These two compounds are tautomers that have interconvert by a process known as tautomerization. All calculations are studied at this level and potential energy surface (PES), activation energy and Gibbs free energy are reported for possible channels.

Materials and methods:

Quantum chemical calculations are carried out using the Gaussian03 program, at the MPWblK level with 6-31+G (d,p) basis sets. All species optimized at this level. The potential energy surfaces (PES) for each pathway are plotted. Harmonic vibrational frequencies are obtained to determine the exactness of transition state and to obtain zero-point vibration energy correction. RRKM theory is used to calculate Rate constant of this reaction. For an unimolecular reaction, $A^* \xrightarrow{k} A^* \longrightarrow P$

Where A^* is the energized reactant, A^{\neq} is the activated complex, and P represents product. This rate constant, k(E), according to the RRKM theory can be expressed as: $k(E) = \frac{\sigma}{h} \cdot \frac{W^{\neq}(E-E^{\neq})}{\rho(E)}$





Where σ is the symmetry factor, $W^{\neq}(E-E^{\neq})$ denotes the total number of states of the TS With activation energy E^{\neq} , and $\rho(E)$ represents the density of states of the energized reactantmolecule [1].

Result and discussion:

Geometries of optimized structure of all species are shown in figure 2.Potential energy surface (PES) is used to calculated activation energy. PES and relative energies of reaction have reported in one dimensional in figure 1 and 2, respectively. PES consists of two transition states (TS₁ and TS₂)and an energized intermediate (Int).



 Figure 1. Potential energy surface
 Figure 2. Relative energies of reaction
 Figure 3. Arrhenius plot for reaction.forreaction at MPWBlK/6-31+G

 at MPWblK/6-31+G(d,p) level. All
 Symbols represent tunneling effect.(d,p) level of theory.
 values are corrected by zero point energy.

As it is shown in scheme 1 in R1 reaction carbon atom number 1 abstract hydrogen atom number 15 to generate intermediate via transition state 1 (with imaginary frequency 1427.7i cm⁻¹). The barrier energy for this reaction is 242.5 (kJ mol⁻¹). In R2reaction, nitrogen atom number 2 abstract hydrogen atom number 15 to produce product via transition state 2 (with imaginary frequency 1412.93i cm⁻¹). The barrier energy for this reaction is 81.1 (kJ mol⁻¹).

Non-linear least-squares fitty used to calculate rate constant expressions for rate constantswhich are plotted in figure 3[2]:

$$k_{nontun} = (\exp 1337.3)(\frac{T}{300})^{167.3} \exp \left[-\frac{52512101.1(T + 4998.3)}{8.314(T^2 + 4998.3^2)} \right]$$

$$E_a = \frac{T^4 + 2(4998.3)T^3 - (4998.3)^2 T^2}{(T^2 + 4998.3^2)^2} + 167.3(8.314)T^4 + 16$$





Conclusion:

Reactant and product are 158.4 and 157.9 kJ mol⁻¹ more stable than Int, respectively. ΔG is - 0.51 kJ mol⁻¹ for the overall reaction, Then thermodynamics results show that reactant is also significant same as product.

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Ultrasonic degradation of 2-hydroxyethylcellulose: Effect of molecular mass, concentration, volume and power input

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Keywords: Ultrasonic degradation, Hydroxyethylcellulose, rate constant, viscosity, kinetic model.

Introduction:

The degradation of polymers can occur because of heat, light, chemical reagents or ultrasonic radiation. Ultrasound has been used for degradation of a wide range of polymers. In the field of polymer chemistry, polymer degradation is usually quantified either by molecular weight distribution or by change in the intrinsic viscosity. In general, it can be said that ultrasonic irradiation does have a significant effect on polymers in terms of its mechanical, mechano-chemical and morphological properties.

Hydroxyethyl cellulose (HEC), one of the most important cellulose derivatives, can be employed in extensive utilizations because of its wonderful water-solution properties and the chemical composition with a large amount of relatively easily accessible hydroxyl units. Understanding the effect of different operating parameters on the extent of degradation of HEC thus becomes very important [1,2].

Materials and methods:

Solutions of 1-5 g/L of HEC in water were prepared. Ultrasonic degradation was performed at fixed temperature (25 ± 0.1 ^oC) and different volume (30,70,100 CC), power(20,40,60,80 W) and molecular weight (250000,720000,1300000). Periodically, samples of the sonicated solution were removed and their viscosities were measured.





Apparatus:

Viscosities were measured using a viscometer (setavic kinematic viscometer, England) thermostated at 25 ^oC. XRD spectra and FTIR spectra were obtained using Bruker (Model Tensor 27) instrument to confirm structure of HEC after and before from degradation.

Result and discussion:

The ultrasonic degradation of (HEC) solutions was carried out in water at 25 $^{\circ}$ C. The effect of different operating parameters such as time of irradiation, solution concentration and volume, molecular mass and power input has been investigated. The degradation behavior of HEC was studied through FTIR, XRD analysis and kinetics of degradation was studied by viscometry. Kinetic analysis of the polymer degradation process has also been performed and rate of reaction calculated for different conditions. Order of reactions of polymer obtained -0.64 for M = 1300,000, -1.2 for M = 720,000 and -1.4 for M = 245,000.

Conclusions:

The experimental results indicated that the degradation rate reduced with increasing solution concentration, solution volume and polymer molecular weight but rate of the degradation of the polymer is increased as power input is increased.

This study confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration, weight molecular can be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around the collapsing bubbles to, therefore, become smaller.

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Thermodynamic and kinetic study of adsorption Direct red 81 on ChamomillaMatricaria

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Key words: Direct Red 81 , ChamomillaMatricaria , Adsorption ,Kinetic Study, Isotherm,Thermodynamic

Introduction:

In recent years, the pollution of the wastewaters with dyes is becoming a major environmental problem due to the growing use of a variety of dyes. Dyes usually have a synthetic origin and complex aromatic molecular structures which are more stable and more difficult to biodegrade. It is known that wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules (particularly Azo dyes), resistant to aerobic digestion, and are stable to oxidizing agents. Textile, paper, plastics, and cosmetic industries use a wide variety of dyes to color their products and discharge large amount of effluents including dyes which are very toxic and could cause serious ecological problems. Therefore, dye pollution in water stream is a major environmental problem. The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption, and oxidation.

The use of cheap, high efficiency and ecofriendly adsorbent has been studied as an alternative source of activated carbon for the removal of dyes from waste water. This study investigates the use of activated carbons prepared from ChamomillaMatricaria as a local low cost, and available in Iran for the removal of direct red dye from aqueous solution.





A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. temperature, initial dye concentration, adsorbent dosage and contact time. Also adsorption kinetic and thermodynamic parameters were calculated.

Material and methods:

Direct red 81 dye was purchased from Germany Aldrich Company.

A stock solution of 1000 mg/L was prepared by dissolving the required amount of dye in double distilled water.

Working solutions of the desired concentrations were obtained by successive dilutions of the stock solution. The concentration of the dye was determined at 510.6 nm, using UV-Vis spectrophotometer.

The tools have been applied for adsorption techniques are suitable. Chamomile Matricariaisdried in electric oven. The concentration of the dye was determined using UV-Vis spectrophotometer(PerkinElmer lambda 25).

Result and discussion:

The results showed that the percentage of dye removal increased as the amount of adsorbent increased but it decreased with the increase of initial dye concentration.

The Maximum dye decolorizing was 87.55% and was observed at temperature of $25\degree$ c.

Adsorption kinetic data were tested using pseudo first order and pseudo second ordermodels that the biosorption followed pseudo second order kinetic model. Langmuir and Freundlich isotherms were used to analyze the equilibrium data. In addition, various thermodynamic parameters, suchas $\Delta G,\Delta H$ and ΔS have been calculated. The biosorption process was found to be spontaneous process. The data were in good agreement with Langmuir isotherm. The results were shown that the adsorption of direct red 81 onto ChamomillaMatricariabest fitted by pseudo second order model. The determination of the thermodynamic parameters indicates the spontaneous and exothermic nature of the adsorption process.





Conclusion:

Adsorption has been found to be superior techniques for waste water treatment natural materials that are available in large quantities may have potential as inexpensive sorbents.

The experimental studies concludes the that the activated carbon prepared from Chamomile Matricaria could be employed as low-cost and an effective adsorbent as alternatives to commercial activated carbon for the removal of direct red 81 from aqueous solution and for the removal of color and dye from wastewater , in general.

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Acid hydrolysis of ion-complex Azidopentaamine Cobalt (III) in different concentrations of Sulfuric acid

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Keywords: acid hydrolysis, UV-Visible spectrophotometery, kinetic, mechanism, H₀

Introduction:

Acid catalytic reactions are possible in Ligand-exchanges which are extremely basic and can make hydrogenated band like F^- , NO_2^- , ONO^- , N_3^- , CN^- , $CO_3^{2^-}$,... Also labile chelates and complexes like $[Fe(bipy)_2]^{2^+}$, $[Nien_3]^{2^+}$, $[Fe(EDTA)]^-$,... ^{[1], [2]} The rate of acid hydrolysis $[Co(NH_3)_5N_3]^{2^+}$ ion complex was studied as an acid concentration function by different concentrations of sulfuric acid through Bunnett, Bunnett & Olsen, and Zucker-Hammett hypothesis to comprehend whether this mechanism depends on water. Kinetical analysis is done by UV-Visible spectrophotometric method. This paper aims to provide analysis for acid hydrolysis of ion complex [Co(NH₃)₅N₃]²⁺ in different concentrations of sulfuric acid.

Materials and Methods:

First of all, $[Co(NH_3)_5N_3]Cl_2$ was prepared ^[3] and washed by salty water solution (10 gr Salt & 800 mL water). Secondly, several concentrations of sulfuric acid prepared (2.0-8.0 M) in 50 mL volumetric balloons. 0.001 mol $[Co(NH_3)_5N_3]Cl_2$ complex were inserted in a 10 mL volumetric balloon and were filled up by 2.0 M sulfuric acid. This mixture was posed in UV-Visible spectrophotometer by using 370 nm⁻¹ wave lengths, in order to receive the reaction progress for several times. The same process was repeated by 3.0-8.0 M concentrations of sulfuric acid.

[H ₂ SO ₄]	log [H ₂ SO ₄]	K	log K	3+log K	-H ₀	3+log K+H ₀	$log [H_2SO_4] + H_0$	3+log K- log [H ₂ SO ₄]	$\log a_w$
2.0 M	0.301	0.0092	-2.036	0.9644	0.2841	0.6803	0.0169	0.6633	0.97
3.0 M	0.477	0.0138	-1.860	1.1404	0.4494	0.6910	0.0276 0.6633		0.95
4.0 M	0.602	0.0161	-1.793	1.2074	0.6143	0.5931	-0.0123	0.6053	0.93
5.0 M	0.699	0.1336	-0.874	2.1257	0.7795	1.3462	-0.0805	1.4268	0.91
6.0 M	0.778	0.1428	-0.845	2.1547	0.9448	1.2099	-0.1668	1.3765	0.89
7.0 M	0.845	0.2764	-0.559	2.4415	1.1097	1.3318	-0.2647	1.5964	0.865
8.0 M	0.903	0.8820	-0.055	2.945	1.2749	1.6706	-0.3764	2.0424	0.84

Table 1- Data related to H_2SO_4 at $20^{\circ}C$





Through changes made to percentage of concentration weight of acid and use of available diagrams, $-H_0$ can be obtained.

These values are collected in table 1 and can be very useful to get necessary data for drawing diagrams 1 to 6.

Results and discussion:

In order to study the mechanism of $[Co(NH_3)_5N_3]Cl_2$ acid hydrolysis, three hypothesis shall be used. These hypotheses are known as Zucker-Hammett, Bunnett, Bunnett & Olsen.^[4]

<u>Zucker-Hammett hypothesis:</u> If the gradiant of logK vs. $-H_0$ diagram be equal to 1.0, the mechanism of reaction is SN₁CA and if the gradiant of logK vs. log[H⁺] diagram be equal to 1.0, the mechanism will be SN₂CA.^[4]







<u>Bunnett hypothesis</u>: Based on equations $\log_{10}K + H_0 = w \log_{10}a_w + C$ and $\log_{10}K - \log_{10}[H^+] = w^* \log_{10}a_w + D$ the values of w and w* will be found from 3 and 4 diagrams:

w values	w [*] values	function of water in rate-determining step			
-2.5 to 0.0	-	Not involved			
+1.2 to +3.3	< -2	As nucleophile			
> 3.3	> -2	As a proton transfer agent			

Table 2- Studying relations between w - w* and water interfering in mechanism

Bunnett & Olsen hypothesis: To get more assurance, we need to use another hypothesis. Based on the equation $(\log K + H_0) = \varphi (H_0 + \log[H^+]) + C$ That C is a constant value, φ was found from diagram 5. By using Bunnett & Olsen hypothesis: ^[4]

If $-0.34 < \phi < 0$, water don't involve in mechanism

If $0.18 < \phi < 0.47$, water act as a nucleophile

If $0.47 < \phi$, water acts as a proton transfer agent

Conclusions:

Based on Zucker-Hammett hypothesis and diagrams 1 and 2, recognizing SN_1CA or SN_2CA mechanisms is absolutely impossible, however combination of Bunnett hypothesis and diagrams 3 and 4 pointed w = -8.115 and w^{*} = -11.32, while these result were not in data range of table 2. Therefore interference of water in the mechanism cannot be recognized by this hypothesis. Based on Bunnett & Olsen hypothesis and understanding that slope in diagram 5 is equal to -2.463, first part of hypothesis is accurate and proves that water does not necessarily meddle the mechanism. Therefore below mechanism is suggested:

 $[Co(NH_3)_5N_3]^{2+} + H_3O^+$ $(Co(NH_3)_5N_3H)^{3+} + H_2O^+$

 $[Co(NH_3)_5N_3H]^{3+} + H_2O \xrightarrow{\text{slow}} [Co(NH_3)_5 H_2O]^{3+} + HN_3$ Rate.D = K.[Co(NH_3)_5N_3H]^{3+} [H_3O]^+ $K_{eq} = [Co(NH_3)_5N_3H]^{3+}.[H_2O]/ [Co(NH_3)_5N_3]^{2+}.[H_3O^+]$ \Rightarrow Rate_{obs}=K.K_{eq}. [Co(NH_3)_5N_3]^{2+}.[H_3O^+]





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A kinetic study on meltingof diphenylamine by thermogravimetric analysis.

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Keywords: Diphenylamine, Non-isothermal, Thermogravimetric analysis, Kinetics study.

Introduction:

Many transformations may occur when a solid sample is heated, such as: melting, sublimation, polymorphic transformation, or degradation [1]. The most widely used stabilizers are from the classes of (a) aromatic amines and (b) urea derivatives.Examples for (a) are diphenylamine (DPA), 2-nitro-diphenylamine (2-NDPA), p-itro-N-ethylaniline (pNEA), p-nitro-N-methylaniline (pNMA) and for (b) akardite-II(1-ethyl-3, 3-diphenylurea; AKA-II) and ethyl centralite (1, 3-diethyl-1, 3-diphenylurea, EC) [2].Our aim was to evaluate thermal experimental data of diphenylamine via thermogravimetricanalysis (TGA) by applying well known kinetic equations such as the Coats-Redfern kinetic equation and also Friedman, Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose kinetic equation at various scanning rates. Some parameters such as activation energy, frequency factor and also model of degradation were determined [3].

Materialsandmethods:

The synthesis of diphenylamine from aniline and phenol has been carried out in the presence of a phosphoric acid catalyst.

Apparatus:

The kinetic study was performed on a TGA thermal analyzer (STA-PT 1000) at several heating rates (5, 10, 15, 20, 25, 30 and 35 $^{\circ}$ C/min) from room temperature to 1000 $^{\circ}$ C. The thermal analyzer was temperature calibrated between experiments using the Curie point of Pb as a reference.

Resultsanddiscussion:





Thermogravimetric analysis were done at seven different heating rates. Then based on Coats-Redfern kinetic equation, kinetics' models and also activation energy were calculated.

Fig. 1 shows calculated models.



Fig. 1 shows relation between Coats-Redfern kinetic equation and regression's of models in 5°C/min rate.

Then by use of Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) kinetic equations, activation energy and model of thermal decomposition in each alpha were calculated and compare with Coats-Redfern equation.

Method	E,(kJ mol ⁻¹),forconversion degree,α									Mainvalue
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
FR	26.54	66.14	51.95	30.91	35.21	84.90	8.43	15.31	11.61	36.78
FWO	125.02	135.17	137.71	140.21	142.16	144.33	147.35	146.68	143.11	140.19
KAS	53.44	57.91	58.97	60.04	60.88	61.83	63.17	62.82	61.14	60.02

Conclusion:

Then thermogravimetric analyses were done in different scanning rates. Based on Coats-Redfern kinetic equation, and also by utilize of Friedman equation, kinetics' models and activation energy were calculated and shows same amounts. Then by use of FR, FWO and KAS kinetic equations, activation energy and model of meltingwere calculated.

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Effect of poly-HEMA hydrophilic gel matrix on photo-physical behavior of Thionine

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Key words: Thiazine dyes, Poly-HEMA, Dye aggregation, Thionine, Ionic dyes

Introduction:

Thionine (TH) dye (Fig.1.) is important class of thiazine dyes. The molecular association of dyes in solutions due to strongly attractive electrostatic forces is a well- known phenomenon. Thiazine ionic dyes such as TH can easily form aggregates in solution that quenches the dye fluorescence emission. Photo-physical behavior of a dissolved dye depends on the nature of its environment. By encapsulation of the dyes in to the pore of PHEMA, it would be interesting to understand the role of the environment on the solute –solvent and solute–solute interactions [1-2].



Materials and methods:

Acrylamide(97%),*N*,*N*-methylenebisacrylamide(\geq 98%), *N*,*N*,*N*,*N*-tetramethylethylenediamine (\geq 99%) (TEMED) and ammonium persulfate (\geq 98%) (APS) were used for synthesizing polyacrylamide gels with compositional 40% (Polyacrylamide/Water (w/w)). The TH dye was procured from Exciton and used without further purification. Deionized water was used for all the dilutions and the polymerization reactions, as well as for the swelling and spectroscopic studies.



The dye-loaded hydrogel was prepared by soaking the hydrogel hosts in aqueous solutions of MB dye with known concentration for various durations of time (1 min to 10 hours) at 22 °C.

Apparatus:

Double beam Shimadzu UV-2450 Scan UV–Visible spectrophotometer was used for recording the absorption spectra over a wavelength range between 300 to 800 nm.

Results and discussion

The absorption UV–Vis. spectroscopy is one of the most suitable methods for quantitative study of dye aggregation as a function of concentration, since in the concentration range used $(10^{-3}-10^{-6} M)$, mainly monomer-dimer equilibrium can be detected.

By systematic variation of K_d and analyzing the straight-line fitness in a series of wavelengths, one obtains optimum dimerization constant as well as monomer and dimer spectra [2].

Table. 1. dimerization constants of TH in water and in hydrogel 40%(w/w) in different soaking times.

Soaking time(min)	30	40	50	100	120	Water
LogK	1/99	2/32	2/45	2/63	2/68	2/55

The calculated dimerization constants for the TH in water and in hydrogel 40% in different soaking times were obtained by linear least square fitting methods [3] and presented in table. 1. These data show that in hydrogel media in initial soaking times the dimeric constants are low and increases with increasing the soaking times. These facts can be explained in terms of hydrogel firmness.

Conclusions

The obtained results explain that in initial soaking time TH molecules interact with free water in hydrogel pores. By increasing this time TH interact with hydrogel interactive functional groups in polymeric chain and freezing water molecules in hydrogel pores. In other words, intermonomeric interaction energy of TH in aqueous solution is higher than hydrogel media.

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Solvent effects on the absorption spectra of Co(II)- tetrasulfonated phthalocyanine

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Keywords: Phthalocyanine, Solvent, Polarity, Absorption spectra.

Introduction:

Metal phthalocyanines are interesting macromolecules in nature. and technological importance in many. In recent years, metallophthalocyanines (MPcs) have been extensively studied in nonlinear optic applications, chemical sensors, catalysis, liquid crystals, photovoltaic cells, semiconductive materials and photodynamictherapy (PDT) [1, 2]. This paper aims at reporting the effect of various solvents on the absorption of Co(II)-phthalocyanine.

Material and Method:

Co(II)-phthalocyanine was obtained from Merck. The following solvents were used in this work: DMF, Acetonitrile, DMSO, Methanol and Ethanol were procured from Merck. UV-Visible spectra were recorded on a SPECORD 205 Analitik-jena spectrophotometer from 200 to 800 nm. In an investigation 5μ m phthalocyanine was mixed with various concentration of solutions made in different solvent from 1.4 to 50 μ M.

Resault and Discution:

Co(II)-phthalocyanine is known to aggregate in solution and is usually depicted as a coplanar association of rings progressing from monomer to dimer. In polar solvents like DMSO, DMF and methanol, when concentration is increased, the intensity of the Q band also increased. The intensity of the monomer peak is very high as compared to the peak arising from the aggregated





species as shown in Fig. 1a, b for DMSO and methanol which has been selected randomely. Thus one can presume that most of the dye molecules are present in the monomeric form in solution. On changing the solvent, the positions of the absorption peaks are shifted and indicate that the absorption wavelengths are sensitive to the environmental factors of the solvents. With the increase of solvent polarity, the Q band of the Co(II)-phthalocyanine molecule was red-shifted more than less polar solvent. Fig. 1 shows that the largest red shift (10 nm) of the Q band was observed for Co(II)-phthalocyanine in DMSO.



Fig. 1. Absorption spectra of Co(II)-phthalocyanine in various solvents at different concentrations $(5 \times 10^{-6} \text{ to } 50 \times 10^{-6} \text{ } \mu\text{M})$. [a=DMSO, b=methanol].

The shift to longer wavelength could be due to either the destabilization of the highest occupied molecular orbital (HOMO) or the stabilization of the lowest unoccupied molecular orbital (LUMO) [3]. In another investigation 50 μ m phthalocyanine was mixed with various volume of added solvent. Fig. 2 shows the UV-vis spectral changes of the 50 μ M Co(II)-phthalocyanine upon addition of various solvent in water. With increasing solvent volume the band of dimmer diminishes, and the band at 660 nm, which can be ascribed to the monomeric species, becomes more intense. When the concentration of solution reaches 33 μ M, the spectrum is typical for monomeric phthalocyanines showing Q-band at 660 nm. Again in polar solvents when solvent volume was increased, the intensity of the Q band also increased.



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Fig. 2. the UV-vis spectral changes of the 50μM Co phthalocyanine upon addition of various solvent a) acetonitrile, b)ethanol, c) DMF, d) DMSO

conclusion :

absorption maxima of Co(II)-phthalocyanine are dependent on solvent polarity.

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Thermodynamic and kinetic investigation of Cationic dye removal from textile waste water via CMK-3

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Keywords: Thermodynamics, Kinetic, dye removal, mesoporous carbon CMK-3.

Introduction:

Environmental problems have become a global concern because of their impact on public health. Nearly 25% of the diseases facing humans today occur because long-term exposure to environmental pollution, including air, soil, and water pollution[1]. Dyeing effluent is one of the largest contributors to textile field and such wastewater has a seriously destructive impact on the human health. Various methods such as advance oxidation, photo catalysis, coagulation, membrane filtration, and adsorption, have been reported to prevent dyes discharge and contamination[2]. Among these methods, the adsorption technique is especially attractive because of its high efficiency, simplicity of design, and ease of operation [3]. Many adsorbents have been tested to decrease the dye concentrations from aqueous solutions, such as clay, peat, chitin, silica and activate carbon[4]. Among these activated carbon is widely used to remove aqueous organic pollutants such as dyes, pesticides, phenols and so on[5]. In recent years mesoporous carbon have been used for Hydrogen storage, microextraction, Adsorption and separation of environmental pollutants[6-8]. In the present work mesoporous carbon CMK-3 adsorbent was prepared, characterized, and used for the removal of Janus green B dye from aqueous solution. Adsorption experiments were carried out as batch studies and the experimental data obtained from the equilibrium studies are fitted to Langmuir, Freundlich adsorption models. In addition, kinetic and thermodynamic studies are also carried out to determine the characters of adsorption process.



Materials and methods:

Mesoporous carbon CMK-3 was prepared by using SBA-15silica mesoporous molecular sieves as hard Template[9]. One gram of SBA-15 was added to 5 mL aqueous solution containing 1.25 g sucrose and 0.14 g H₂SO₄. The resulting sludge was heated in an oven at 100 °C for 6 h and then 160 °C for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 5 mL aqueous solution containing 0.8 g sucrose and 0.09 g H₂SO₄ was added again and the mixture was subjected to the thermal treatment describedabove. Then, it was carbonized in an argon flow at 900 °C for 6 h with a heating rate of 5 °C min⁻¹. Finally, the mesoporous carbon (CMK-3) was obtained by removing the silica matrix using a 4 mol/L NaOH solution (50 vol.% ethanol-50 vol.% H₂O) at room temperature followed by filtration, washing, and dryingat 120 °C for 4 h. All materials used in the investigation were purchased from Merck (Germany) but Except Janus green B dye copolymer P123 and was supplied from Aldrich Co.

Apparatus:

The oven by Exciton Company has been applied For the carbonized CMK-3[Model: Ex-1300-33L]. Also adsorbtion investigations were carried using a UV–visible spectrometer (UVIKON 923).

Result and discussion:

The negative free energy changes (ΔG^0) suggested that the adsorption of Janus green B onto CMK-3 adsorbent was feasible and spontaneous thermodynamically. Also the Langmuir isotherm with correlation coefficient of 0.998 represents a better fit of experimental data than Freundlich model with correlation coefficient of 0.899. It indicates that monolayer adsorption of Janus green dye takes place on the homogeneous surface of carbon mesoporous adsorbent.

Conclusions:

Fitting equilibrium data to Langmuir and Freundlich isotherms showed that Langmuir model was more suitable to describe the Janus green B adsorption with maximum monolayer adsorption





capacity of 182.3 mg/g at 25 °C. The adsorption kinetics was found to follow closely the pseudosecond-order kinetic model. The negative values of ΔG^0 and ΔH^0 showed that the adsorption was a spontaneous and exothermic process[10].

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Thermodynamic and Kinetics investigation of adsorption of anionic surfactant sodium dodecyl sulfate using spent tea leaves

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Keywords: spent tea leave, Sodium dodecyl sulfate, Adsorption, Thermodynamic, Kinetics

Introduction:

Many industrial effluents such as wastewater from cosmetic and detergent industries, laundry and car washing services contain mixtures of surfactants. They create much hazardous health like dermatitis and harmful for the aquatic flora and fauna [1]. So, the water treatment process is necessary in order to remove surfactant from industrial and domestic wastes to reduce its concentration. In this study, two types of spent tea leaves were used for adsorption of sodium dodecyl sulfate (SDS) from aqueous solutions.

Materials and methods:

Spent Green and black tea leaves (SGTL, SBTL) were employed as green nonconventional adsorbents for removal of SDS from aqueous solutions. Adsorption experiments were carried out using batch system and the various empirical parameters such as adsorbent dose, initial SDS concentration, contact time and temperature were studied. Unadsorbed SDS measurements were carried out spectrophotometrically [2].

Result and discussion:

Kinetics study is very important in explaining the efficiency of any sorption process. In this investigation, aliquots of adsorbent (0.50 g) were treated with 50 mL of SDS solutions (10 mg L^{-1}) for periods of two hour at room temperature. The pH of solution was selected as the natural pH test solution (pH= 6-7). The results obtained are shown in Table 1. As the data show, high correlation





coefficient as well as good agreement between the experimental (q_{exp}) and theoritical (q_{e2}) sorption capacities interestingly suggests that adsorption of SDS onto SGTL and SBTL followed the pseudo-second-order kinetics model and therefore a chemisorptions mechanism.

	Table 1: Adsorption kinetic parameters of SDS onto SGTL and SBTL adsorbents							
	Pseudo first order				Pseudo second order			
Adsorbent	K_1	q _e	\mathbf{P}^2	K ₂	q _e	P ²	q _{exp}	
Ausoroent	(\min^{-1})	$(mg.g^{-1})$	K	$(g.mg^{-1}.min^{-1})$	$(mg.g^{-1})$		$(mg.g^{-1})$	
SGTL	0.016	0.363	0.6628	0.073	0.927	0.9923	0.906	
SBTL	0.013	0.453	0.4219	0.155	0.555	0.9853	0.544	

The effect of temperature on the adsorption of SDS onto SGTL and SBTL was investigated at various temperatures (298-343 K). The obtained results are presented in Table 2. Negative values of ΔG° in all temperatures indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of SDS for all adsorbents. Positive values of ΔH° indicate the endothermic nature of the process.

Adsorbent	T (K)	$\Delta G^{\circ} (kJ.mol^{-1})$	$\Delta H^{\circ} (kJ.mol^{-1})$	$\Delta S^{\circ} (J.mol^{-1}.K^{-1})$
	288	-2.30		
SGTL	298	-3.17	26.31	99.10
$\mathcal{O}_{\mathcal{X}}$	308	-4.26		
	318	-5.25		
	288	-2.14		
SBTL	298	-2.37		
	308	-4.46	25.67	95.69
	318	-4.72		

Table2: Thermodynamic parameters for adsorption of SDS on SGTL and SBTL





Conclusion:

SGTL was found to be more effective for removal of SDS from water solutions. SGTL is a biomaterial waste which was found an efficient and green adsorbent for removal of SDS from aqueous solutions.

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The role of Formation Chemically Activated Intermediates on the Mechanism and Kinetics of the Reaction of Methoxy Radical with Hydroxyl Radical.

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Keywords: Kinetics; Hydroxyl radical; Methoxy radical; Hydroxy methyl radical

Introduction:

Chemically active species like hydroxyl radical, methoxy radical (CH₃O), and hydroxy methyl radical (CH₂OH) play important role in the atmospheric and combustion processes. Methoxy radical undergoes isomerisation process to produce hydroxy methyl radical. Both methoxy and hydroxy methyl radicals are the key intermediates in the combustion of methanol in oxygen rich regime. The kinetics of the reactions of CH₃O or CH₂OH with hydroxyl radical has been studied in some extent. Methoxy radical is 36.6 kJ mol⁻¹ more stable than hydroxy methyl radical with 125.5 kJ mol⁻¹ activation energy at the CCSD(T)/Aug-cc-pVTZ level of theory. The major product of the reaction of methoxy radical with hydroxyl radical is reported to be formaldehyde and water. The reaction is highly exothermic and the products are 401.9 kJ mol⁻¹ more stable than the reactants. Another path for the reaction of methoxy radical with hydroxyl radical is 174 kJ mol⁻¹ more stable than the reactants. Formation of this chemically activated intermediate increase the possibility of formation of some other products like methane, molecular oxygen and methanol. To the best of our knowledge no data is available for the mechanism and formation of these products.

This is the purpose of the present work to investigate the possibility of formation of CH₃OOH* intermediate and calculating the branching ratio of different channels in this system.



Potential Energy Surface:

Using Gausssian09 program, the energy of the stationary points are calculated at the CCSD(T)/Aug-cc-pVTZ//UMp2/Aug-cc-pVTZ level of theory. Figure 1 shows the schematic of the potential energy surface at the CCSD(T)/aug-cc-pVTZ level. The reported energies in Figure 1 are corrected for the zero point energies. As shown in Figure 1, the presence of two intermediates int1 and int2 should be important for the formation of the other products.



Rate Constant Calculations:

The ab initio data in Figure 1 were used to calculate the overall and individual rate constants. Canonical variational transition state method (CVT) was used to calculate the rate constant for reaction Rx. Zero and small curvature tunneling approximations are used to include the quantum effects in calculating the rate constants. GAUSSRATE9.1¹ program, which is an interface between POLYRATE9.3.1² and Gaussian 03 program, was employed in our CVT calculations.

For those channels proceed through the chemically activated intermediates int1 and int2, RRKM-TST method suggested by Dean³ was used to calculate the overall and individual rate constants.





The quantitative and qualitative effect of the tunneling process on the rate constants and rate constant branching ratios will be discussed in detail.

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Interplay between inter and intra molecular addition of n-methylaniline and side-chain amine group of neurotransmitters

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Keywords: kinetic study, Michael addition, catecholamine, rate constant

Introduction:

Among the organic compounds, catechols and catecholamines can be easily oxidized chemically or electrochemically to the corresponding reactive *o*-quinones. It is worth mentioning that catechols are used in a variety of applications including photography, dying, rubber and plastic production and pharmaceutical industry [1]. In addition, catechol derivatives play an important role in mammalian metabolism, and many compounds of this type are known to be secondary metabolites of higher plants. Aromatic vic-diols are catechol derivatives in which 3 or 4 position is unsubstituted and these positions are sterically blocked. These derivatives are drugs and now, are widely used in the treatment of bornchail asthma, hypertension, Parkinson's disease myocardial infarction and cardiac surgery.

Materials and methods:

All experiments were performed with reagent grade chemicals purchased from E. Merck. These chemicals were used without further purification. The stock solutions of, catechol, dopamine, epinephrine, potassium periodate and N-methylaniline were prepared fresh, daily by dissolving them in distilled water. The buffered solutions were prepared based on Kolthoff tables, and the concentration of the prepared buffers was 0.15 M [2]. The kinetic experiment was initiated by the addition of stock solution of periodate to mixture of n-methylaniline and catechol or catecholamines with desired pH in a 5 ml flask. All of the solutions were thermostated at 25 °C





before mixing and measurements were also performed at this temperature. The reaction mixture was shaken and transferred to the spectrophotometer quartz cell immediately. The cell placed in cell holder and reaction monitored by full spectral scan with time.

Apparatus:

Absorption spectra were obtained with a Scinco UV–vis Spectrophotometer S2100. In each experiment, the sample placed in a 1 mm path length quartz cells, and the measurements were performed at 25 °C.

Result and discussion:

Chemical oxidation of catechol, dopamine and epinephrine, by periodate at mild acidic conditions, have been studied in the presence of N-methylaniline. The details of their nucleophilic addition and comparison of inter and interamolecular reactions have been studied by cyclic voltammetry and spectrophotometric methods. The intramolecular reaction is the addition of side chain amine group of dopamine and epinephrine and the intermolecular reaction is the Michael addition of N-methylaniline. Interestingly the half-wave potential of these products and their λ_{max} are completely different due to electron-donating character and the ability of resonance for side chain amine group and N-methylaniline. All of these reactions and their reactivity have been confirmed by electrochemical and spectrophotometric results. Also some of the final products have been characterized by NMR and MS spectroscopy.

Conclusion:

The reactions of *a*-quinone from oxidation of catechol only followed by Michael addition of Nmethylaniline and the reaction products is its diphenylamine derivative. For the oxidation of epinephrine; the results indicate that the intramolecular cyclization reaction is the dominant reaction and drastically faster than intermolecular reaction of N-methylaniline. In the case of dopamine there is interplay between inter and intramolecular reaction depends on solution pH. At the pHs lower than 6 the foremost reaction is the intermolecular addition while the possibility of intramolecular reaction increase by increasing the pH. The most sticking result of this study is the





reaction of dopamine in the presence of N-methylaniline at mild acidic condition; the primary product of its oxidation is the diphenylamine derivative that undergoes an intramolecular substitution that produces the cyclization product again.

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Investigation of the Antibacterial activity of Cu, Ag, and Aumodifiednanocomposites contain a magnetic core-polymeric shell

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Keywords:Magnetic nanoparticles, PEG, PPG, Antibacterial activity, Escherichia coli, Staphylococcus aureus

Introduction:

Magnetic nanoparticles are widely used in recent researches. They have many potential applications in Biology, Catalyst, and some other fields of research in science. Drug delivery, Antibacterial activity and imaging with magnetic resonance (MRI)are some examples of their applications that are reported in the articles and literatures [1], due to their high saturation magneitzation, low toxicity, and biocompatibility.For Biological usage,because of their Biological fitness and chemical stability, nanostructures of Fe₃O₄are the first choices.

Although there have been many important developments in the synthesis of magnetic nanoparticles, the stability of these particles for a long time without agglomeration or precipitation is still remain an important subject [2]. Therefore, it is necessary to develop efficient methods to improve the chemical stability of magnetic nanoparticles. All the protection strategies result in magnetic nanoparticles with a core–shell structure, its meaning, the naked magnetic nanoparticle as a core is coated by a shell, isolating the core against the materials that surround around it.

Silica Coatingis one of the most strategies that are used for this purpose. A silica shell does not only protect the magnetic cores, but can prevent the direct contact of the magnetic core with additional agentlink to the silica surface too, thus avoiding unwanted interactions [3]. Silica layers



have several advantages because of their stability under aqueous conditions (at least if the pH value is sufficiently low), easy surface modification, and easy control of interparticle interactions, both in solution and within structures, through variation of the shell thickness.

The biological activities of silver make it a suitable candidate for applications in industry and hospitals as a microorganism inactivator. Silver is also known for its water and air purifying ability [4]. In spite of these findings, research is going on to develop still more convenient methods to exploit the beneficial properties of silver in newer applications. In this context, we studied the interaction of metallic nanoparticles with Microorganisms like bacteria. In addition, the antibacterial activity of Silver compared with Gold and Cupper according to role of the polymers which embedded the metallic particles into polymer branches.

Material and Methods:

Chemicals including $FeCl_{3} \cdot _{6}H_{2}O$, $FeCl_{2} \cdot _{4}H_{2}O$, NH_{3} ,HCl, NaOH, Ethanol, Polyethylene glycol (PEG), Polypropylene glycol (PPG) were analytical grades and purchased from Merck (Darmstadt, Germany). Reaction between $FeCl_{3} \cdot _{6}H_{2}O$ and $FeCl_{2} \cdot _{4}H_{2}O$ performed under N₂ gas to prevent unwanted oxidation. The composites were washed with deionized water (DIW) and then dried at 90C in the oven.

Apparatus:

Characterization of prepared samples in this project was performed withFT-IR, TEM, TGA and VSM analysis methods. For antibacterial test, using of sterile instruments such as laminar, oven, special shaker, autoclave and a cultivation media (Agar) was necessary.

Result and discussion:

All the prepared nanocomposites were characterized by FT-IR, TEM, VSM and TGA analysis method. For instance the results for VSM analysis have shown in the Figure. A decrease in the amount of magnetic saturation from pure magnetic core to core-shell nanocomposite is observable. Bacterial inactivation diagrams for each composite were depicted.



Figure. The results for VSN analysis

Unlike Fe₃O₄/SiO₂/Polymer, Fe₃O₄/SiO₂/Polymer-Metal nanocomposite exhibited a high activity for E. coli (as a gram negative) and Staphylococcus aureus (as gram positive bacterium) degradation. Theinactivation kinetic of the bacteria, the effect of composites dosage and reusing ability of composites were studied and furthermore we found a mathematical equation which is suitable for this treatment andthe rate of releaseof metal into the solution. In one experiment when we used 10 mg of the prepared nanocomposite, the number of the growth colonies was reduced from 10⁷ to zero after 30 minutes. According to the results for antibacterial activity, we concluded that copper can be trapped in both PEG and PPG branches, while PPG layer showed a better role and activity for Cu nanoparticles.In addition, Silver only can penetrate in PPG polymeric branches on the surface and Gold nanoparticles only can penetrate in PEG polymeric branches. The inactivation of Bacteria is mainly due to interaction between metal nanoparticles and deoxyribonucleie acid (DNA) [5] and the mechanism was discussed in elsewhere [6].

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Kinetic study of reactive oxygen species production upon photoexcitation of sun care agents such as TiO₂, ZnO and ZrO₂

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Key words: Reactive oxygen species, Kinetic Monte Carlo, Inorganic oxides, simulation.

Introduction:

Reactive oxygen species (ROS) are free radicals that continuously produced through a variety of normal metabolic processes.[1]Reactive oxygen species, include singlet oxygen, superoxide and hydroxyl radicals, and hydrogen peroxide.[2]The uncontrolled production of ROS may lead to inflammation, aging, neurodegenerative disorders and cancer. Many sunscreens contain light-reflective agents such as TiO₂, ZnO and ZrO₂,to achieve high SPF(Sun Protection Factor) ratings.TiO₂, ZnO and ZrO₂have been reported to be an effective photocatalyst agent, which is able to generate reactive oxygen species.[3] In uric acid(UA) assay TiO₂, ZnO and ZrO₂irradiated, UA oxidize by produced ROS by inorganic oxides.

Purpose of this paper is identification of kinetic mechanism of ROS production by irradiation of TiO₂, ZnO and ZrO₂by using kinetic Monte Carlo simulation.

Theory :

In this project, we have tried to attain of mechanism by applying kinetic Monte Carlo simulation. In this method the reaction mechanism is considered as a collection of several steps: [4] $nN + mM + ... \rightarrow products (1)$

The input data for simulation are the steps and their rate constants, k_i . The rate of the it's step, R_i, is taken to be proportional to the probability, P_i, of its occurring in a particular time interval. $P_i \propto R_i = k_i [N]^n [M]^m (2)$





The algorithm is based on a reaction probability density function, $P(\tau,i)$, is obtained by Mater equation: $P(\tau,i) = k_i C_i \exp\{-\Sigma k_i C_i \tau\}$ (3)

The time step Δt between occurrences of any of the reaction steps is the mean time for a system obeying Poisson statistics:

$$\Delta t = \frac{-\ln\rho}{\sum R_i} (4)$$

Where ρ is a random number between 0 and 1. This stochastic numerical simulation method has been used to simulate several chemical kinetics reactions.[5]

Results and discussion:

Suggested mechanism that using CKS program was attained, is:

$$TiO_{2} \rightarrow TiO_{2}^{*}$$
$$TiO_{2}^{*} + O_{2} + H_{2}O \rightarrow ROS$$
$$ROS + UA \rightarrow UA - OX$$

 TiO_2^* is excited state of TiO_2 that under irradiation of TiO_2 one electron is excited from the valance band to the conduction band.Fig.1 shows rate of ROS creation by TiO_2 (rutile and anatas), ZnO and ZrO₂that irradiated. As can be seen, calculation diagram fit to experimental graph in perfect way.



Fig.1. Kinetic data for the photo-oxidation of uric acid by inorganic oxides, (Δ) ZnO, (\Diamond) TiO₂ (anatas), (\circ) ZrO₂, (\Box) TiO2 (rutile), experimental data (open circles) and theoretical data (solid line).





Conclusion

Our results demonstrate that using kinetic Monte Carlo simulation, we attain to mechanism which ROS is produced by irradiation of TiO₂, ZnO and ZrO₂. Graphs which attain with this mechanism fit to experimental data.

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Kinetic Study of Reactive Oxygen Species by Using 2,7-dichlorofluorescein Diacetate Assay

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Key words: Reactive oxygen species, Free radical, Kinetic Monte Carlo, Simulation.

Introduction

Reactive oxygen species (ROS) are chemically reactive molecules including oxygen. Examples contain oxygen ions, superoxide and hydroxyl radicals.[1]This may result in significant damage to cell structures. Generally, damage of reactive oxygen species on the cell are most often: damage of DNA, oxidations of polyunsaturated fatty acids in lipids,oxidations of amino acids in proteins.In biological systems, use 2,7-dichlorofluorescein diacetate (DCHF-DA) for measurement of intracellular ROS.[2] It has been demonstrated that the nonfluorescent DCHF-DA can cross cell membranes and deacetylizes by cellular esterase enzymes and form the nonfluorescent,oxidant-sensitive 2,7-dichlorofluorescein (DCHF). In the presence of hydrogen peroxide (H_2O_2) DCHF is oxidized to highly fluorescent DCF.

Purpose of this paper is study of mechanism of enzyme reaction which is used to determinate ROS by chemical kinetic simulation.

Theory

In this project, kinetic Monte Carlo simulation has been used to find the mechanism of an enzyme reaction. In this method the reaction mechanism is considered as a collection of several steps: [3] $nN + mM + ... \rightarrow products$ (1)

The input data for simulation are the steps and their rate constants, k_i . The rate of the *i*th step, R_i , is taken to be proportional to the probability, P_i , of its occurring in a particular time interval. $P_i \propto R_i = k_i [N]^n [M]^m (2)$





The algorithm is based on a reaction probability density function, $P(\tau, i)$, is obtained by Mater equation: $P(\tau, i) = k_i C_i \exp\{-\Sigma k_i C_i \tau\}$ (3)

The time step Δt between occurrences of any of the reaction steps is the mean time for a system obeying Poisson statistics:

$$\Delta t = \frac{-\ln\rho}{\sum R_i} (4)$$

Where is a random number between 0 and 1. This stochastic numerical simulation method has been used to simulate several chemical kinetics reactions.[4]

Results and discussion

The mechanism that has been suggested for enzyme reaction is:

$$DCHF - DA + E \leftrightarrow E.DCHF - DA$$
$$E.DCHF - DA \rightarrow DCHF$$
$$DCHF + ROS \rightarrow DCF$$

In above mechanism E is equal to esterase enzyme. The values of rate constant are obtained as adjustable parameters. Calculated data which were obtained by applying this mechanism are in good agreement with experimental data (fig.1).



Fig.1.Kineticof DCHF-DA oxidation for different concentrations of K562 cells: (Δ) 1E5, (◊) 2E5, (○) 4E5,experimental data (open circles) and theoretical data (solid line).





Conclusion

By applyingkinetic Monte Carlo simulation, the mechanism of deacetylation of DCHF-DA by cellular esterase enzymes has been found. The obtained results which have been attained by using this mechanism are in perfect agreement with experimental data.

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Ab initio computations on zigzag (10,0) carbon nanotube-phosphoryl halides

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Keywords: Carbon nanotube; Phosphoryl halide, DFT, NQR

Introduction:

The chemistry of carbon nanotubes (CNT) has shown a great development for these molecular systems in nanoscience and nanotechnology. CNTs have important applications in several areas of science such as physics, chemistry, biology, materials science and pharmacology [1]. The CNT are classified by their numbers of layers into two classes: multi-wall (MWNT) and single wall (SWNT) nanotubes [2–4]. The functionalization of nanotubes may lead to electronic and mechanical properties that are substantially different from their non-functionalized analogues [1].

Computational details:

The structures of zigzag (10,0) carbon nanotube and compounds **1** and **2** were optimized in using Gaussian 98 program [5] at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set. Nuclear quadruple coupling constants (χ) were calculated from the equation $\chi = e^2 q_{zz}Q/h$, supposing that the electric quadrupole moments (Q) of ²H, ¹⁷O and ¹⁴N nuclei are 2.860, -25.58 and 20.44 mb, respectively.

Results and discussion:

In this research, the structures of zigzag (10,0) carbon nanotube and compounds $P(O)Cl_3$ (1) and $P(O)Br_3$ (2) were optimized at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set, Figure 1. The binding energies were measured from the equation $E(bind) = E(molecule) - \Sigma_i E(i)$, i = atom. Table 1 indicates the binding energies and dipole moments. It reveals that the





biding energies of grafted CNTs are more negative at both methods. Also, the hydrophilicities increase very much for the grafted CNTs than that of pristine CNT. The NQCCs of ²H and ¹⁴N, ¹⁷O nuclei were computed about 200-250 kHz and 4.0-5.0, 11.0 MHz, respectively.

Table 1. The stabilization energies and dipole moments of CNT and compounds $1, 2$						
Compound	ΔE (stabilizatio	on)/kcal.mol ⁻¹	Dipole moment/Debye			
	B3LYP B3PW91		B3LYP	B3PW91		
Zigzag (10,0)-CNT	-20858.599	-21314.291	1.495	1.942		
$P(O)Cl_{3}(1)$	-21138.324	-21643.661	3.505	3.587		
$P(O)Br_{3}(2)$	-21131.474	-21639.201	5.127	0.738		
	•	•				

Table 1. The stabilization energies and dipole moments of CNT and compounds 1,2



Figure 1. The optimized structures of compounds P(O)Cl₃ (1) and P(O)Br₃ (2).

Conclusion:

The structures of a zigzag (10,0) carbon nanotube and CNT-grafted phosphoryl halides **1** and **2** were optimized at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set. Results revealed that the grafted CNT becomes more stable and its hydrophilicity increases greatly. In addition, the NQCCs were computed for the ²H and ¹⁴N, ¹⁷O atoms about 200-250 kHz and 4.0-5.0, 11.0 MHz, respectively.

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Grafted zigzag (10,0) carbon nanotube with phosphoramides

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Keywords: DFT calculations, Phosphoramide, Carbon nanotube, Grafting

Introduction:

Recently, there has been an increased interest in materials with non-linear optical (NLO) properties with potential applications in the areas of optical computing, telecommunications and signal processing [1,2]. Carbon nanotubes are considered potentially useful molecules after their functionalization with various molecular systems to enhance the non-linear responses [3].

Computational details:

The structures of zigzag (10,0) carbon nanotube and compounds **1** and **2** were optimized in using Gaussian 98 program [4] at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set. Nuclear quadruple coupling constants (χ) were calculated from the equation $\chi = e^2 q_{zz}Q/h$, supposing that the electric quadrupole moments (Q) of ²H, ¹⁷O and ¹⁴N nuclei are 2.860, -25.58 and 20.44 mb, respectively.

Results and discussion:

In this study, the structures of zigzag (10,0) carbon nanotube and compounds $Cl_2P(O)(NH_2)$ (1) and $ClP(O)(NH_2)_2$ (2)were optimized at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set, Figure 1. Table 1 indicates the binding energies and dipole moments. The binding energies were measured from the equation $E(bind) = E(molecule) - \Sigma_i E(i)$, i = atom. It can be deduced from the Table that the grafted CNTs with more negative biding energies at both methods are more stable than pure CNT. Moreover, the hydrophilicities increase very much in the case of the grafted CNTs than that of pristine CNT. The NQCCs of ²H and ¹⁴N, ¹⁷O nuclei were also calculated about 200-250 kHz and 4.0-5.0, 11.0 MHz, respectively.





Table 1. The stabilization energies and dipole moments of CNT and compounds 1,2

Compound	$\Delta E(stabilization)$	on)/kcal.mol ⁻¹	Dipole mo	moment/Debye	
	B3LYP	B3PW91	B3LYP	B3PW91	
Zigzag (10,0)-CNT	-20858.599	-21314.291	1.495	1.942	
$Cl_2P(O)(NH_2)(1)$	-21331.233	-21831.965	8.091	11.228	
$ClP(O)(NH_2)_2(2)$	-21523.788	-22022.236	12.419	12.781	



Figure 1. The optimized structures of compounds Cl₂P(O)(NH₂) (1) and ClP(O)(NH₂)₂ (2).

Conclusion:

The structures of a zigzag(10,0) carbon nanotube and CNT-grafted phosphoramides **1** and **2** were optimized at DFT (B3LYP and B3PW91) level of theory with standard 6-31G* basis set. The binding energies of the grafted CNTs are more negative and their hydrophilicities enhance greatly in comparison with prinstine CNT. The NQCCs were computed for the ²H and ¹⁴N, ¹⁷O atoms about 200-250 kHz and 4.0-5.0, 11.0 MHz, respectively.

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Photodegradation of Acid Orange 7 over AgBr/TiO₂ Nanocomposite under UV Light Illumination

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Keywords: Photodegradation, Ag/TiO2 nanoparticles, AgBr/TiO2 nanocomposite, Acid Orange 7

Introduction:

Dye containing waste water generated from textile industries represents an increasing environmental pollution owing to its non-biodegradability, toxicity, and potential carcinogenic nature. Azo dyes, which are widely used in textile industry designed to resist degradation [1]. In the past two decades, much attention has been focused on photocatalytic degradation of these pollutants mediated by TiO₂ particles under UV light illumination [2]. These organic pollutants are oxidized by photogenerated positive holes (h^+) or by reactive oxygen species (OH⁺, HOO⁺, O₂⁻⁺) formed on the TiO₂ surface under UV light irradiation [1]. The high band gap, low quantum efficiency, and high rate of recombination of photo generated positive holes (h^+) and electrons (e⁻) have limited the use of TiO₂ as photocatalyst. In recent years, some researches were done in order to promote the photocatalytic property of TiO₂. The aim of this work was to synthesize TiO₂, Ag/TiO₂ nanoparticles, and AgBr/TiO₂ nanocomposite by the sol-gel method to investigate the degradation of Acid Orange 7 (AO7). The effect of calcination tempereture, initial dye concentration, TiO₂ loading, pH, and the adding of H₂O₂ on the rate of photodegradation of AO7 was also examined.

Materials and methods:

AO7 ($C_{16}H_{11}N_2NaO_4S$) was provided from Iran color research center, Tetraisopropylorthotitanate (Tipt), Ethanol, 2-aminoethanol, AgNO₃, Hexane, Cetylmethylammonium bromide (CTAB), Decanol were supplied by Merck. Three photocatalysts were employed in this study, namely





 TiO_2 nanoparticles, Ag/TiO_2 nanoparticles, and AgBr/TiO 2 nanocomposite prepared by the solgel method.

Apparatus:

Irradiation experiments were carried out in a pyrex UV reactor which was surrounded by a circulating water jacket to maintain constant temperature. The UV source was an OSRAM 125 W high-pressure mercury lamp placed above the reactor. UV-GBC Cintra 40 spectrophotometer was used for determining the concentration of dye at the maximum wavelength, 484 nm. Characterization of synthesized catalysts was performed using FT-IR, XRD, DRS and SEM techniques [2].

Results and discussion:

The optimum conditions for degradation were found to be, calcination temperature (400°C), dye concentration (20 ppm) and amount of photocatalysts (100 ppm).



Figure. The degradation efficiencies ($x_{\%} = \frac{c_{0} - c}{c_{0}} \times 100$) of AO7 on three photocatalysts at pH=2

The results showed that the degradation of AO7 in comparision to other dyes is more difficult with common photocatalysts, such as TiO_2 or Ag/TiO₂ nanoparticles due to adsorption of AO7 as a bidentate ligand on the surface of the photocatalyst [3]. Therefore, the active sites of TiO_2 are





covered stronger by AO7. The designation of AgBr/TiO₂ nanocomposite is a novel way to decolorize AO7. Silver bromide with a band gap of 2.6 eV has high photocatalytic activity in the visible light region and can be used to modify TiO₂ to have visible light activity [4]. It was found that AO7 degradation efficiency, of AgBr/TiO₂ increases with decreasing pH values to 2. Therefore a marvellous way to decolorize AO7 on AgBr/TiO₂ is to decrease pH up to 2, by this way the surface of the catalyst became protonated, so AO7 dye can adsorbed more on the surface of the photocatalyst [5]. Although in pH=2 the surface of the other catalysts such as TiO₂ and AgBr/TiO₂ is positive and this effect may improve the photocatalytic activity of these but this effect is much stronger in AgBr/TiO₂.

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A Theoretical Study on the Solvent Effects in pericyclic Reactions Part I: 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxide

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Keywords: Solvent effects; Transition State; 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide

Introduction:

Cheletropic reactions were defined by Woodward and Hoffmann as pericyclic reactions in which two σ bonds are made or broken in a single atom. Some authors consider these reactions to be a sub-class of cycloaddition. Experimental work has shown that a Diels-Alderadduct is the kinetic product of reactions of sulfur dioxide with conjugated dienes but that the adduct is thermally unstable and readily undergoes a retro-Diels-Alder reaction to 1,3-butadiene and sulfur dioxide according to scheme 1 [1]. On the other hand, the analysis of the wave functions of the transition structures by means of a theoretical method (HOMO-LUMO analysis), allows us to throw some light on the stability of the TS through which the retro Diels-Alder reaction proceeds. The next step of our investigation inferred the influence of the solvent on the retro-cheletropicene reaction in detail from the theoretical point of view, in order to examine the presence of specific interactions between three different solvents and reactant/TS.

Computational methods:

Density functional theory (DFT) calculations have been carried out at the B3LYP level using the Gaussian 09 package of Programs [2]. All structures were fully optimized with the 6-311++G(d,p) basis set followed by vibrational frequency calculations which confirmed that reactants (and products) and transition structures (located by means of Schlegel's algorithm) have zero and one imaginary frequency, respectively. Solvation energies were computed by the SCRF-(CPCM/UFF) continuum models as implemented in Gaussian 09 computational package.

Ô





Scheme 1

Results and discussion:

Rate constants of the reaction in the gas phase and different solvents of acetone, benzene, and DMF at 393 K were calculated by means of transition state theory. Comparison between the gas phase and solvated TS confirmed a small solvent effect in terms of donor properties of the solvent. Higher reaction rates below to solvents with a higher degree of basicity. To explain the influence of the solvent on the reaction rate, using the dipole moment (μ) is of importance. Calculated ushows that it is different between the reactant, TS and products. Different polarities in different solvents induces different $\Delta \mu^{\neq}$ (μ_{TS} - μ_{R}), which in turn causes different reaction rates. Our theoretical calculations in different solvents confirmed that the dipole moments of all TSs are between the reactant and the products. For example computed values of μ 's of the reactant, TS and products in acetone are 3.75, 3.45 and 2.12D, respectively. From the obtained data, this reaction seems to be sensitive to both the solvent acidity and basicity, being only influenced by the polarity of the solvent. The rate constants will be characterized by opposite effect of the polarity which means that k will slightly decrease with the increase of solvent polarity. Other calculations on the frontier molecular orbitals of the TSs in different solvents show that HOMO-LUMO energy differences of the TSs can be influenced by the solvent polarity. In other words the solute-solvent interactions will highlighted the FMO effects. Computed rates and activation parameters of the retro-cheletropicene reaction of 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide (Reactant) in the gas phase and different solvents are accordance to experimental data. Positive singe of activation entropies in acetone, benzene and DMSO are 3.2, 9.1 and 5.5 calmol⁻¹K⁻¹





implies that degrees of freedom at the TS increases and confirmed the ring opening in the rds of the reaction.

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Molecular Photochromic System: Experimental Investigation of Nickel(ll)Dithizonate in Different Solvent by Diode Laser

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Key words: Photochromism, Nickel(ll)dithizonate, Diode laser.

Introduction:

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having differenta absorption spectra. The thermodynamically stable form A is transformed by irradiation into form B[1].

The photochemistry of different metal dithizonates has been studied extensively by Meriwether et al [2]. The photo- and thermo-chromisms of organometallic compounds have been intensively studied during the last 20 years. Different coordination compounds of the monoanionic HDz⁻ species in tetrahedral or square-planar geometries $[M(HDz)_2, M = Zn, Cd, Hg, Pt, etc.]$ have been previously synthesized and characterized and it has been suggested that the photochromic reaction involves a trans–cis isomerization about the C=N bond and an N to N hydrogen transfer, as shown in Scheme 1.



This paper evaluates $Ni(HDz)_2$ in terms of color response range on the basis of its photochromic behaviour in different solvents and radiation conditions.





Materials and methods:

Ni(HDz)₂ was synthesized and purified by the procedure described in [3]. Chloroform (CHCl₃), dichloromethane (CH₂Cl₂), benzene (C₆H₆), CCl₄ were used as solvents. All were of spectral grade and used without further purification. Typical concentrations employed were around 4.69×10^{-5} mol L⁻¹.

Result and discussion:

We directed our attention to two points of view: the photochemical behaviour of Ni(HDz)₂ in different solvents and usage laser (λ = 532 nm, 50 mW) for photochromic behavior of Ni(HDz)₂. The absorption spectra of the complex in different solvents are described in Table 1. In all the solvents used, the complex displays bands in the 450 and 610 nm region (normal form A). The absorption of the activated form was monitored at maximum in the 530–550 nm region. Ni(HDz)₂ was photochromic under our test conditions with visible light in CHCl₃, CH₂Cl₂, CCl4 and C₆H₆. A visual color difference between the samples before and after irradiation was taken as a negative evidence of photochromism.

Solvent	Dielectric Constant	Form A λ max (nm)	Form B λmax (nm)
CHCl ₃	4.7	450-610	530
CH ₂ Cl ₂	6.7	440-610	540
CCl ₄	4.2	430-620	550
C ₆ H ₆	9.87	460-630	540

Table 1 The spectral data of the normal A and activated forms B of $Ni(HDz)_2$ in different solvents and irradiation with visible light.

Conclusion:

The photochromism of Ni(HDz)₂ using laser observed in CHCl₃, CH₂Cl₂, CCl4 and C₆H₆.

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Laser Induced Tunable Photochromism of Dithizone via Metal Coordination

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Key words: Photochromism, Metal dithizonate, Palladium, Mercury, laser.

Introduction:

Photochromism can be defined as a reversible transformation of a chemical species induced by electromagnetic radiation between two states with light absorptions in spectral regions. Colour changes in photochromic compounds typically are the result of the shift of optical absorption due to changes in molecular structure or conformation.

These photochromic molecules can play a key role in materials for photonic switches, memories, sensors or actuators and this wide range of applications involve large-size devices (e.g., sunglasses) as well as miniaturized ones (e.g., memory media). A combination of metal-ion recognition moieties with photochromic molecules has been reported to afford metal-ion responsive photochromic molecules [1]. The most widely adopted functional groups that form metal-ion complexes are crown ethers, and the photochromic chromophores. Different coordination compounds of the monoanionic Dithizonate (HDz⁻) species in tetrahedral or square-planar geometries [M(HDz)₂, M = Zn, Cd, Hg, Pt, etc.] have been synthesized and characterized and it has been suggested that the photochromic reaction involves a trans–cis isomerization about the C=N bond and an N to N hydrogen transfer.

The case study of $[M(HDz)_2, M = Zn, Cd, Hg, Pd, Pb]$ in different solvents and radiation conditions was performing.

Materials and methods:

 $M(HDz)_2$ was synthesized and purified by the procedure described in [2]. Chloroform (CHCl₃), dichloromethane (CH₂Cl₂), benzene (C₆H₆), Carbon tetrachloride (CCl₄) were used as solvents.





All were of spectral grade and used without further purification. Typical concentrations of complexes employed were around 4.69×10^{-5} mol L⁻¹.

Result and discussion:

We directed our attention to two points of view: the photochemical behaviour of $M(HDz)_2$ in different solvents and usage He-Ne laser (λ = 632 nm, 5 mW) for photochromic behavior of $M(HDz)_2$. In this conditions, only Hg(HDz)₂ and Pd(HDz)₂ are shown photochromic behavior in all solvents. The absorption spectra of the Pd(HDz)₂ complex in different solvents are described in Table 1. In all the solvents used, the complex displays bands in the 450 and 610 nm region (normal form A). The absorption of the activated form was monitored at maximum in the 530– 550 nm region. Hg(HDz)₂ was photochromic under our test conditions with visible light in CHCl₃, CH₂Cl₂, CCl₄ and C₆H₆, that changes from orange colour to royal blue. In all the solvents used, the complex displays band in the 480 nm (normal form A) and λ_{max} of activated form was monitored in 630 nm. Photochromic behavior of this two complexes in different solvent is different because of their different geometry and this changes occurs in different times.

Table 1

The spectral data of the normal A and activated forms B of Pd(HDz)₂ in different solvents and irradiation with visible light.

Solvent	Dielectric	Form A λ_{max} (nm)	Form B λ_{max} (nm)
	Constant		
CHCl ₃	4.7	450-610	540
CH ₂ Cl ₂	6.7	450- 620	530
CCl ₄	4.2	440- 630	530
C ₆ H ₆	9.87	460-630	540

Conclusion:

The photochromism of $Hg(HDz)_2$ and $Pd(HDz)_2$ using laser observed in CHCl₃, CH_2Cl_2 , CCl_4 and C_6H_6 in different times.

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Kinetic of Sonocatalytic degradation of Methylene blue

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Key words: Ultrasonic irradiation, Fenton process, Methylene blue, Kinetic

Introduction:

Various treatment methods have been developed to remove azo dyes from waste water. Fenton process is one of the advanced oxidation processes (AOP) that is widely used for degradation of dyes. Also as one of AOPs ultrasonic irradiation has been employed in the degradation of textile dyes [1]. Sonochemistry is principally based on acoustic cavitation which includes the formation, growth and implosive collapse of bubbles in loquid [2]. Combination of these two methods can improve the degradation rate. In this work we used this combined method for degradation of Methylene blue (MB). The reaction orders for all of the reagents determined by kinetic study of degradation process in various concentrations of MB, H_2O_2 and Fe^{2+} . Also effect of pH and ultrasound power on the degradation rate investigated.

Materials and methods:

Methylene blue, Hydrogen peroxide, NaOH, FeSO₄, and H₂SO₄ were purchased from Merck Chemical Co. and were used without further purification.

Results and discussion:

Degradation of MB was carried out at constant temperature, Fe^{2+} concentration, H_2O_2 concentration and MB concentration (t=23°C, [MB]=2.5×10⁻⁵ M, [Fe²⁺]=5.0×10⁻⁴ M, [H₂O₂]=3×10⁻⁴M)with various pH values in order to studying the effect of initial pH. The effect of initial pH on the degradation was illustrated in Fig. 1. The results of Fig.1 show that the rate





of degradation were decreased by increasing the pH. this is caused by the fact that at higher pHs ferrous and ferric hydroxides are formed wich inhibit the reaction between Fe^{2+} and H_2O_2 and thus the 'OH production. Degradation of MB was carried out at constant temperature, Fe^{2+} concentration, H_2O_2 concentration and MB concentration (t=23°C,[MB]=2.5×10⁻⁵ , $[Fe^{2+}]=1.0\times10^{-4}$ M, $[H_2O_2]=0.09$ M)with various ultrasound power in order to studying the effect of ultrasound power. The result of this study was illustrated in Fig.2 that show the rate of degradation were increased by increasing the power. Degradation of MB was carried out at constant temperature, pH and Fe^{2+} concentration(t=23°C, pH=2.6 [MB]=2.5×10⁻⁵ and $[Fe^{2+}]=1.0\times10^{-4}$ M) with various concentrations of Hydrogen peroxide in order to studying the effect of Hydrogen peroxide concentration on the degradation. The result showed that the rate of degradation were increased by increasing the dosage of H_2O_2 from 1.0×10^{-5} M to 1.0×10^{-3} but further increase of the dosage decreased the rate. This is attributed to the scavenging effect of excessive H₂O₂ to OH. Degradation of MB was carried out at constant temperature, pH and H₂O₂ concentration (t=23°C, pH=2.6 [MB]= 2.5×10^{-5} and [H₂O₂]= 3.0×10^{-4} M) with various concentrations of Fe^{2+} in order to studying the effect of Fe^{2+} concentration on the degradation. The results showed that the rate of degradation were increased by increasing the initial concentration of Fe²⁺ and this behaviors can be attribute to the higher production of 'OH with increasing Fe²⁺ in Fenton reaction. The order of reactants was evaluated by initial rate method and it found that the equation rate as follow:



Fig.1.Effect of pH on the degradation rate of MB

Fig.2.effect of ultrasound power on the degradation rate of MB





Conclusion:

This study showed that the combination of ultrasound and the Fenton process could enhance the degradation rate of MB. The orders of reactants obtained from studying the initial rates.

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Kinetic study of degradation of methylene blue by Fenton process

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Keywords: Fenton process, Kinetic study, Methylene blue

Introduction:

Several advanced oxidation processes (AOP) have been developed and applied to waste water treatment [1]. Fenton process is a homogeneous catalytic AOP using a mixture of hydrogen peroxide and ferrous ions [2]. The Fenton process uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants[3]. In this research degradation of methylene blue(MB) have been studied by Fenton process and some parameters that influence the degradation rate, such as initial concentration of MB, H_2O_2 and Fe^{2+} and temperature have been investigated.

Materials and methods:

Methylene blue, Hydrogen peroxide, NaOH, FeSO₄, and H₂SO₄ were purchased from Merck Chemical Co. and were used without further purification.

Results and discussion:

Degradation of MB was carried out at constant temperature, pH and Fe²⁺ concentration(t=23°C, pH=2.6 [MB]= 2.5×10^{-5} and [Fe²⁺]= 1.0×10^{-4} M) with various concentrations of Hydrogen peroxide in order to studying the effect of Hydrogen peroxide concentration on the degradation. The effect of Hydrogen peroxide concentration on the degradation was illustrated in Fig.1. The results of Fig.1 show that the rate of degradation were increased by increasing the dosage of H₂O₂ from 1.0×10^{-5} M to 1.0×10^{-3} but further increase of the dosage decreased the rate. This decrease is attributed to the scavenging effect of excessive H₂O₂ to 'OH.Degradation of MB was



carried out at constant temperature, pH and H₂O₂ concentration (t=23°C, pH=2.6 [MB]=2.5×10⁻⁵ and [H₂O₂]= 3.0×10^{-4} M) with various concentrations of Fe²⁺ in order to studying the effect of Fe²⁺ concentration on the degradation. The effect of Fe²⁺ concentration on the degradation was illustrated in Fig. 2. The results of Fig. 2 show that the rate of degradation were increased by increasing the initial concentration of Fe²⁺ and this is due to the higher production of 'OH with increasing Fe²⁺ in Fenton reaction. Degradation of MB was carried out at constant temperature, pH, Fe²⁺ and H₂O₂ concentration (t=23°C, pH=2.6, [Fe²⁺]=1×10⁻⁴ and [H₂O₂]= 0.09M) with various concentrations of MB in order to studying the effect of MB increased by increasing the results showed that the degradation rate of MB increased by increasing the MB concentration. The order of reactants was evaluated by initial rate method and it found that the equation rate as follow:

 $R = K [MB]^{1.25} [H_2O_2]^{-0.96} [Fe^{2+}]^{2.164}$

To obtain the activation energy of degradation, degradation of MB were studied at different temperatures. The activation energy were calculated by using the usual Arrhenius treatment(K=Aexp(- E_a/RT)). The obtained activation energy is 90.755 kj/mol.



Fig.1.effect of initial H₂O₂ concentration on the degradation rate

Fig.2.effect of initial Fe^{2+} concentration on the degradation rate

Conclusion:

In this work the degradation of MB was studied by Fenton process at different experimental conditions and a suitable operating condition was selected as: [MB] =0.0166 mM,





 $[Fe^{2+}] = 4 \times 10^{-5}$ M and $[H_2O_2] = 0.001$ M. The orders of reactants obtained from studying the initial rates.

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Kinetically dimerization of α -methylstyren by $H_6P_2W_{18}O_{62}$ catalyst: Temperature and time aspects

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Key words: Heteropolyacids, Catalysis, Dimerization, α-Methylstyrene

Introduction:

The dimerization of aryl alkenes is atom-economical reaction that gives access to useful intermediates. Considerable attention has been focused on the transformations because of the demand for the formation of important intermediates in the fields of material engineering and pharmaceuticals. Acid-catalyzed dimerization of α -methylstyrene (1) can lead to 2,4-diphenyl-4-methyl-1-pentene

(2), 2,4-diphenyl-4-methyl-2-pentene (3) and 1,1,3-trimethyl-3-phenylindan (4) which are industrially relevant in several contexts. The unsaturated dimers of α -methystyrene, particularly 2 are industrially important and are useful as chain-transfer agents or molecular weight regulators in the production of polymers such as polystyrene, AS resin, ABS resin, SBR, and the like, furthermore derivatives of 4 are utilized in the electronic industry, in the production of polymers and as flame retardants. In this work, we report the effect of different reaction times and temperatures on producing dimers in the present of catalytic amount of the Dawson (H₆P₂W₁₈O₆₂) heteropolyacid (HPA-D) [1-3].

Materials and methods:

Dawson heteropolyacid was prepared by passing a synthesized [2] aqueous solution of $K_6P_2W_{18}O_{62}$ through a Dowex-50W-X₈ ion exchange column followed by evaporation of water under reduced pressure and drying at 120 °C overnight. A mixture of α -methylstyrene (118 mg, 1





mmol), HPA (0.01 equiv.) and DEC as a solvent (5 mL) was stirred at determined time and temperature under nitrogen atmosphere. After cooling to room temperature, the mixturewas filtered through a short pad of silica. The solvent was evaporated under vacuum. The residue was analyzed by GC.

Apparatus:

FT-IR (Bruker IFS-88) and GC (Varian.CP- 3800).

Result and discussion:

The influence of the reaction time, amount of catalyst and reaction temperature with HPA-D has been examined. These results demonstrate that chemoselectivity towards, 2 and 3 dimers are obtained by kinetically controlled conditions, while thermodynamic control reaction, produce 4 dimer. So by increasing the temperature, the amount of 2and 3 decrease and convert to 4 cyclic dimer. In

according to this results, change of reaction temperature from 40°C to 80 °C for 3 h leads to produce 4 dimer and limited 2 and 3 liner dimers (Fig. 1). Also, the reactions carried out in different times. Results demonstrated that the amounts of 4 increases from 35% to 65% by enhancing the reaction time from 15 min to 3h. Under these conditions, heating at 60 °C is required to selectively obtain 4.





Conclusion:

Our study shows that, the dimerization of α -methylstyrene catalyzed with HPA-D is efficient and can be tuned kinetically toward the selective production of cyclic dimer by controlling the temperature and the reaction time.





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Macroscopic and Microscopic Protonation Constants of Alanine in Aqueous solutions of 1-propanol

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Keywords: Potentiometry ; Alanine ; 1-Propanol; Mixed Solvent; Micro and Macro Protonation Constants.

Introduction

The acidic macroscopic and microscopic dissociation constants are among important physicochemical property of all amino acids, specially in ADMET (absorption, distribution, metabolism, excretion, and toxicity) processes. In this way, potentiometry technique is very useful and wellestablished in current determination of pharmaceutical or biological interest. When the compounds are sparingly soluble in water, the pK_a determination is commonly done in organic solvents or better in aqueous organic mixture. Alcohol-water mixtures are often used because they have a lower polarity than pure water, but keeping a similar environment.

Experimental

The macroscopic and microscopic protonation constants of L-alanine have been determined in different aqueous solutions of 1-propanol containing (0 to 50 % v/v 1-propanol) using potentiometric method at 25 °C and constant ionic strength (0.1 mol dm⁻³ sodium chloride).

Results and Discussion





The micro constants values were evaluated using a non-linear least squares method in computer program (Microsoft Excel Solver and Linest). The effect of solvent composition on the





macroscopic and microscopic protonation constants in the mixed solvents were analyzed using Kamlet, Abboud, and Taft (KAT) solvatochromic parameters (α , β , π^*). Single-parameter correlation of the micro constants versus α (hydrogen bond donor acidity), β (hydrogen bond acceptor basicity) and π^* (dipolarity/polarizability) are poor in all solutions, but dual-parameter (α and π^*) correlation represent significant improvement with regard to the single or multi-parameter models. Linear correlation is observed when the experimental micro constants values are plotted versus the calculated ones, while the KAT parameters are considered.

Conclusions:

According to the obtained results, it is characterized that the first macroscopic protonation constant of alanine is decreased with increasing the percentages of 1-propanol in solution and the second one increased when the solution is richer in the organic solvent, and also π^* (dipolarity/polarizability) parameter has a major role in correlation analysis in all cases. This indicates that an increase in the polarity of the mixed solvents increases the solvation of the anionic species and thus can explain why the second macroscopic protonation constant increase by increasing the organic solvent in the mixtures and decreases the first protonation constant of alanine [1-2]. Finally, the results are discussed in terms of the solvent effect on macroscopic and microscopic protonation constants.

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Mechanism of Stable Phosphonate Ester Derived from 2-fluro Anilin: a Kinetic Study

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Keywords: Stable Phosphonate Ester ; NH-acid; Rate constant; Kinetic studies.

Introduction:

These reactions have not been investigated yet. Herein, we describe a kinetic investigation of a facile synthesis of the reactions between **1**, **2** and **3** (as NH-acid) (Figure 1) [1,2]. Numerous kinetic investigations over a large area of different reactions have been reported previously using UV analysis [1,5]. To gain further insight into the reaction mechanism, a kinetic study of the reactions was undertaken by UV spectrophotometeric technique.





Material and Methods

Et

Bu

R

Me

Dialkylacetylenedicarboxilates, triphenylphosphite and 2-floro Anilin were purchased from Fluka (Buchs, Switzerland) and used without further purification. All extra pure solvents including dichloromethane, ethylacetate and 1,2-dichloroethane also were obtained from Merk (Darmstadt, Germany). A Cary UV-Vis spectrophotometer model Bio-300 with a 10 mm light-path black quartz spectrophotometer cell was employed throughout the current work.





Result and Discussion

First 1mL aliquot from the 3×10^{-3} *M* solutions of each compound of **1**, **2a** and **3** was pipetted into a quartz spectrophotometer cell and the reaction monitored by recording scans of the entire spectra every 10 min over the whole reaction time at ambient temperature. The ultra-violet spectra shown in Figure 2 are typical. From this, the appropriate wavelength was found to be 330 nm. Since at this wavelength, compounds **4**, **2a** and **3** have relatively no absorbance value, this provided the opportunity to fully investigate the kinetics of the reaction between **1**, **2a** and **3** at 330 nm in the presence of 1, 2-dichloroethane as solvent.







Figure 2. The UV spectra of the reaction between 1, 2a and 3a with 10-3M concentration of each compound as reaction proceeds in 1, 2 dichloroethane with 10 mm light-path cell.



Figure 3. Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between compounds 1, 2a and 3 at 330 nm and 25.0°C in 1,2-dichloroethane.

In order to gain further insight into the reaction mechanism, the reaction kinetics was followed by plotting UV absorbance against time. The original experimental absorbance curves (dotted line) accompanied by the second order fit curves (full line), which exactly fit experimental curves (dotted line), is shown in Figure 3 at 25.0°C and 330 nm (Figure 3). The results show that the rate of reaction in each case was increased at higher temperature. In addition, the rate of reaction was accelerated in a higher dielectric constant environment (1, 2-dichloroethane) in comparison with a lower dielectric constant environment (Mix 50:50 of 1, 2-dichloroethane and ethyl acetate) at all temperatures.

Conclusion

The results can be summarized as follow:1-The overall reaction order followed second-order kinetics and the reaction orders with respect to triphenylphosphite, dialkylacetylenedicarboxylate were one and 2-floro anilin zero order respectively. 2-The values of the second-order rate constants of all reactions were calculated automatically with respect to the standard equation, using the software associated with the Cary-300 UV equipment. 3-The rates of all reactions were accelerated at higher temperatures.

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Solvent polarity, hydrogen-bonding and solvophobicity effects on the nucleophilic substitution of benzenesulfonyl chloride with aniline in aqueous and non-aqueous solutions of methanol

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Introduction

It is generally accepted that solvent characteristics such as dipole moment, permittivity, refractive index, cohesive pressure and polarizability are important in the rate and mechanism of chemical reactions [1]. The solvent effect on a typical property is described by a general correlation model which gives a simultaneous separate calculation of the contributions of non-specific solute – solvent interactions [2].

In this paper, the reaction of aniline with benzenesulfonyl chloride in methanol-ethyl acetate, methanol-water and methanol-propan-2-ol mixtures has been studied. We made an attempt to investigate the use of the linear free energy relationship correlations LFERs to establish the role of solvent in reaction rates [3].

Experimental section

The reaction of benzenesulfonyl chloride with aniline was followed conductometrically by running the reaction in the thermostated cell at 25°C. Kinetic investigations were carried out at various mole fractions of methanol in ethyl acetate, propan-2-ol and water. The concentrations of benzenesulfonyl chloride and aniline were 6.5×10^{-5} and 0.1 - 0.01 M, respectively, i.e. the reaction was carried out under pseudo-first-order conditions. All rate determinations were carried out at least in duplicate and averaged rate coefficients were utilized.

Results and discussion





The nucleophilic substitution reaction of benzenesulfonyl chloride with aniline was studied in various compositions of methanol with ethylacetate, propane-2-ol and water at 25°C.

In methanol-ethyl acetate mixtures, the rate coefficient is reduced sharply with ethyl acetate content. This is in accordance with decreasing of all solvent parameters. However, single-parameter correlations of $\log k_2$ values versus solvatochromic parameters don't show acceptable results. Dual-parameter correlations were considered and the best results were observed as followed:

$$\log k_2 = -0.709(\pm 0.555) + 7.482(\pm 0.601) E_T^N - 10.021(\pm 1.349) \beta$$

 $n=10, r^2=0.962, s=0.078, F=89.151$

where n, r^2 , s and F are number of data, square of regression coefficient, standard deviation and statistical Fisher number, respectively.

In methanol-water mixtures, the second-order rate coefficients go up rapidly with increasing the mole fraction of the water. It can be seen that the rate coefficients have a fair correlation with solvophybicity (*Sp*) of the media. Dual-parameter regression of $\log k_2$ versus E_T^N and *Sp* produces a good correlation.

$$\log k_2 = -6.501(\pm 0.818) + 6.549(\pm 1.126) E_T^N + 1.556(\pm 0.174) Sp$$
(2)

$$n = 9, r^2 = 0.998, s = 0.029, F = 1670.4$$

In methanol-propane-2-ol mixtures, second-order rate coefficients demonstrate a slight decreasing with increasing the mole fraction of propane-2-ol. The best correlation is observed between $\log k_2$ with E_T^N and α which is in accordance with the similar results in methanol-ethylacetate and methanol-water mixtures.

$$\log k_2 = -3.930(\pm 0.480) + 8.059(\pm 2.368) E_T^N - 3.104(\pm 1.219) \alpha$$
(3)

$$n = 11, r^2 = 0.982, s = 0.022, F = 221.54$$

Equation 3 shows the opposite effect of the normalized polarity and hydrogen bond donor ability of the media on the reaction rate.

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Linear and Non-linear Free Energy Relationships in Nucleophilic Substitution Reaction of 2-Bromo-5-Nitrothiophene with Morpholine

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Introduction

Solvents can considerably change both the rate and the mechanism of a chemical reaction. Solvent effects are closely related to the nature and extent of solute-solvent interactions [1]. In many physical and chemical processes taking place in solution, binary mixtures of solvents are frequently used as a media in which solvent-solvent interactions as well as solute-solvent interactions are considered. The solvent effect on a typical property is described by a general correlation model, which gives a simultaneous separate calculation of the contributions of non-specific solute-solvent interactions (such as polarity and polarizability) and specific solute-solvent interactions (such as hydrogen bond donor-acceptor abilities) [2]. In this work, the relation of the kinetic data of the S_NAr reaction between 2-bromo-5-nitrothiophene (BNT) and morpholine (Mo) with the solvent composition was studied in binary mixtures of solvents.

Experimental section

The kinetics of the reaction was spectrophotometerically studied, by running the reactions in the thermostatted cells of spectrophotometer at 25 °C. A Perkin-Elmer UV-vis 25 spectrophotometer coupled with a thermocell was used with 1.00 cm silica cells. Absorbance was measured at wavelength 430-455 nm, depending on the type of solvent was used. Concentration of 2-bromo-5-nitrothiophene and morpholine were 5×10^{-4} and 0.20 mol.L⁻¹, respectively. Therefore, the reaction was studied pseudo-first-order. On the other hand, the reaction rate was slow enough to enable us to study the kinetics of reactions by initial rate method. Reaction was carried out in different composition of aqueous solutions of methanol, ethanol, and 2-propanol and methanol-ethyl acetate mixtures.

Results and discussions



The second-order rate coefficients of the reaction under pseudo-first order conditions were determined in different molar compositions of binary solvents at 25°C. Figures 1 and 2demonstrate the variation of the reaction rate coefficients with solvent composition. In order to determine the incidence of each type of solvent properties on the kinetics of the reaction, the linear free energy relationship (LFER) correlation was applied. The best correlations were considered in dual-parameter regressions of $\log k_A$ with π^* and $\alpha \text{or}\beta$. These correlations show that the reaction rate is controlled with non-specific interactions of the media (except that in methanol-ethyl acetate mixtures). The specific interactions of solvents such as hydrogen bond donor-acceptor abilities have negligible effects on the reaction rate in aqueous solutions. High standardized coefficients of the π^* in all dual-parameter regressions confirm this claim.

Preferential solvation model was applied to analyze the solvation effect on the reaction rate. Obtained parameters showed that the transition state of the reaction are preferentially solvated by alcohol in aqueous solutions.Likewise, these parameters reveal preferential presence of alcohol molecules or the absence of the mixed solvent in the microsphere solvation of the transition state of the reaction.





Figure 1. Second-order rate constants of the reaction *versus* mole fraction of water (x_2) in aqueous solutions of methanol (**•**), ethanol (**•**), and 2-propanol (**▲**) at 25°C.

Figure 2. Second-order rate constants of the reaction *versus* mole fraction of ethyl acetate (x_2) in ethyl acetate-methanol mixtures at 25°C.

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Kinetic investigation of photocatalytic decolorization of a metachromatic dye using nano-structure zinc oxide at buffer solution

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Keywords: Photocatalytic, decolorization, Lauth's violet, Kinetic .

Introduction:

In photocatalytic decolorization, light is absorbed by an photocatalyst. The photocatalytic activity depends on the ability of the photocatalyst to create electron-hole pairs, which generate free radicals (hydroxyl radicals: •OH) able to degrade a target substance. Photocatalytic degradation (or mineralization) of chemical pollutants, such as environmentally toxic organic and inorganic compounds under aerated conditions have extensively been investigated in recent years [1–5]. In this work, photocatalytic degradation and kinetic studies of a metachromatic dye (thionine) was carried out using anatase nano-structure zinc oxide at buffer solution in a photocatalytic reactor under irradiation with 400W high pressure mercury lamp.

Materials and methods:

All chemicals were purchased from Merck and Fluka. Nano-structure zinc oxide was used as photocatalyst. The photodecolorization experiments were done by illumination of 20 mL continuous aerated, stirred buffer solutions of thionine in various pHs as well as optimum dosage of photocatalysts in photoreactor cell under 400W high pressure mercury lamp at constant temperature. After effective decolorization, photocatalyst was separated by centrifugation and title compound concentration was followed by spectrophotometric method. A photoreactor equiped with high pressure mercury lamp, 400W, air pump and a magnetically stirrer was used for irradiation of sample solution containing dye.

Results and Discussion:





Reaction order and observed photodegradation rate constants:

The observed photodegradation rate constants, k_{obs} at various buffer pHs were evaluated from the plots of the $ln(C_0/C_t)$ vs. time(Figure 1) based on the below equation with some approximations: $ln(C_0/C_t) = k_{obs}t$



Figure 1- The Plots of $\ln(C_0/C_t)$ vs. time and 1/R versus $1/C_0$

Kinetic model for dye at various buffer pHs:

Kinetic parameters of photodegradation of thionine were obtained based on Langmuir-Hinshelwood model from the diagram of 1/R vs. $1/C_0$ at various buffer pHs(R= rate and C_0 = initiated concentration)(figure 1). The slope and intercept of this diagram results the absorption constants K_A , and photocatalytic degradation rate constants, $k_r(1/R=1/k_rK_A+1/k_r)$

The effect of pH on photodecolorization kinetic parameters of dye:

Based on the related plots, higher k_{obs} is related to pH=11 while the higher value of K_A is evaluated at pH=11. The maximum of k_r is observed at pH=2. the value of K_A is 5.877 for pH=2, 4.804 for pH=7 and 7.95 for pH=11. The value of k_r is 12.33 for pH=2, 5.75 for pH=7 and 1.77 for pH=11. the value of k_{obs} is 1.38×10^{-2} for pH=2, 3.6×10^{-2} for pH=7 and 7.09×10^{-2} for pH=11.

Conclusion:

In this research we reported kinetic investigation of thionine photocatalytic degradation. The nanostructure zinc oxide was used as photocatalyst. Rate constants span are evaluated at different





buffer pHs. Also the Langmuir-Hinshelwood (L-H) rate constant, (k_r) and adsorption constant, (K_A) at various buffer pHs are presented.

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DFT Study of kinetics and thermodynamics of proton transfer and proton-bound dimer formation of methyl isobutyl ketone and 2,4-dimethyl pyridine

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Keywords: Proton transfer, Proton-bound dimer, DFT, Kinetics, Thermodynamics

Introduction:

Protonation and proton-bound dimer formation are the most important ion-molecule reactions occuring in ion mobility (IMS) and mass spectrometry based experiments [1,2].

$$(H_2O)_nH^+ + M \rightleftharpoons MH^+(H_2O)_m + (n-m) H_2O \qquad \text{protonation} \qquad (1)$$

$$MH^{+}(H_{2}O)_{n} + M \rightleftharpoons M_{2}H^{+}(H_{2}O)_{m} + (n-m)H_{2}O \qquad \text{proton-bound dimer formation} \quad (2)$$

The number of water molecules (*n*) depends on the water content of the gas in which the reaction happens. It strongly affects the kinetics and thermodynamics of the reactions. The kinetics of the reaction 1 and 2 have been experimentally studied [2]. In this work, the kinetics and thermodynamics of protonation and proton-bound dimer formation of methyl isobutyl ketone (MIBK), dimethyl methyl phosphonate (DMMP) and 2,4-dimethyl pyridine (DMP) are theoretically studied using density functional theory (DFT) methods at 298 K.

Method:

Generally ion molecule reactions such as protonation and formation of proton-bond dimer have no activation energy [2]. Hence, calculation of their activation energy, using conventional computational quantum methods, is unfeasible. In this work, the Langevin collision rate equation [3] was used to obtain the rate constant of the forward reactions in Eqs. (1) and (2)

$$x_{forward} = q(\pi \alpha / \mu \varepsilon_0)^{1/2} \tag{3}$$

where q is the ion charge, μ is the reduced mass, α is the polarizability of the neutral reactant, and ε_0 is the permittivity of the free space. The polarizibilities(α), and ΔG° of the reactions (Eqs. (1) and (2)) were calculated at the B3LYP level of the theory using 6-311++G(2df,p) basis set. The calculated ΔG° was used along with Eq.(4) to obtain the equilibrium constants of the reactions.





 $K_{eq} = exp(-\Delta G^0/RT)$

(4)

The rate constants for the reverse reactions (dissociation of protonated molecues and dimers) were calculated by $k_d = k_f / K_{eq}$ where k_f is obtained from Eq. (3).

Results and discussion:

Protonated molecules $MH^+(H_2O)_n$ (*n*=0-5) and symmetric proton-bound dimers (MHM⁺; M= MIBK, DMP, DMMP) were optimized at the B3LYP/6-311++G(2df,p) level of theory. In addition the frequency calculations were performed to obtain the thermodynamic properties of the molecules and the imaginary frequency. The equilibrium and rate constants for proton transfer reaction or formation of $M(H_2O)_nH^+$ (M=MIBK, DMP and DMMP) were also calculated. As an example, the calculated rate constant for reaction 1 when n=m=0 are 7.937×10^{-9} , 8.578×10^{-9} and 7.520×10^{-9} cm³s⁻¹ for MIBK, DMP and DMMP, respectively. It is evident that the values of rate constants decreases with increasing the size of ion. We also concluded that the rate constant reduces when the number of water molecules of hydronium ion increases. Similarly, the equilibrium and rate constants for the proton-bound dimer formation and its dissociation reaction were calculated. The calculated rate constants for (MIBK)₂H⁺, (DMP)₂H⁺ and (DMMP)₂H⁺ are 1.117×10^{-9} , 1.164×10^{-9} and 0.953×10^{-9} cm³s⁻¹, respectively, which are in good agreement with the experimental results [2].

Conclusion:

In general, the rate constants of proton transfer between M and $(H_2O)_nH^+$ and proton-bond dimer formation reaction, decreased with the increase in the size of ion and the number of water molecules. It was found that the fraction of the protonated molecule, $M(H_2O)_nH^+$, with n=2-5 is negligible and the protonated molecules are mostly in the form of MH⁺ and $M(H_2O)H^+$ at 298 K.

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Electrochemical and morphological study on green nano-ceramic reinforced conversion coating

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Keywords: Nanoceramic based conversion coating; Polarization; AFM; EIS; FE-SEM

Introduction

For improving corrosion protection and adhesion to the next layer (organic paints, finishes), pretreatments are used on metal surfaces. One of these pretreatments is the application of chemical conversion coatings for example phosphating process. However, this process has several limitations: eutrophication, requires frequent desludging, requires additional sealing step to reduce porosity and requires expensive energy input. Consequently, research on new surface pretreatments to replace phosphating has been performed. In the last decade, one promising new pretreatment was the application of zirconium oxide (ZrO_2) on the metal surfaces by immersion in a hexafluorozirconic acid solution. Electrochemical Impedance Spectroscopy (EIS) as technique provides qualitative and quantitative data and plays an important role in corrosion phenomenon studies. The nanoceramic reinforced H₂ZrF₆ conversion process is a novel study, but the study does not address the correlation between practical immersion parameters and the microstructure and anticorrosive performance of conversion coatings.

Experimental

Cold rolled steel (CRS) sheets were chosen to investigate conversion coating properties. Before immersion treatment, samples were cleaned with cold deionized (DI) water and then with KOH solution, afterwards rinsed with deionized water again. 4% volume of Bonderite NT-1 was used for each treatment solution.

Results and discussion



The OCP plot of a CRS plate comprises steady and unsteady stages. At the unsteady stage, the potential decreases clearly with increasing immersion time. The initial decrease of the OCP was probably caused by the surface activation of substrate and dissolution of substrate in the acidic medium accompanying with simultaneous hydrogen evolution. After about 100 s of immersion the OCP curve reached a plateau, which is indicative of the establishment of a steady-state situation related to a complete coverage of the surface with the film. After immersion in solution for 60 s, some oxides or reacted products are deposited on the surface of the cold rolled steel, as shown in Fig. 1b. The surface morphology of samples treated for 60 and 90 s looks very similar to each other. When the immersion time increased to 90 s, the deposition proceeded to form a more compact film (Fig.1c).



Fig. 1: The AFM topography images of bare polished (a) and samples that were treated 60 s (b) and 90 s (c) in the conversion solution (pH=4 and solution temperature of 25 °C)

Nyquist plots indicate a single semicircle for all samples, which is indicative of one reaction between electrolytes and coatings. The coatings immersed in solution with conversion time of 90 and 60 s show larger semicircles in comparison with 120 and 180 s, indicating that these coatings have better anti-corrosion performance.

Conclusions

Experimental results showed that the immersion time strongly affects the microstructure and anti-corrosion resistance of the conversion coatings. According to polarization tests, all samples treated in the conversion solution had a better corrosion performance in comparison with bare CRS sample. Many obvious cracks were generated on the coating surface when the conversion time extended to 120 s and 180 s. With increasing the immersion time, the thickness of conversion layer increased until 180 s and uniformity decreased after 120 s.

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Theoretical Investigation of the Thermal Unimolecular Decomposition of Ethylacetate

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Keywords: Kinetics study, Unimolecular reaction, Ab initio, Ethylacetate.

Introduction:

The gas phase unimolecular decomposition of ethylacetate is important from theoretical and experimental standpoints. The mechanisms of the thermal unimolecular degradation of many simple sters are studied as a model for biofuel pyrolysis [1]. Theoretical studies have revealed that a cyclic six-membered ring transition state is involved in the decomposition of estes. In this research, the kinetic and mechanism of the thermal unimolecular reaction of ethylacetate is studied by employing ab initio quantum chemical methods. The computed rate constants are compared with the available experimental data.

Method:

The ab initio calculations are performed using Gaussian 09 program. The geometries of all the stationary points, i.e., minimum energy structures and the saddle points, are fully optimized at MP2 level of theory with the 6-311+G(2d,2p) basis set. Harmonic vibrational frequencies and zero-point energies of all species are calculated at the same level of theory. To improve the description of the stationary points, single-point calculations are made at the CCSD(T)/6-311+G(2d,2p). Additional calculations are performed at the BB1K, M06-2X and the composite CBS-QB3 methods. A modified strong collision/RRKM model is employed to calculate the thermal rate coefficients for the formation of major products as a function of temperature and pressure.

Results and Discussions:

Three important possible reaction channels are supposed for unimolecular reaction of ethylacetate.

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$$\begin{array}{c} \mathrm{CH_3COOC_2H_5} \rightarrow \mathrm{CH_3COOH} + \mathrm{C_2H_4} & \qquad \mathbf{R1} \\ \rightarrow 2 \ \mathrm{CH_3COH} & \qquad \mathbf{R2} \end{array}$$





\rightarrow CH₃CH₂OH + CH₂CO R3

The calculated barrier heights for the reaction channels R1, R2 and R3 at the CCSD(T)/6-311+G(2df,2p) level of theory are 211.3, 307.0 and 318.4 kJ mol-1 respectively. The higher barrier heights of the reaction channels R2 and R3 show that these reaction channels do have smaller rate constant in comparison with the reaction channel R1. It is revealed by many experimental measurements that the important pathway for gas-phase unimolecular decomposition of ethylacetate is the reaction channel R1. The present calculation reveals that the computed P_{1/2} (the pressure at which $k_{uni} = k_{\infty}/2$) for k₁ at 500, 1000 and 1500 K are about 0.01, 3.0 and 70.0 Torr, respectively.

Conclusion:

The high-pressure limiting rate constants for the reaction channel R1 computed in the temperature range of 500-2500 K are in good agreement with experimental data and can be fitted to a Arrhenius expression as $k_1 = 7.78 \times 10^{13} \times exp$ (217.23 kJ mol⁻¹/RT) s⁻¹.

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The study of photo degradation kinetics of PVC-TiO₂ nano-composites and determination of their hydrophobicity under artificial UV radiation

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Key words: Nanocomposite, Photocatalyst, Photodegradation, Hydrophobicity

Introduction:

Poly(vinyl chloride) is one of the most widely used polymers in the world, because it exhibits a good price/performance balance that allows penetration into many applications such as pipes, cable insulation, packaging foils, and medical products [1]. In outdoor applications all polymers degrade. The degradation rate depends on the environment and on the type of polymer. The PVC– TiO_2 composite represents a unique case of the photocatalytic degradation of solid wastes while most of photocatalytic remediation systems have dealt with aquatic or air pollutants [2].

Materials and methods:

As the first step, TiO_2 nano particles were prepared with irradiation ultrasonic. The polymer solution was prepared by dissolving of PVC and di- octyl phthalate in tetrahydrofuran (THF) under stirring. Then TiO_2 powder and other additives were suspended in PVC stock solution and were sonicated for 1 h to prepare a uniform suspension. The total loading of TiO_2 varied from 1.35 to about 2.1 Wt. % in the solution. Prepared suspension was spread on a cast and dried. All the films were irradiated under a 300W high pressure mercury lamp during different periods of time.

Result and discussion:

During irradiation, weight changes of samples used for rate constant calculations. The weight loss of the PVC film or the extent of its degradation under artificial UV radiation is predictably a function of the process variables – namely the loading of the photocatalyst and the intensity of the UV radiation. Light energy excites the semiconductor catalyst to generate hole and electron pairs:

 $\text{TiO}_2 + hv \xrightarrow{k_1} \text{TiO}_2(h^+ + e^-)$





Trapping of these holes and electrons lead to the formation of hydroxyl radical. OH[•] free or adsorbed on the catalyst surface may attack neighbouring PVC chain to produce PVC[•] radical. PVC[•] may also be produced by attack of UV or visible radiation onto PVC surface: $PVC + hv \xrightarrow{k_6} PVC^{\bullet}$

The rate of degradation of the polymer can be expressed as a first order process in the mass of undegraded polymer (W): $-dW/dt = d[PVC^{\cdot}]/dt = kW$

The rate constant being a function of the concentrations of the photocatalyst (TiO₂) and the intensity of the UV radiation (I_f), density (ρ) and thickness (l):

$$k = (I_{\rm f}/\rho l) \cdot (2k_1[{\rm TiO}_2] + k_6)$$

Results show that rate of photocatalytic degradation is larger than that of photodecomposition of PVC[3]. The SEM images reveal that the degradation of the PVC matrix started from the $PVC-TiO_2$ interface and led to the formation of cavities around TiO_2 particle aggregates[2]. After irradiation, by formation of cavities on nanocomposite surface, it was expected that hydrophobicity would increase. But water absorption increased and hydrophobicity decreased, because TiO_2 nanoparticles witch came out of polymer matrix due to degradation, have strong hydrophilic property.

Conclusion:

Photocatalytic activity of nanoparticles depends on intensity of radiation, concentration of oxygen and moisture, therefore shelf life of nanocomposites depends on weather and season. Loss or reduction of polymer's hydrophobicity causes serious effects, such as reduction in electrical insulation and pollution withstands performance, or influences the aging process.

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Equilibrium isotherms and kinetic for adsorption of methylene blue from aqueous solution on activated carbon prepared from wood of khinjuk tree

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Key words: khinjuk tree, Methylene blue (MB), Kinetic , Isotherm.

Introduction:

The textile industries such as textile, metal plating, packaging, and paper industry generally produce a large amount of wastewater dye containing and that may cause serious environmental impact and lead to mutagen containing aquatic biota or humans and cause carcinogenic. Methylene Blue (MB) is selected as a model compound for evaluating the potential of tripoli to remove dye from wastewaters. MB is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. The objective of this study was to assess the suitability and efficiency of active carbon prepared from the wood of khinjuk tree pretreated for the removal of Methylene blue (MB) in batch method was studied. The influence of variable including pH, contact time, initial dye concentration, adsorbent dosage, sieve size of adsorbent were studie. MB contents and its removal percentage were determined using a UV-Vis spectrophotometer before and after adsorption. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. The graphical correlation of various adsorption isotherm models like Langmuir, Freundlich, Tempkin have been carried out for this adsorbent [1-3].

Materials and methods:

All chemicals including NaOH, HCl , KCl, Methylene Blue (MB) and AC with the highest purity available are purchased from Merck Stock MB solution was prepared by dissolving its accurately weighted amount in double distilled water and the test solutions were prepared by diluting stock solution. The removal percentage of MB was calculated using the following relationship: % MB removal = $((C_0 - C_t)/C_0) \times 100$

Where C0 (mg.L-1) and Ct (mg.L-1) is the dye concentration at initial and after time t respectively.





Apparatus:

During this study following pH optimization in all experiments, the Methylene Blue (MB) concentration was determined at 664 nm against a reagent blank. The pH measurements were done using pH/Ion meter model-686 (Metrohm) and absorption studies were carried out using Jusco UV-Visible spectrophotometer model 160-shimadzo.

Result and discussion:

in this test , it was shown that the MB dye can be adsorbed on the surface of the active carbon prepared from the wood of khinjuk tree by electrostatic adsorption.in this work dye elimination on series of similar solution whit 50 ml volume in concentration of 10 mg.L⁻¹ in the various pH from 1 to 8 was investigated and showed that in pH=3, there is maximum percent of dye elimination. synthetic studies to determinate dye absorption effciency in optimum values namely solution with concentration of 10 mg.L⁻¹ in pH=3 in the 10 time with 1.4 gr absorbent with elovich synthetic models and inter particle diffusion was investigated and observed that dye absorption follows two-order synthetic. investigation of adsorption isotherms carried out in afew different concentration in 50 min with optimal condition of another parameters, and showed that dye absorption follow by langmuir isotherm.

Conclusion:

The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. active carbon prepared from the wood of khinjuk tree is identified to be an effective adsorbent for the removal of MB from aqueous solution. it was observed that bath sorption using active carbon prepared from the wood of khinjuk tree was dependent on parameters such as initial concentration of dye, time, pH, amount of adsorbent and type of dye. Analysis of experimental data for the Langmuir, Freundlich and Temkin isotherms were determined and the equilibrium data were best described by the Langmuir model. The kinetics process is can be successfully fitted to pseudo-second-order kinetic model respectively.

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(Liquid + liquid) equilibria for phosphoric acid with dichloromethane and water using GMDH-type neural network

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Introduction:

Studies of phase equilibria of ternary systems are very importantin both theoretical and industrial. Precise LLE data of aqueous mixtures with organic solvents are needed in the evaluation of industrial units for solvent extraction processes.

Phosphoric acid is one of the most widely used inorganic acids, which has many industrial applications. Therefore, the efficient separation of phosphoric acid from aqueous solutions, by solvent extraction technique, is of considerable economic importance in the chemical industry [1,4].

In this work, LLE results for the aqueous mixtures of phosphoric acid with dicholoromethane at T = 298 Kwas obtained for the ternary system with usingGMDH type-neural network in prediction of LLE data for the ternary system.

GMDH method

GMDH(group method of data handling)model was applied in great variety of areas for data mining and knowledge discovery,forecasting and systems modeling,optimization and pattern recognition.inductive GMDH algorithms give possibility to find automatically interrelations in data,to select optimal structure of model or network and to increase the accuracy of existing algorithms. This original self-organizing approach is substantially different from deductive methods used commonly for modeling.it has inductive nature –it finds the best solution by sorting –out-of possible variants.By sorting of different solutions GMDH networks aims to minimize the influenceof the author on the results of modeling.Computer itself finds the structure of the model and the laws which act in the system. Group method of data handling is a set of several algorithms for different problems solution.

It consists of parametric, clusterization, anaoguescomplexing, rebinarization and probability algorithms. This inductive approach is based on sorting-out of gradually complicated models and selection of the best solution by minimum of external criterion characteristic [5].

Result and discussion:





(Liquid + liquid) equilibrium data for ternary mixtures (water + phosphoric acid + dichloromethane)were determined at T = 298.2 K. The experimentalLLE data were satisfactorily fitted by the GMDH model. The averageRMSD value between the observed and calculated mass percent obtained.

Conclusion:

Tie-line data for the ternary system containing of(water+ phosphoric acid + dichloromethane) were obtained at T = (298.2) K. The GMDH modelwas used to correlate and analyze the experimental LLE data. The average RMSD value between the observed and calculated mass percent was good agreement.

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The photodegradation of 4-nitrophenol at presence of Fe₂O₃ and Fe₂S₃ nanoparticles as photocatalyst

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Abstract

The Fe₂S₃ and Fe₂O₃ nanoparticles are produced by using controlled precipitation and aqueous colloidal solutions methods, respectively. The prepared nanoparticles are characterized by UV-Visible spectroscopy and transmission electron microscopy. The Fe₂O₃ and Fe₂S₃ nanoparticles are used as photocatalyst in photodegradation of 4-nitrophenol as pollutant. The calcinations temperature, pH of samples and photocatalyst dosage are optimize in order to increasing of photodegradation rate. The highest photodegradation efficiency is obtained at presence of 1.0 g/L nanoparticles at time 180 min under UV-Visible irradiation, pH of 10 and 10 mg/L of 4-nitrophenol.

Keywordes: Fe₂O₃, Fe₂S₃, Nanoparticles, 4-Nitrophenol, Photodegradation

Introduction:

Nanoparticles of magnetic metals and oxides have attractedgreat interest in recent years because of their unique physical and chemical properties. Due to their suitable surfacechemistry, ferric oxide magnetic (Fe_2O_3) nanoparticles offer agreat of interest for biomedical applications, such as drugdelivery, cell engineering, magnetic carriers for bioseparationand for enzyme and protein immobilization, tissue repair, diagnostics, and as a contrast-enhancing medium [1]. Semiconductor photocatalysis, as one of the advanced physicochemical processes, has beenextensively studied for solving existing environmental problems such as wastewater treatment [2]. Phenol is a major pollutant of surface water and ground water, and there are strict limits on the amounts which can be discharged in the effluent. Owing to its stability to a level of safety inthe range of 0.1-1mg/L is not easy [2].





Experimental:

0.1-1.2 g/L of Fe_2O_3 and Fe_2S_3 nanoparticles added on specific content from 10 mg/L of 4nitrophenol (4-NP) solutions on pH=3-12. Since irradiations of hours 1-4, nanoparticles separated by insulator and solutions absorbance dimensioned on max wavelength of 4-nitrophenol solutions.

Results and discussion:

The UV-Vis absorption spectra of Fe_2S_3 and Fe_2O_3 nanoparticles calcined at 300°C show absorbance band in the wavelengths of 525 and 514 nm, respectively. The particles size distribution is obtained at range 4-50 nm by using TEM.

The results showed on pH=3-10, photodegradation efficiency of Fe_2O_3 and Fe_2S_3 nanoparticles increased with increasing of solutions pH. Increasing concentration ⁻OH on pH>10 and to react with [•]OH due to product H_2O_2 and HO_2^{\bullet} with lesser activity ratio [3]. Hence, pH=10 is optimize pH. With increasing of photocatalyst quantities until 1g/L, 4-NP photodegradation increased. 4-NP photodegradation due to aggregation of photocatalyst particles on above quantities of 1g/L and decreased specific surface area decreased [2]. Hence 1g/L is optimizing quantity.

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Humidity and scaning rate effects on the glass transition (Tg) of ABS (acrylonitrili butadiene styrene)

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Keywords: acrylonitril butadiene styrene (ABS), glass transition (Tg), differential scanning calorimetry (DSC)

Introduction:

Acrylonitrile-butadiene-styrene terpolymer is a high performance thermoplastic containing two amorphous phases; a rubbery phase provided by butadiene, and a strength-lending styreneacrylonitrile(SAN) copolymer two-component phase. It has two glass transitions. The low temperature glass transition is due to the butadiene phase, and the high temperature one is due to the SAN phase [1]. Glass transition is a physical property of an amorphous material that defines the change from an iso-viscous glassy state to a rubbery state (and vice versa) at a temperature, which is referred to as the glass transition temperature, Tg [2]. According to previous research, the influence of scan rates and molecular weight (900 to 1.8×10^6) on the glass transition temperature of low polydispersity polystyrene has been studied by DSC at different heating rates [3]. The effect of water observed on the extent of physical ageing is related to the plasticizing effect of water on Tg [4]. Our aim was to investigate the effect of scan rate and humidity on the glass transition temperature of ABS polymer via differential scanning calorimetry (DSC).

Materials and methods:

Acrylonitrile butadiene styrene (ABS) Granules –ABS powder (we solved ABS granules in THF (tetra hydro furan) solvent then adding methanol as anti-solvent until formed a precipitate). Then Let the powder dry during the two days. We measured the moisture for ABS whit weight loss. We created different humidity on the ABS powder whit different concentrations of the H_2SO_4 during the 3 days. Then we measured the glass transition temperature for the ABS with different humidity.





Apparatus:

Glass transition properties of the ABS were investigated by DSC (DSC823e; METTLER TOLEDO, Switzerland). The DSC was calibrated by indium and tin.

Results and discussion:

Many transitions are kinetic events; they are a function of both time and temperature. For example the glass transition temperature for ABS with 10°C/min rate is 103.07°C and with 80°C/min rate will shift to 117.32°C. Therefore the Tg will shift to a higher temperature when heated at a higher rate because it has less time at any specific temperature. This shift is the result of two different factors. The first is that the sample has low thermal conductivity and, therefore, the temperature of the center of the sample lags the temperature of the surface. The size of the temperature lag increases with heating rate and causes the glass transition on heating to shift to a slightly higher temperature. The second factor is that the glass transition is associated with a change in molecular mobility, and this mobility has a small time-dependent or kinetic contribution. Moisture absorption in the ABS is 2.87%. Water absorption by polymers causes of the reduced ability of these materials. The effect of water observed on the extent of physical ageing is related to the plasticizing effect of water on Tg.. Increasing the humidity content shifts Tg to a lower value, thus for samples stored at the same temperature and at a smaller [T-Tg], the structural relaxation is facilitated in glasses with increasing moisture content [4].

Conclusion:

We investigated various humidity and different scan rates on the glass transition temperature of ABS. Data shown Tg will shift to a higher temperature with increase of heating rates and results shown decrease the Tg with increase the humidity. The glass transition is used in light-emitting diodes for organic materials, nano-lithography, the pharmaceutical industry, food industry and in making rubber.

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Solid-state kinetics calculation of a new synthesized oxovanadium(IV) complex using differential scanning calorimetry

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Key words: Solid-state kinetic, Diffrential scanning calorimetry, Direct differential method

Introduction:

Solid-state kinetic studies of oxovanadium complex calculate of kinetic parameters (activation energy, frequency factor, reaction model) using differential scanning calorimetry (DSC) technique, condition of non-isothermal and with model-fitting of direct differential method. Experimentally, solid-state kinetics was studied either isothermally or nonisothermally. These methods generally fall into one of two categories: model-fitting and model-free. Solid-state kinetics can be studied with thermal analytical methods for example by differential scanning calorimetry (DSC). [1].Solid-state kinetic studies have appeared in the pharmaceutical literature over many years. Before the discovery of insulin and its clinical trials for treating diabetes mellitus (DM), inorganic salts of vanadium have long been known to act as orally viable mimics [2]. Since insulin is not orally active, great effort has therefore been made to synthesize oxovanadium(IV) complexes of organic ligands of high biological activity (hydro/lipophilicity) therefore we have synthesized a new oxovanadium complex and during our research discovered this complex is a high-energy material by thermal analysis technique (DSC).

Materials and methods:

Chemicals and solvents used for the preparation of Schiff base ligands and metal complexes

are: 5-Boromosalicylaldehyde, 1,3-diamnopropane, Oxovanadium(IV) sulphate, methanol. Oxovanadium(IV) sulphate (6mmol) was dissolved in hot absolute methanol (300 mL)





and added to mixture Schiff base (6mmol), dissolved in methanol (20 mL) and therefore oxovanadium(IV) complex synthesized.

Apparatus:

Solid-state kinetic studies were investigated by DSC (DSC823e; METTLER TOLEDO, Switzerland). The DSC was calibrated by indium and tin.

Result and discussion:

By DSC curves with 10 °C.min⁻¹ rate and using MATLAB software , α changes (the progress of the reaction) and $d\alpha/dT$ (rate of reaction) with increasing temperature was calculated. Then we used model-fitting of direct differential method that it is according equation of $\left(\ln \frac{d\alpha}{dT} = \ln \frac{A}{\beta} - \frac{Ea}{RT}\right)$. The plot of $\ln \frac{d\alpha}{dT}$ versus $\frac{1}{T}$ (T is absolute temperature and $f(\alpha)$ is reaction model) gives activation. energy (Ea)and frequency factor (A) from the slope and intercept, respectively [3] and Model that creat regression maximum was selected as a model reaction.

Conclusion:

Thermal decomposition study of oxovanadium complex with using DSC technique characterize that decomposition enthalpy of this complex is very large. Also kinetic parameters obtain with model-fitting of direct differential method by differential scanning calorimetry (DSC) technique.

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Photodegradation of methylene blue using Sb-doped ZnO nanostructures prepared by microwave irradiation method

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Keywords: Semiconductor, Photocatalyst, Microwaveirradiation, Nanostructures

Introduction:

Semiconductor photocatalysts have been a potential field for treating various water pollutants [1]. Among thephotocatalysts,ZnO is a very attractive semiconductor photocatalyst. Major limitation to achieve high photocatalytic efficiency is the quick recombination of photo-generated charge carries. Doping is a powerful way to enhance the separation of charge carries in semiconductor photocatalyst[2]. Microwave irradiation is becoming an increasingly popular method forprepration of nanostructures [3]. In this work, we have prepared Sb-doped ZnO nanostructures in water by microwave irradiation method and effects of some operational parameters on photocatalytic activity of them were investigated.

Materials and methods:

The chemicals were obtained from Merck, and employed without further purification. Photocatalysis experiments were performed in a cylindrical Pyrex reactor. A UV Osram lamp with 125 W was used as light source.

Results and discussion:

Photocatalytic activity of Sb-doped ZnO nanostructures toward photodegradation of MB was evaluated under UV irradiation. The results indicate that the nanostructures with 0.1 mole fraction of Sb cations exhibit highest photocatalytic activity among the prepared samples. Influence of various operational parameters on photodegradation of MB has been studied to achieve maximum degradation efficiency. The results demonstrate that microwave irradiation time has not remarkable effect on the photodegradation reaction. A series of experiments were carried out to find the optimum catalyst amount by varying weight of the nanostructures between 0.025 and 0.2 g. The reaction rate constant increases with weight of the photocatalyst and then decreases. Indeed, maximum value of





the rate constant was achieved at 0.15 g of the photocatalyst. Also, the results demonstrate that the reaction rate constant decreases with calcination temperture. Moreover, the rate constant of the reaction suddenly increases with pH and then decreases. These results were described by electrostatic interactions. In order to know reusability of the photocatalyst, the photodegradation experiments were carried out on the photocatalyst in optimized conditions and the results were demonstrated in Fig. 1. As can be seen, the degradation percent decreases to 83 % after four runs, indicating that the photocatalyst has a better reusability.

Conclusion:

Photocatalytic activity of Sb-doped ZnO nanostructures for degradation of MB molecules under UV irradiation is higher than that of pure ZnO. The nanostructures with 0.1 mole fraction of Sb cations demonstrate better results. Moreover, calcination of the photocatalyst decreases degradation rate constants. Influence of the catalystweigh, concentration of MB and pH of solution on the photodegradation reaction was studied and the results were discusseed.



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Preparation and characterization of Sb-doped ZnO nanostructures by a simple and green refluxing method

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Keywords: Sb-doped ZnO, Nanostructures, XRD, SEM.

Introduction:

Controlled preparation of nanomaterials is an important topic in nanoscience because it is the prerequisite for applications of these materials [1]. Recently, semiconductor nanomaterials have been extensively studied due to their vital applications in numerous technologies such as microelectronics, electro-optics, nonlinear optics, light energy conversion, photocatalysis and biological fluorescence labeling. Among semiconductors, ZnO and cation-doped ZnO known as an important ones which have been studied extensively in the past few years due to their fundamental and technological characteristics [2,3]. There are various methods for preparation of these nanomaterials. Generally, these methodologies employ harmful chemicals, high temperatures, or longer reaction times. For this reason, in this work, we have prepared Sb-doped ZnO nanostructures in water by a simple refluxing method.

Materials and methods:

The chemicals were obtained from Merck, and employed without further purification. The X-ray diffraction (XRD) patterns were recorded on Philips Xpert X-ray diffractometer. Surface morphology of particles was studied via LEO 1430VP scanning electronic microscopy (SEM). Diffuse reflectance spectra (DRS) recorded by a Scinco 4100 apparatus.

Results and discussion:





The phase and purity of the prepared nanostructures (with 0, 0.03, 0.06, 0.10 and 0.20 mole fractions of Sb) were determined by XRD, whose typical diffraction patterns are shown in Fig. 1. As can be seen the diffraction peaks are in agreement with the JCPDS file of ZnO (JCPDS 36-1451), which can be indexed as a wurtzite hexagonal crystalline phase and no characteristic peaks are observed for other impurities. The sharp diffraction peaks manifest that the as-prepared nanostructures have high crystallinity.

Morphologies of the nanostructures were investigated by scanning electron microscopy (SEM). The nanostructures are mainly nanoplates with different sizes and although the particles are agglomerating however the boundaries between single crystallites are clearly observable (Fig. 2).

Diffuse reflectance spectra (DRS) of the nanostructures with different Sb contents showed that there are not any significant changes in UV-Vis. region.





Conclusion:





Sb-doped ZnO nanostructures were prepared using a simple, mild and template-free method in water by 3 h refluxing at about 95 °C without using any organic compound. The nanostructures were characterized by XRD, SEM, DRS and FT-IR techniques.

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Visible light degradation of methylene blue using Sb-doped ZnO nanostructures prepared under microwave irradiation

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Keywords: Photocatalysis, Pollutant, Microwave irradiation, Methylene blue.

Introduction:

Photodegradation of organic pollutants for water treatment has attracted wide attention due to its effectiveness, easy operation and ideally producing nontoxic products [1]. ZnO is of interest as a photocatalyst in the degradation of environmental pollutants [2]. To expand the usage of this photocatalyst, many studies employed modifications onto ZnO nanoparticles in order to improve its catalytic efficiency through enhancements of absorbance in the visible-light region [3]. In this work, we have prepared Sb-doped ZnO nanostructures in water by microwave irradiations and effects of some operational parameters on photocatalytic activity were investigated.

Materials and methods:

The chemicals were obtained from Merck, and employed without further purification. Photocatalysis experiments were performed in a cylindrical Pyrex reactor. A tungsten lamp with 500 W was used as visible light source.

Results and discussion:

Photocatalytic activity of Sb-doped ZnO nanostructures toward photodegradation of MB was evaluated under visible light irradiation. The results indicate that the nanostructures with 0.1 mole fraction of Sb cations exhibit highest photocatalytic activity among the prepared samples. Influence of various operational parameters on photodegradation of MB has been studied to achieve maximum degradation efficiency. The results demonstrate that microwave irradiation time has not remarkable effect on the photodegradation reaction. A series of experiments were carried out to find the optimum catalyst amount by varying weight of the nanostructures between 0.05 and 0.25 g. The reaction rate





constant increases with weight of the photocatalyst and then decreases. Indeed, maximum value of the rate constant was achieved at 0.2 g of the photocatalyst. The results demonstrate that the reaction rate constant decreases with calcination temperature. Decreasing photocatalytic degradation of MB with calcination temperature may be due to aggregation of the catalyst. Moreover, the rate constant of the reaction suddenly increases with pH and then decrease. These results were described by electrostatic interactions and solution of the nanostructures. In order to know reusability of the photocatalyst, the photodegradation experiments were carried out on the photocatalyst in optimized conditions and the results were demonstrated in Fig. 1. As can be seen, the degradation percent decreases to 83 % after three runs, indicating that the photocatalyst has a better reusability.

Conclusion:

Photocatalytic activity of Sb-doped ZnO nanostructures for degradation of MB molecules under visible light irradiation is higher than that of pure ZnO. The nanostructures with 0.1 mole fraction of Sb cations demonstrates better results. Moreover, calcination of the photocatalyst decreases degradation rate constants. Influence of the catalyst weigh, concentration of MB and pH of solution on the photodegradation reaction was studied and the results were discussed.





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Study of structural and magnetic properties of nanoparticles manganese ferrite synthesized by laser ablation

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Key word: Mn ferrite, Laser Nd:YAG, nano particle

In this work, Mn ferrite nanoparticles were synthesized by pulsed nanosecond laser ablation in deionized water using Nd:YAG laser. The aim is to investigate the structure and magnetic properties nanoparticles of MnFe2O4.

Manganese ferrites (MnFe2O4) belong to a group of soft ferrite materials characterized by high magnetic permeability and low losses. (1)

In the present work, nanoparticles of Mn ferrite are prepared by pulsed laser ablation in liquids(PLAL).Characterization of the samples were supported by transmission electron microscope(TEM),Fourier transform infrareds(FTIR),and magnetic force microscopy(MFM).

TEM measurement :

TEM (Philips EM280) was carried out for the accurate determination of diameter, shape, and microstructure of the Mn nanoparticles.

The TEM micrographs of the Mn nanoparticles fabricated by the Nd:YAG laser are shown in Fig. 1.The smallest nanosize were observed around 3nm.

Fig. 1 depict the size distribution of the nanoparticles fabricated by the Nd:YAG laser, obtained by statistical analysis of the particles in TEM images.





Fig.1 TEM image, size distribution histograms with fitted Gussian curves of Mn ferrite of nanoparticles.

FTIR measurement:





FTIR spectra of the Mn nanoparticles were recorded in KBr medium in the wave number range 400-4000cm-1 with a Bomem Canada FTIR(2-4).



2927 cm-1	Hydrogen Carbon
1453 cm-1	Oxygen Carbon
556.735 cm-1	Manganese Oxide
520.036 cm-1	Iron Oxide

MFM measurement :

A quantitative MFM technique to determine the magnetic orientation in longitudinal media at the microscopic level is described. The remained magnetization orientation ratio measured by this MFM technique correlates well with the orientation ratio measured using a VSM.



Fig.3 MFM image of the nanoparticles MnFe2O4

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Studies of Kinetic and Thermodynamic of competitive adsorption Of Cu⁺² and Zn⁺² on modified multi-walled carbon nanotubes

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Key words: Carbon nanotubes, Thermodynamic, Kinetic, Competitive adsorption

Introduction:

The presence of toxic heavy metal ions in the water and wastewater over the permissible limits pose a significant threat to the environment and public health. In view of the toxicity, incremental accumulation in the food chain and persistence in the ecosystem, wastewaters containing heavy metals are required to be properly treated prior to discharge into receiving waters [1]. Several treatment methods have been investigated for the removal of metal ions from water and wastewater. These methods include chemical precipitation, membrane filtration, ion exchange, and adsorption. Carbon nanotubes (CNTs), a new form of carbon, have come under intense multidisciplinary study because of their unique physical and chemical properties, CNTs include single-wall (SWCNTs) and multiwall (MWCNTs) depending on the number of layers comprising them [2]. The objectives of this investigation were to adsorption kinetic, equilibrium isotherm and thermodynamic parameters.

Materials and methods:

MWCNTs, obtained from Research Institute of Petroleum Industry (RIPI) (Iran). The surfaces of MWCNTs were modified by NaOCl to remove the amorphous carbon. In the modification of NaOCl, the as-produced CNTs (3 g) were immersed in NaOCl (60%) and shaken in an ultrasonic bath for 30 min; they were then continuously stirred for 3 h at 358 K. The modified CNTs were washed repeatedly using distilled water until the solution reached pH 7. Finally, the modified CNTs were dried at 343 K for 12 h. The modified CNTs were used to remove of both copper and zinc ions in aqueous solution competitively. All concentration detection was performed by atomic adsorption system (Philips Spectra PU9100X).





Result and discussion:

The functional groups on the surfaces of oxidized CNTs can be quantitatively measured by Boehm's method. In order to find the best kinetic model correlate the adsorption process, the kinetic models are used with regression of the experimental data. The value of R^2 calculated from pseudo second order kinetic is near 1. These results indicate that the competitive adsorption of Cu⁺² and Zn⁺² on the modified MWCNTs follows pseudo second order kinetics. Regression of equilibrium data of the process using both Langmuir and Freundlich models was used. The regression determination results shown that Freundlich isotherm model has a better fitting than Langmuir model. This shows that adsorption occurs on heterogonous surface. The Freundlich constants were determined from the slope and intercept of a plot of log Q versus log C. Thermodynamic parameters of the process such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated. ΔH° and ΔS° were obtained from the slope and intercept of linear plots of lnKc versus 1/T and The standard Gibbs free energy ΔG° values (kJ/mol) were calculated from the equation.

Conclusion:

The adsorption kinetics data were modeled using the pseudo-first order and pseudo-second order and elvich and bangham's kinetics equations. It was shown that the pseudo-second order kinetics described best the competitive adsorption kinetics for copper and zinc. The experimental results have been analyzed by Langmuir and Freundlich adsorption isotherms and the results show that the Freundlich isotherms can be fitted well to the equilibrium data. The thermodynamic parameters ΔG° , ΔH° and ΔS° values of Cu⁺² and Zn⁺² adsorption onto MWCNTs show that the adsorption process is a spontaneous, physical and endothermic. Thus, the results show that the MWCNTs can be effectively applied for the removal of copper and zinc ions from wastewater.

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Preparation and properties of nanorotaxane from α-Cyclodextrin and Poly (ethylene glycol) with Poly (vinyl alcohol)

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Keywords: "Cyclodextrin"," Poly (ethylene glycol)"," Poly (vinyl alcohol)", "Sonication", "Hexagonal microstructures".

Introduction:

Poly (ethylene glycol) makes a reversible complex inclusion compound with α - cyclodextrin. Meanwhile, cyclodextrins (CDs) are a series of natural cyclic oligosaccharides composed of 6, 7, or 8 D(+)-glucose units which are connected through α -1,4-bondings namely α -, β -, or γ -CD, respectively. Various molecules can be fitted into the cavities of CDs to form supramolecular inclusion complexes, which have been widely studied as models to explain mechanism of the molecular identification. The current work aims to prepare and examine regularly shaped, hexagonal complexes of α -CD using PEG in the presence of PVA. The sonic energy was found to have major effect on the formation of discrete size microcrystals for complex inclusion compounds of PEG- α -CD in PVA solution. Both the time and the sonic energy at room temperature (25^oC) were effective factors of this process. Right concentration of PVA could facilitate the formation of discrete hexagonal microcrystals.

Formation of *a* – CD / PEG Complex without Sonic Energy:

The inclusion complexes of α – CD and PEG were prepared by adding an aqueous solution of PEG (5.0 mL of 5.0 wt %) to the aqueous solution of α - CD (5.0 mL of 14.5 wt %) followed by mixing for 1, 2, 4 and 6 hours at 0, 25, 40 and 50°C[1, 2].

Production of PEG/ α-CD in PVA:

The new complex of α - CD/ PEG in PVA was first developed from PEG and α -CD under sonic energy (Table 1).Afterwards, the sonicated complex was dissolved in the aqueous solution of PVA (5.0, 10, 15 and 20 wt %) at room temperature and stirred for one hour at 50°C. The solution was





finally centrifuged and kept one day to form the new complex. At the end, the solid complex was easily separated by dissolves in water to cast films.

Results and discussion:

The effect of sonication time on microstructure of the complex is depicted. This figure shows that apart from sonication time (30 min) or temperature (25 °C), PVA concentration has also played a critical role in formation of discrete and stable microcrystals of the α – CD / PEG complex in PVA[3]. The absence of crystals at higher concentrations of PVA is PVA/ ($\alpha - CD/PEG$) = 2/1 wt% solution can imply that a dissolution of the complex has taken place. Microstructures of the stable complex crystals indicate the effect of sonication at 30 min or longer times on PVA/ (α – CD/ PEG) =1/4 wt %, where no excess PVA can be found in the solution. The broad XRD peak at $2\theta = 19.260^{\circ}$ and a narrower one at $2\theta = 10.85^{\circ}$ (of the film) imply that PVA solution may act like a phosphate buffer to facilitate the formation of a stable hexagonal microcrystalline complex of about 10µm dimensions [3]. The sonication has provided enough energy to overcome the viscosity effect of PVA solution in this reaction. However, the chemical potential may give enough energy to assist dissolution of the crystalline complex at higher concentration of PVA. Furthermore, the effect of sonication time on concentration ratio of PVA introduces different microstructures . A new complex with different characteristic peaks is reported at similar PVA/complex ratios. After 30 min of sonication, PVA ratio is far less than 1 or about 1.4, and different inclusion complexes can be produced in this case.

Conclusion:

The crystalline structures of inclusion complexes of α -CD / PEG/ PVA were studied by SEM, XRD, FTIR and HNMR. SEM images of crystals showed that sonication of the reaction in poly (vinyl alcohol) solution having different ratios of PVA/complex was utilized to develop hydroxyl groups of desired ionic strength and chain mobilities required for the formation of one new inclusion complex between α -CD with PEG. It is possible to achieve a tricomponent inclusion compound (TIC) at similar ratios. The size of its underlying microcrystals is approximately 10 µm with almost uniform geometry

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Novel microfibers of rotaxanes from the Inclusion Complex Reactions of α , β , γ -Cyclodextrins with copolymer of poly(thiourethane)

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Keywords: sulfide polymer, α , β , γ -cyclodextrin, macromolecular microfibers, inclusion complex compound.

Introduction:

Although the reactions of toluene diisocyanates with many organic materials are known; their bulk reactions with organic sulfur polymers and formation of hexagonal microstructures of the copolymer have not been studied. In this study, we have found that inclusion complex formations of this copolymer with α , β , γ -Cyclodextrins can transform the hexagonal crystalline copolymer structures into novel microfibers; indicating that cyclodextrins cavity may not only forms a complex, but it controls the diameter of the microfibers and formation of new microfibers from inclusion complex of cyclodextrins with thiourethane.

Preparation of Thiourethane from TDI and Sulfide groups

Sulfide polymers (3 gr) was added to 30 cc TDI (which is liquid) and mixed for one hour at $60^{\circ}C$. The FTIR of thiourethane from TDI and sulfide polymer is with peaks at $3416.07 cm^{-1}$ ($CH_3 - S$), $2821.37 cm^{-1}(-CH_2 - S)$, $1658.51 cm^{-1}(H-S)$, $1378 cm^{-1}(-CH_2 - CH_2 - S)$, $1101.20 cm^{-1}(-S-)$ (Fig 2) [4].

Inclusion Complex Formation of CDs (α , β , γ - cd) with Thiourethane of TDI and Sulfide groups

The inclusion complex of CDs and the crystalline thiourethanes was prepared by adding a thiourethane solution (5.0 mL of 5.0 wt % in DMF) to a solution (5.0mL of 10 wt % in DMF) of α – CD; and mixing was continued for 2 hours at 25°C. The same method was used for β and γ -cyclodextrin at 60°C. The inclusion complexes were then separated and investigated by XRD and SEM.





Results and discussion:

Scheme 1 shows our suggested route to the formation of microfibers rotaxane (CD+ thiourethane) from the crystalline thiourethanes, assigning a new role to cyclodextrins, making a route for transformation of an ordered polymer into microfibers of a specific diameter. The crystalline structures of thiourethane with DMF and α -CD are shown. The result showed two kinds of microfibers of discrete structures of columnar and cage arrangments from the reaction at 25 ° *C*. In ^{25°}*C*, microfibers are mixture of strip like and rod like microfibers which strips are clearly wider from rode like kind. When the complexing temperature was increased to 60°*C*, the microfibers arrangement were lost from strip geometry to rod like structures and reappeared in smaller geometries of disordered structures. The increase in temperature may CD active sites turn in to a random orientation loosing the specific geometries needed for the fine microfibers arrangements. S-C bond in sulfides exhibits a Trans geometric pereferences, the Trans geometry have been reported [1,2].Figures compares the microfibers made by the Inclusion Complex of α , β and γ - cyclodextrins with thiourethane under the same conditions. In this process, the cavity size controls the size of the fibers, making the Van der-Waals radius of –OH groups within the cavity a determing factor in controlling the diameter of the fiber with a fixed ratio about 5.



Scheme1. Formation of crystalline microfibers from CD and thiourethane

Conclusion:

The inclusion complex of TDI with sulfide polymer (thiourethane) with α , β , γ -cyclodextrin makes specific microfibers of strip or rod like geometries. In formation of strip microfibers, there is more than one thiourethane chain in cyclodextrin cavity which crosses liked to each other. But in rod like microfibers, there is more than one thiourethane chain in cyclodextrin cavity. The thiourethane in the form of hexagonal crystalline structures change to microfibers with cyclodextrins in DMF. The microfibers diameters are controlled by the cavity size of cyclodextrins. Higher temperature, the complex is rods like, and with larger cavity size of cyclodextrins, larger microfibers of specific structures are formed.





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Microwave-assisted method for preparation of Sn-doped ZnS nanostructures in water and their photocatalytic activity

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Keywords: Sn-doped ZnS, Photocatalysis, Microwave irradiation, Nanostructures.

Introduction:

Nanocrystalline semiconductor materials are the subject of intense research due to their remarkable size, shape and surface dependent physical and chemical properties [1]. Photocatalysis, an advanced oxidation technology employing semiconductors as photocatalysts, is a promising method for treatment of contaminated ground, surface, and wastewater containing various organic pollutants [2]. This method is generally based on generation of OH radicals which interact with organic pollutants leading to degradation and, subsequently, mineralization [3]. Recombination of electron and hole, produced in photocatalytic degradation of the pollutants, decreases the photocatalytic activity. Doping of ZnS nanostructures with various cations can reduce the recombination rate.

For this reason, we have prepared Sn-doped ZnS nanostructures in water with various dopant contents by microwave irradiation. In addition, photocatalytic degradation of methylene blue (MB) under UV irradiation was investigated.

Materials and methods :

Zinc acetate was dissolved in water, and solution of high purity tin (IV) chloride was added to the solution. The solution was transferred into microwave oven and irradiated for 5, 10 and 15 min. After completion of the reaction, white colored product was centrifuged and washed three times with water to remove impurities. Finally the product was dried using a simple conventional oven at 60 °C. A UV Osram lamp of 125 W with the major fraction of irradiation occurring at 365 nm was used. The reaction kinetics was investigated by a spectrophotometer at 664 nm corresponding to λ_{max} of MB.





Results and discussion:

The XRD patterns for the prepared nanostructures demonstrate that the products have the same crystal structure and the diffraction peaks are corresponding to $(1 \ 1 \ 1)$, $(2 \ 2 \ 0)$ and $(3 \ 1 \ 1)$ planes of cubic crystal system (Fig.1). Photodegradation of MB on the photocatalysts with dopant content ranging from x = 0.00 to 0.15 were studied. The photocatalyst with 0.75 mole fraction of Sn have highest activity. In addition, influence of various parameters such as calcination temperature, catalyst weight, pH of solution and initial concentration of methylene blue (MB) on the photocatalytic degradation of MB was studied to achieve maximum degradation efficiency and the results were discussed. The reaction rate constant increases with catalyst weight up to 0.1 g and then decreases. Moreover, the degradation rate constant decreases with calcinations temperature.



Conclusion:

The nanostructures of Sn-doped ZnS were prepared in water without using any template under microwave irradiation. The photocatalysts were characterized using XRD, SEM and UV–Vis DRS techniques. The photocatalytic activity of the products was investigated by degradation of MB under UV irradiation.

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Investigation of Kinetic isotope effects on reaction of methane with radical of thrifluoromethane

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Key words: Kinetics, Potential energy surface, Transition state theory, Rate constant.

Introduction:

In this investigation, reaction of methane with radical of thrifluoromethane has been studied. This reaction is a hydrogen abstraction reaction and produce two kind of products. We study these two channels and determine the kinetic isotope effect in these reactions.

		(R_1)
		(R ₂)
de.		(R ₃)
	(R_4)	
		(R ₅)
Co.	(R_6)	
	Calchemin	(R ₄) (R ₆)

In 1967 Giles, R.D.; Quick, L.M. and Whittle, E. investigated reaction R_4 by Gas chromatography technique and reported it's rate expression equal to $1.34\pm1.3\times10^{-1} e^{7.11 [\pm 0.43 \text{ kJ/mole}]/\text{RT}}$ (cm³ molecule⁻¹ s⁻¹), at 417 - 625 K [1]. In 1964 Carmichael, H. and Johnston, H.S. used IR absorption technique and reported rate constant of reaction R_4 1.58x10⁻¹² [cm³/molecule s] $e^{-46.06 [\pm 0.46 \text{ kJ/mole}]/\text{RT}}$ at 357 - 534 K [2].

Materials and methods:

Gaussian03 program is used to calculated quantum chemical calculations. All species have been optimized at the MP2 /6-311++G(d,p) level of theory. Transition states along the minimum energy path have been obtained with scanning techniques and frequency test shows the accuracy of these transition states. Each transition states have one imaginary frequency, which is reasonable. Rate





constant of reactions R_1 - R_6 are calculated according to generalized transition-state theory (TST). TST explains the reaction rates of elementary chemical reactions. The general expression for transition state theory is as follows:

$$k(T) = \Gamma \frac{k_B T}{h} \sigma \frac{Q^{*}}{Q_A Q_B} \exp(-\frac{V_{MEP}(s)}{k_B T})$$

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That k_B and h are Boltzmann's and Planck's constants. σ is the degeneracy of reaction and Γ is the tunneling factor. The Q parameters are the sum of translational, vibrational, rotational and electronic partition functions for spices.

Result and discussion:

Optimized structures of reactants, products and transition states are shown in scheme 1. Isotope replacement doesn't have any effect on structure of molecules but has high effects on calculation zero point energy. The Arrhenius plots for these reactions are shown in Figure1 and 2. According to Arrhenius plots, rate constants of reactions compare with each other.



Scheme1. Optimized structure at the MP2/6-311++G(d,p) level. Distance and angle are shown in angstrom and degree respectively.



Figure 1. Arrhenius plot for reaction R₄-R₆. Solid line, open square triangle show R₄, R₆ and R₄, respectively.

Figure 2. Arrhenius plot for reaction R₁-R₃ Solid line, open square open With line and triangle with line show R₁, R₃ and R₂, respectively.

Conclusion:

According to potential energy surface of these reactions, reaction R_4 has lower activation energy than R_1 so it accomplishments more than R_1 .

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Study on the adsorption of caffeine on magnetic nanoparticle coupled with carbon prepared from almond nutshell

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Key words: Caffeine, Magnetic nanoparticles, Almond shell, Sorption.

Introduction:

Caffeine is a naturally occurring substance found in the leaves, seeds or fruits of coffee and tea plants[1]. Caffeine stimulates the central nervous system, enhances immunity, strengthens the heart and induces diaeresis. However, excessive caffeine intake can lead to adverse reactions, such as over-stimulation of the central nervous system, increased blood pressure, and it can be a risk factor for rheumatoid arthritis and premature birth[2]. Various methods have been attempted to remove caffeine from the aqueous solutions including using activated carbon[3], molecular imprinted polymers[4], and polymeric resins[5, 6]. Most of methods reported to remove caffeine are based on adsorption. Magentic nanoparticles (MN) are interesting materials have attracted much attention because of their unique magnetic properties and widespread application in different fields such as mineral separation, magnetic storage devices, catalysis, and magnetic refrigeration system, heat transfer application in drug delivery system, magnetic resonance imaging (MRI), cancer therapy, and magnetic cell separation. The application of MN or MN composites in the field of adsorption of materials from aqueous media is becoming an interesting area of research[7]. The main goal of this study was to adsorb caffeine from the aqueous solutions by incorporating of MN and almond shell carbon.

Materials and methods:

To prepare MN, 0.425 g of ammonium ferrous sulfate and 0.6275 g of ammonium ferric sulfate were poured in a beaker and 8 mL of 15 M NH_4OH solution was added slowly at constant temperature of 40 ^{0}C under nitrogen atmosphere with the aid of ultrasonic stirring for 10min. The pH of the final mixture was controlled in the range of 10–11. The reaction was allowed to be continued for 30 min,





which resulted in the suspension changing from black to a brown color. After the completion of the reaction, the suspension was allowed to cool at room temperature. Almond shell carbon was prepared by ashing the crushed nutshell in an oven at 800 °C for an hour and finally it was milled. Subsequently, an amount of 0.25 g of almond carbon was suspended in 100mL of MN solution and mixed thoroughly to obtain a composite of MN and carbon. Caffeine solutions were treated with various amounts of the composite and amount of caffeine removed were measured spectrophotometrically. Factors affecting the adsorption such as pH, temperature, time, and interferences from other molecules were studied and optimized. The method was applied to remove caffeine from the real sample of caffeine containing beverages.

Apparatus:

Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (Tensor 29, Brucker) at resolution 1 cm⁻¹. Caffeine concentrations were measured by UV-Visible spectrophotomer Lambda 25 (Perkin-Elmer, USA) equipped with UV Win Lab software.

Results and discussion:

Results showed that carbon prepared from almond shell was coupled with MN, hence its adsorption capacity and efficiency was improved significantly. A simple spectrophotmetric method was used and validated for caffeine analysis. Result showed that spectrophotometric method for the determination of caffeine had a linear range of 0.5-60 mg/L. Precision of the method on the basis of RSD% was lower than 3.6%. Error percent of the method was lower than 3.8% that shows good accuracy for the method. LOD and LOQ of the method were 1.47 mg/L and 1.51 mg/L, respectively. Result showed that if caffeine solution be protected from heat and light it has good stability. Optimum condition to remove caffeine from aqueous solutions was obtained as follows: caffeine concentration: 10 mg/L; adsorbent amount: 0.1 g; temperature: 25°C; time of adsorption to equilibration: 5 minutes; pH of the solution: 6.6. In optimum conditions, more than 89% of caffeine can be removed from the solution. Adsorption mechanism was evaluated by fitting the data on various isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Tempkin[8]. Results depicted that data are best fitted on Freundlich isotherm that means caffeine is adsorbed in a multilayer manner. Kinetic of the adsorption was studied through the fitting data on three kinetic models commonly used in adsorption including Elovich, pseudo first order and pseudo second order kinetic models[8]. Pseudo second order adsorption kinetic was the best model of





kinetic of adsorption of caffeine on MN-carbon. Adsorption capacity of MN-Carbon was calculated to be 1.4 mg/g. Results showed that modified nanoparticles prepared have the proper efficiency to remove caffeine from aqueous solutions.

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Thermodynamic investigation of the removal of titan yellow dye from aqueous solution

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Introduction

The industrial wastewater usually contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic. It is well known that textile industries, pulp mills and dyestuff manufacturing discharge highly colored wastewaters which have provoked serious environmental concerns all over the world [1]. Dyes can be classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [2]. Milling of rice crop produced rice husk as agriculture waste material having no commercial significance. Approximately 80 million tons of rice husk are obtained annually.

In the present work, it is aimed to investigate the adsorption equilibrium of titan yellow on rice husk, at 10, 15, 25, 30, 35, 40 and 45 °C. This study was also undertaken to evaluate thermodynamic parameters of the adsorption at different temperatures above.

Methods:

Rice husk was collected from local rice mills. The husks were thoroughly washed with water to remove all dirt and were oven-dried at 80°C till constant weight. Then the material was grinded and sieved through the sieves of 300µm size. The dried husks were stored in a pre cleaned air tight container and were used as such without any physical or chemical pretreatment.

A stock solution of titan Yellow (3478.6 mg L⁻¹) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out of 200 rpm agitation speed (mechanical shaker) at room temperature ($25 \pm 1^{\circ}$ C) under batch mode 11 as per the experimental conditions. All absorbance measurements O.D at 408 nm (λ_{max}) using a double beam UV/VIS spectrophotometer (Cary 100) and the standard curve is drawn optical density against concentration and the straight line is obtained. From this line, the concentrations of dye solution before and after





adsorption were calculated. In all five different sets of adsorption experiments were carried out by varying the following experimental parameters with other parameters kept constant.

Results and discussion:

The thermodynamic parameters such as standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated from the temperature data obtained from the biosorption of titan Yellow onto rice husk biosorbent. According to the Van't Hoff equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\log K = \frac{-\Delta G^{\circ}}{2.303 \,\text{RT}} = -\frac{\Delta H^{\circ}}{2.303 \,\text{RT}} + \frac{\Delta S^{\circ}}{2.303 \,\text{R}}$$
(1)
(2)

The values of different thermodynamic parameters are collected in Table 1. The negative value of ΔG° reflected the spontaneity and feasibility of biosorption of dye on the biosorbent. Thermodynamic parameters showed that biosorption of titan Yellow were spontaneous at all temperatures (10–45 °C). The positive value of ΔH° indicated that the biosorption of titan Yellow on the rice husk was endothermic in nature. The biosorption capacity increased with increase in temperature. This might be due to increase in diffusion of titan Yellow dye into the pores of the biosorbent surface and formation of new binding sites at higher temperature [1]. The positive value of entropy (ΔS°) showed the increase in randomness at the solid/liquid interface during the biosorption mechanism of titan Yellow dye. The results indicated that dye removal capacity increased with an increase in temperature. This might be due to an increase in the motion of dye molecules.





T (K)	К	$\Delta G^{\circ} kJmol^{-1}K^{-1}$	$\Delta H^{o}kJmol^{-1}K^{-1}$	Δ S ° Jmol ⁻¹ K ⁻¹
283.0	1.92	-1.53		190.21
288.0	2.59	-2.28		189.50
298.0	5.18	-4.07	52.29	189.16
303.0	7.58	-5.10		189.42
308.0	11.75	-6.31		190.26
313.0	17.13	-7.39		190.68
318.0	19.49	-7.85		189.13

Table 1: Thermodynamic parameters for the biosorption of titan Yellow onto rice husk

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Rheology and morphology of Polyamide/Polyethylene blends filled with different clays

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Key words: Rheology- Morphology- Blend- Nanocomposite

The main objective of the present work was to study rheology and morphology of PA / LDPE blends filled with different nanoclays (Closite30B and Closite15A). The effect of PE-g-MA compatibilizer was also studied. All the compounds were prepared via melt intercalation method and the samples were analyzed using XRD and SEM. The rheological properties of all the samples were also measured using a stress controlled rheometer.

Using the rheological analysis it was concluded that both Closite30B and Closite15A can intercalated in PA and Closite30B was more affine to PA, while they showed no interaction with PE. Affinity of Closite30B to PE was not affected using PE-g-MA, while in the presence of PE-g-MA intercalation of PE chains into the Closite15A inter layers was occurred. Using rheological and XRD analysis, it was shown that both Closite30B and Closite15A exhibited higher degree of dispersion in PA/PE blend than that of pure PA. This was attributed to the detachment process of clay layers in PA phase due to the stress transfer effect of PE particles. The presence of PE-g-MA compatibilizer showed two different effects in PA/PE/Closite30B and PA/PE/Closite15A blend nanocomposites. In latter case adding of compatibilizer decreased modulus of elasticity particularly at low frequency region, while in former case it increased the viscoelastic properties. Using this results and the result of SEM and XRD analysis, it was concluded that in the blend nanocomposite consist of Closite30B, presence of PE-g-MA increases the interfacial interaction via formation of PA-g-PE copolymer which in turn leads to more stress transfer of PE particles to clay tactoids undergo exfoliation. Although, in blend nanocomposite consist of Closite15A, the presence of PE-g-MA also leads to formation of PA-g-PE copolymers it also facilitate the migration of clay tactoids into the dispersed PE particles. Using of both clays simultaneously led to an intermediate behavior of both single clays.





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Kinetic of Decomposition of Hydrogen Peroxide Over MnO₂ and MnO₂ Suported on Z-Al₂O₃

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Key words: Kinetics of Decomposition, Hydrogen Peroxide

Introduction:

The catalytic decomposition of Hydrogen peroxide by solid metals has gained conciderable attention. The reaction has been treated by many authors from the point of view of the radical mechanism[1-4]. On the basis of the electron theory ,the metal could be considered as a source and as a sink of electrons. Although ,the high activity of solid metals towards the decomposition of H_2O_2 has been well-known for sometime, very little work has been reported on the catalytic decomposition of that reaction using Over MnO₂. In this article we investigate the decomposition of H_2O_2 over MnO₂ Suported on \mathbb{Z} -Al₂O₃.

Materials and methods:

The Al_2O_3 (90, active neutral, 70–230 mesh) and MnO_2 were purchased from Merck . Hydrogen peroxide (35% in water) was purchased from Fluka and its concentration (11.4 M). Place the solution in a 1 cm quartz call and measure the absorbance at 229 nm .

Result and discussion:

The decomposition of Hydrogen peroxide solution:

 $2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$

At room temperature Hydrogen peroxide decomposes very slowly. The presence of a catalyst may cause it to decompose quickly. The reaction is started by adding a catalyst to the Hydrogen





peroxide. The catalyst is manganese(IV) oxide(MnO2) and manganese(IV) oxide supported over \Box -alomina(MnO₂-Al₂O₃). Alumina is one of the most important ceramics for their potential applications in, e.g., electronics, catalysis and optics. The catalyst MnO₂-Al₂O₃was prepared by reaction of MnO₂ and Al₂O₃ in methanol. Finally a gray colored solid was obtained.

The concentration of Hydrogen peroxide decreases as the reaction proceeds.

The concentration of Hydrogen peroxide can be noted every 15 minute and a graph of concentration against time can be plotted. The gradient of the plot (the steepness of the slope) shows how fast the reaction is going. The rate of the reaction can be followed by recording the concentration of Hydrogen peroxide with decreases absorbance .This implies that the absorbance becomes linear with the concentration (or number density of absorbers) according to :

A=elc

Conclusion:

One of the catalyst used is Manganese(IV) oxide - $MnO_2(s)$ Using more catalyst will show an increase in reaction rate. This is because more catalyst will have a greater surface area for the reaction to take place. The reaction can be performed using (the same amount) of manganese(IV) oxide supported over \mathbb{Z} -alomina(MnO_2 -Al₂O₃) catalyst to compare how well each catalyst works for the same reaction.





As you can see from the graph and rate constants, Manganese(IV) oxide supported over \mathbb{Z} -alomina(MnO₂-Al₂O₃) catalyst is the best catalyst. The gradient of the plot is greater (steeper) than the Manganese(IV) oxide (MnO₂(s)), also it was found that the rate of decomposition of H₂O₂ obeyed a first order rate equation.

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Complete Gas-Phase Proton Microaffinity Analysis of Hematoxylin. A DFT Study

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Key words: Hematoxylin, DFT Study, Proton microaffinity, Proton macroaffinity.

Introduction:

For each polybasic molecule there may be several ways for protonation depending on which site is protonated. Protonation of different sites for each polybasic molecule will release different amounts of energy and therefore the term "proton affinity" for protonation of a special site on a polybasic molecule can be replaced by term "proton microaffinity". Two other types of defined gas-phase proton affinities for such molecules are "proton macroaffinity" and "proton overallaffinity"[1]. The proton macroaffinity is a weighted mean of various proton microaffinities involved in each step of protonation of a polybasic molecule and corresponds to its protonation macroconstant in solution. For calculation of proton macroaffinities, \overline{PA}_n , of polybasic molecules with any type of symmetry, Eq. (1) is used.

$$\overline{PA}_{n} = \frac{\sum_{j=1}^{l} \sum_{i=1}^{m} PA_{n,i} \times R_{n,j} \times S_{n,j}}{\sum_{j=1}^{l} \sum_{i=1}^{m} R_{n,j} \times S_{n,j}}$$
(1) Where $R_{n,j} = \sum_{j=1}^{K} R_{n-1,j} \times S_{n-1,j}$

The proton overall affinity, PA_{ov} , is also defined as the negative of the electronic energy difference between L and it's fully protonated form together. According to Hess's law the summation of the calculated proton macroaffinities for one polybasic must be the same as or very close to its \overline{PA}_{ov} .

$$\overline{PA}_{ov} = \sum_{n=1}^{m} \overline{PA}_{n}$$
(2)

So far, the proton microaffinity analysis for Hematoxylin (Fig. 1), a polybasic molecule, in the gas phase has not investigated.





Computational details:

The geometries of all microspecies in the gas phase were fully optimized at standard $6-31++G^{**}$ basis set by BP86 level of theory using the Gaussian 03[2] set of programs.

Result and discussion:

Proton macroaffinity (\overline{PA}_n) obtained from proton microaffinities for each step of protonation for Hematoxylin was calculated. The summation of the calculated proton macroaffinities (\overline{PA}_{ov} ; see Eq. (2)) is very close to its PA_{ov} value.

As can be seen in Fig. 1, there is a good correlation between the calculated $\log PA_n$ in the gas phase and corresponding measured $\log K_n$ in solution (calculated by experimental techniques in our research group) for all four successive protonation steps of Hematoxylin.



Conclusion:

The results of this work show that the reliable theoretical calculation of the gas-phase proton macroaffinities and proton overallaffinities of Hematoxylin according to the complete proton microaffinity analysis is potentially possible.



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Studies on the Adsorption Kinetics for the Removal of Methyl Orange using Modified Sawdust

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Keyword: Methyl Orange, Modified sawdust, Diethylenetriamine, FT-IR.

Introduction:

Dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants [1]. Methyl orange (MO) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products and has to be removed from water due to its toxicity[2]. Various chemical and physical processes such as adsorption [3,4], Solvent Extraction Using Reverse Micelles [5], and Photocatalytic degradation [6,7] were used for the removal of Methyl Orange from water samples. In the present study the modified sawdust by diethylenetriamine (DETA-Sawdust) composite as a novel adsorbent was prepared by a two-step method. The structure and morphology of the synthesized adsorbent were characterized by powder the fourier transform of infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The adsorption was considered as the pseudo-first-order and pseudo-second-order kinetic models.

Preparation of absorbance:

Sawdust supplied by a local wood processing factory, was washed with distilled water to remove impurity, and then dried overnight at 50 °C. Dried sawdust was sieved to retain the 0.5 mm fractions for further chemical synthesis. HCl was added to 10 gr of sawdust then 60 mL of DETA was added to that. After keeping it for 2 h, the product filtered, washed with distilled water, and dried in oven at 50 $^{\circ}$ C for 24 h.





General procedure:

In each adsorption experiment, 50 mL of dye solution of known concentration and pH=3.5 was added to the modified adsorbent in a 250 mL erlenmeyer flask in room temperature (25 ± 1 °C) and it was stirred by a shaker at 100 rpm. After 50 min, the mixture was filtered and the concentration of Methyl Orange in the solution was measured by the spectrophotometeric method to be at 464.0 nm with Perkin-Elmer UV Visible Spectrophotometer (model: Lambda35).

Kinetic studies:

For evaluating the adsorption kinetics of MO, the pseudo-first-order and pseudo-second-order kinetic models (for 100 and 200 mg L^{-1} of MO) were used to fit the experimental data. Model of the pseudo-second-order kinetics better fitted the adsorption data according to the results (table 1).

		5
Kinetic parameters	$100 (mg L^{-1})$	200 (mg L ⁻¹)
$q_{e, exp} (mg g^{-1})$	28.90	43.00
Lagergren-first-order	•	
$K_1 (min^{-1})$	6.12×10 ⁻²	5.69×10 ⁻²
$q_e (mg g^{-1})$	8.16	31.44
\mathbb{R}^2	0.988	0.9616
Pseudo-second-order equation		
$K_2 (gmg^{-1} min^{-1})$	2.27×10 ⁻²	2.35×10 ⁻³
$q_e (mg g^{-1})$	28.66	47.84
\mathbb{R}^2	0.9992	0.9963

Table 1. Kinetic parameters for the removal of MO dye

Real ample:

The researchers studied dye removal from real samples of the waters from Ahvaz city, Karoun River, and the industrial wastewaters. Different amounts of MO were added to them and the removal process explained above was studied on them. Dye removal, in all the samples, was more than 92% which reveals the effectiveness of this method for all samples.





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Studies on the Adsorption Kinetics for the Removal of Methyl Orange using Modified Sawdust

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Removal of bromo phenol blue from aqueous solution on activated carbon prepared from wood of astragalus bisulcatus tree: kinetics and isotherm study

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Key words: Astragalus bisulcatus tree, Bromo phenol blue, Kinetic, Isotherm

Introduction:

Most of the dyes are resistant to be decolorized by chemicals,heat, and light due to their complex chemical structures. Therefore,the biodegradation of dyes is a typically slow and undesired process. There are several methods available for color removal from waters and wastewaters such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, and reverse osmosis. This study investigates the potential use of activated carbon prepared from the astragalus bisulcatus for the removal Bromo phenol blue dye from simulated wastewater. The effects of different system variables, adsorbent dosage, initial dye concentration, pH, sieve size of adsorbent and contact time were investigated and optimal experimental conditions were ascertained. Bromo phenol blue contents and its removal percentage were determined using a UV-Vis spectrophotometer before and after adsorption. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. The adsorption data at equilibrium was evaluated and fitted by different isotherm models like Langmuir, Freundlich and Tempkin to evaluate the ongoing adsorption process [1-3].

Materials and methods:

All chemicals including NaOH, HCl, KCl, bromo phenol blue and AC with the highest purity available are purchased from Merck.Stock bromo phenol blue solution was prepared by





dissolving its accurately weighted amount in double distilled water and the test solutions were prepared by diluting stock solution. The removal percentage of bromo phenol blue was calculated using the following relationship:

% removal = $((C_0 - C_t)/C_0) \times 100$

Where C_0 (mg.L⁻¹) and C_t (mg.L⁻¹) is the dye concentration at initial and after time t respectively.

Apparatus:

During this study following pH optimization in all experiments, the bromo phenol blue concentration was determined at 436 nm against a reagent blank. The pH measurements were done using pH/Ion meter model-686 (Metrohm) and absorption studies were carried out using Jusco UV-Visible spectrophotometer model 160-shimadzo. The removal percentage of MB was calculated using the following relationship: % MB removal = $((C0 - Ct)/C0) \times 100$ Where C0 (mg/L) and Ct (mg/L) is the dye concentration at initial and after time t respectively.

Result and discussion:

in this work dye elimination on series of similar solution whit 50 ml volume in concentration of 10 mg.L⁻¹ in the various pH from 1 to 9 was investigated and showed that in pH=1, there is maximum percent of dye elimination. synthetic studies to determinate dye absorption effciency in optimum values namely solution with concentration of 10 mg.l⁻¹ in pH=1 in the 10 time with 2 gr absorbent with elovich synthetic models and inter particle diffusion was investigated and observed that dye absorption follows two-order synthetic. investigation of adsorption isotherms carried out in afew different concentration in 60 min with optimal condition of another parameters, and showed that dye absorption follows by langmuir isotherm.

Conclusion:

The copper sulfide nanoparticles loaded on active carbon have been synthesized and characterized with SEM, and then these new adsorbents have been applied for removal of SY. It was observed that batch sorption using ZN(OH)₂-NP-AC were dependent on parameters such as initial concentration of dye, time, pH, dose of adsorbent. Analysis of experimental data for the





Langmuir, Freundlich and Temkin isotherms were determined and the equilibrium data were best described by the Langmuir model. The kinetics process is can be successfully fitted to pseudo-second-order kinetic model respectively.

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Solvent parameters effect on the rate constant of the solvolysis of 2-chloro, 2-methyl propane in aqueous solution of alcohols

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Keyword: 2-chloro,2-methyl propane, Rate constant, Solvatochromic parameters, Solvolysis.

Introduction:

solvent is one of the components of the reaction and determining factor of reaction rate. The solubility rate of a solute in the solvent significantly depends to the nature and strength of the attractive forces between solute-solute, solvent - solvent and solute – solvent. for measurement of reaction rate, reactant or product concentration can be followed as a function of time [1]. Due to extensive interactions of solvent – solute, solute- solute to define solvent polarity, experimental scales such as solvachromic Dymurt - Richard (E_T) and Kamlet - Taft parameters can be used. Solvatochromic parameters Kamlet - Taft indicate dipole / polarizability, π^* , hydrogen bonding donor , α , hydrogen bonding acceptor, β , [2]. Other solvatochromic parameter is the normalized polarity ,Dymort – Richard, (E_T^N). Solvolysis is one of the reactions that solvent is directly influence, The purpose of this research is comparison of the solvent effect on the rate of solvolysis reaction, 2 - chloro 2 - methyl propane (t-BuCl) in different mole fractions of water and methanol, water and ethanol and water, and 2 – propanol

Method:

2-chloro,2-methyl propane, sodium hydroxide, methanol, ethanol, and 2-propanol were purchased from Merc and were used without further purification. Doubly-distilled water was used in all solvent samples. The kinetic of solvolysis of t-BuCl in aqueous methanol, ethanol, and 2-propanol solutions was studied by titration method at 298K.





Because of the reaction product for each cases is HCl, variation of volume (v) of NaOH standard solution to naturalize HCl with time was recorded. In all cases the infinity volume, V_{∞} , was determined experimentally for each kinetic run. The reaction rate constant was obtained from eq

(1):
$$\ln\left(1 - \frac{v}{v_{\infty}}\right) = -kt \tag{1}$$

Result and discussion:

The rate constants of the reaction, *k*, demonstrate that the rate constants of reactions increase with water content up to a maximum at $X_w=0.9$ and then decrease to pure water. Solvatocromic parameters have been used to model kinetic data. The values for π^* , α , and E_T^N taken from literature [3]. Analysis of obtained data indicated single-parameter correlation of log *k* versus π^* , α , and E_T^N not to good results in all aqueous solutions. Therefore, multi-regression analysis was carried out. The only model that has good correlation is dual-parameter regression of log *k* versus α and π^* which are summarized in eqs. 2, 3, and 4 for aqueous solution of methanol, ethanol, and 2-propanol, respectively.

$$\log k = -5.305\alpha + 3.631\pi * -0.929 \qquad (R=0.940, n=11)$$
(2)

$$\log k = -3.668\alpha + 3.430\pi * - 3.026 \qquad (R=0.948, n=11)$$
(3)

$$\log k = -2.395\alpha + 4.618\pi * -5.907 \qquad (R=0.975, n=11)$$
(4)

Where, n and R are number of data and regression error.

This correlation is also seen in all aqueous solutions of alcohols for all solvent compositions: $\log k = -0.436\alpha + 3.650\pi * - 6.436$ (R=0.964, n=31) (5) As we can see α and π * have opposite effect on the reaction rate. If the intermediate of the

As we can see α and $\pi *$ have opposite effect on the reaction rate. If the intermediate of the reaction is a carbocation, the activated complex of the reaction has higher polarity than reactant. Hence the reaction rate increases with increasing $\pi *$. However the reaction rate decreases with α and there is evidence of strong hydrogen-bonding interaction. Therefore, the reaction media is stabilized via hydrogen bonding interaction and the reaction rate decreases.

Conclusion:

Results of this investigation demonstrate that solvolysis reaction of t-BuCl is first-order substitution nucleophilic reaction $(S_N 1)$ mechanism. The relationship of reaction rate constants





and solvatochromic parameters of media is multiparameter regression. It is clear that this mechanism can be generalized to other reaction behaviors.

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Modification of sawdust and using for removal of Pb : kinetic and real samples studies

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Key words; Lead, Removal, Adsorption, kinetic.

Introduction:

Heavy metal are considered the most important pollutants.in marine, ground and industrial waste waters they are highly toxic. Lead is one of the most dangerous heavy metals for humans and living organisms.all the compounds containing lead are considered as cumulative poisons. Lead poisoning in human couses severe damage to the kidney, nervous system, reproductive system, liver and brain. Therefore, the removal of exessPb ions from waste water is essential to protect human and environmental health. sawdust is prodused in large quantities at sawmills as a solid waste.interest in the use of sawdust as an adsorbent has been stimulated by the good resits that have been obtained.

Materials and methods:

All the used chemicals had an analytical grade and doubled distilled water was used throughout the study.

The sawdust supplied by a local wood processing factory was washed with distilled water to remove impurity, and then dried overnight. The dried sawdust was sieved to retain the 0.5 mm fractions for further chemical synthesis. HCl concentrated (Merck) was added to 10 gr of sawdust. After diethylentriamine(Merck) was added too. Then, the product was filtered, washed with distilled water, and dried in oven at 50 $^{\circ}$ C for 24 h.

In each adsorption experiment, 100 mL oflead solution (50mg/L)and pH=4.0 was added to the modified adsorbent in a 250 mL erlenmeyer flask in room temperature (25±1 °C) and it was





stirred by a shaker at 120 rpm. The mixture was filtered and the concentrationlead of in the solutionwas measured by the flame atomic adsorption spectrometric method.

Result and discussion:

Sawdust was chemically modified by a two-step procedure consisting of acidification with HCl and subsequent modification with diethylenetriamine. This chemical modification procedure was studied to compare the fouriertransform of infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) before and after the modification. The modified sawdust used for the removal of lead.Pseudo-first-order and pseudo-second-order are used to test the experimental data and thus elucidate the adsorption kinetic process. The pseudo-second-order model fit the data very well and provided better correlation coefficients than the pseudo-first-order model.q_e(mg.g⁻¹) was 50.0 and R^2

Equal 1.00.

The researchers studied lead removal from real samples of the waters from Dezfool city, KarounRiver,Dez River and the industrial wastewaters. Lead removal, in all the samples, was more than 99% which reveals the effectiveness of this method for all samples.

Conclusion:

The present investigation evaluated the fact that the chemically modified sawdust with diethylenetriamine can be used as an effective adsorbent for the removal of lead from different water samples. The SEM photographs clearly showed that after chemical treatment, a lot of pores were produced and the FTIR spectra showed that a chemical modification occurred. Pseudo-first and pseudo-second-order kinetics models were tested with the experimental data, and pseudo-second-order kinetics was the best. This study showed that the modified sawdust is useful as a promising adsorbent for the remove of lead in wastewater treatment


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The effect of ligand substitutions on catalytic activity of Heme – Imidazole derivatives – SDS complex as a nano artificial enzymes

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Artificial enzymes are manufactured from synthetic materials by simulation of natural enzyme functions. Heme group has the functional role in many hemoproteins like peroxidases. The microenviroment of heme and also it's ligands are very significant in catalytic activity of hemoproteins. Because of Heme tendency to dimerization in aqueous solutions, It's own catalytic activity is decreased in aqueous media. In critical concentration of detergents like SDS, the strong hydrophobic interactions between detergent and porphyrine group can overcome the porphyrine – porphyrine forces and porphyrine can be solubilized. In hemoproteins proximal heterocyclic nitrogen ligands like histidine can catalyze the oxidation of variety of substrates via reacting with hydrogen peroxide. In biomimetic chemistry, simulation of histidine is done by imidazole containing ligands. A surfactant - imidazole derivative - heme is known as nano artificial enzyme. Herein two sulfonyl imidazole analogues (1-(benzensulfonyl)-1H-imidazole, 1-tosyl-1H-imidazole) were compared in terms of activation of heme – SDS complex as a peroxidase like nano artificial enzyme. The catalytic activity of the designed models was evaluated by the oxidation reaction of guaiacol with H₂O₂ at 470 nm (λ_{max} for the product of the catalytic reaction) using a model Shimadzu-3100 spectrophotometer. Obtained kinetic parameters showed that catalytic efficiency of Tosyl imidazole is about 2.2 times of Benzen imidazole's catalytic efficiency. It is known that heterolytic cleavage of O-O bond of H₂O₂ is the key step of peroxidase mechanism that leads to generation of compound I. Tosyl group provide a favored





stereoelectronic environment for the active site of heme-peroxidase which promotes the heterolytic cleavage of O-O bond in hydrogen peroxide.





Thermokinetics Modeling of Claus Furnace Unit in the Presence of NH₃ for Determining the Optimum Operating Conditions

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Key words: Claus furnace unit, Ammonia, Thermodynamic, Kinetic, CHEMKIN

Introduction:

The Claus process is one of the most common processes to convert sulfur compounds into elemental sulfur. Claus process is formed from a high temperature furnace and several bed catalytic Claus process to enhance the production of elemental sulfur. In the sulfur recovery unit, the furnace is one of the key stages [1]. Researches show that the input feed to the sulfur recovery unit is not only containing H_2S , but also other compounds (such as ammonia) are into this unit. In the refinery operations, ammonia as a byproduct is entered into the furnace of Claus unit. Studies show that the presence of ammonia product ammonium salts in the furnace downstream units that these substances cause the catalyst deactivation and plugging of downstream equipment. Hence, the presence of ammonia in the feed of Claus unit, should be destroyed in the furnace and prevented from entering to the downstream units of furnace. Therefore in this study thermokinetics evaluation of presence of ammonia in the furnace of Claus unit has been investigated by CHEMKIN software to determine the optimum process conditions from perspective of thermodynamics and kinetics to maximum removal of ammonia.

Operating conditions and assumptions:

To calculate the distribution of products in Thermodynamic models, minimization of the total Gibbs free energy has been used. Also, in the kinetic modeling, the furnace can be assumed as a plugged and isothermal reactor with a length of 10 m and diameter of 1 m. In this study





Chernysheva [2] and Duynslaegher [3] kinetic models for the oxidation of ammonia and hydrogen sulfide have been used. The sum of these two kinetic models defines the reaction that have over 350 mechanisms. To evaluate the thermokinetics parameters, H_2S , NH_3 , H_2O containing feed in different proportions and in the temperatures range of 1000-1500 K have been considered. All calculations have been carried out at atmospheric pressure. All calculations have been done based on the amount of oxygen needed to convert one-third of the hydrogen sulfide to sulfur dioxide. In addition, the effect of increasing oxygen on the conversion of compounds has been studied.

Results and discussion:

Thermodynamic modeling results show that with increasing the ammonia concentration in the feed inlet, the conversion of nitrogenous compounds increases and conversion of hydrogen sulfide decreases. While kinetic modeling results show that increasing the ammonia concentration in the feed inlet, reduces conversion of nitrogen compounds. Increasing temperature will increase the conversion of hydrogen sulfide and nitrogenous compounds. In this case, both models of thermodynamics and kinetics, are compatible (see fig. 1). Thermodynamic and kinetic modeling results show that with increasing the air concentration (contain oxygen), conversion of nitrogenous compounds and hydrogen sulfide increases (see fig. 1).



Fig. 1. Effect of NH₃ Concentration on the: (a) conversion (b) equilibrium conversion of nitrogen compounds;(c) Effect of O₂ Concentration (in air) on the conversion of nitrogen compounds (At the cte: H₂S:NH₃:H₂O:70:20:10 mol)

Conclusion:

In this study thermokinetic modeling of the Claus process in the presence of the ammonia has been studied. Results confirmed that for maximizing of the ammonia removal in the furnace, two





major approaches can be utilized: enhancing the air concentration in the input feed and increasing the operating temperature. These results are quite consistent with experimental data.

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Removing Crystallization Water of Holmium Nitrate: Drying vs. Degradation

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Keyword: Holmium nitrate, Brachytherapy, thermal drying, holmium decomposition

Introduction:

Brachytherapy is a therapeutic choice in different cancer types *e.g.*, cervical, prostate, breast, skin cancer, *etc* to using β -emitting radioisotope source[1]. Radioisotope source must be dispersed within a matrix or trapped inside ligands forming a complex structure to prevent its leakage into biological milieu[2]. Holmium (Ho) as a commonly used brachytherapeutic candidate has a relatively short half life and can be used as hydrated chloride or nitrate salts. Metal-ligand complexes but it needs dry, extra pure starting materials [3]. Here, we report on water of hydration in hydrated Ho nitrate and optimal heating program needed for its thermal drying. The effect of drying atmosphere on the thermal decomposition of the material is also reported.

Materials and methods:

Thermal stability of Ho(NO₃)₃, 5H₂O, HoNit, was studied by TGA in temperature range of 20-600°C at 20°C/min. ATR-FTIR spectra were recorded in the range of 600-4000 cm⁻¹ for samples treated isothermally.

Results and discussion:

Complete removal of water of hydration takes please at temperatures relatively close to the salt decomposition temperature [3]. Fig. 1 shows TGA thermograms recorded for HoNit samples under air or N_2 atmosphere while a 10 min hold time was applied at different temperatures for each individual ru





The hold temperatures (250, 260C) were chosen in a way that while avoiding decomposition of the salt, allow complete removal of water of hydration. The weight loss observed at the end of 10 min hold at 250 and 265C were recorded as about 24 and 25%, respectively(Table 1), which is higher than that theoretically expected (20.4%) for losing the 5 water of hydration. This 4% difference can be attributed to the surface-adsorbed water. To ensure the claim, the salt was vacuum-dried at 90°C for 2 h (dried*) and TGA test was done(Fig.) .13 % weight loss at 250 °C, equals to losing 3 moles of crystallization water from the salt. Hence, 2 moles of water of hydration is removed along with the surface water during pre-conditioning, and HoNit decomposition does not occur until 350°C. No significant change was observed between thermal stability of HoNit in N₂ and air atmospheres



Figure 1: TGA thermograms of HoNit samples with no pre-treatment heated at 20°C/min under N2 or air atmosphere.

Figure 2: Isothermal TGA thermograms for HoNit hydrated samples with temperature hold in 200, 220 and 250°C.

Figure 3: ATR-FTIR results of HoNit samples treated at different temperatures.

Table1: Isothermal TGA findings at different temperatures

Temp. (°C)	200 (dried*)	220 (dried*)	250 (dried*)	250	265
Weight loss (%)	11	11	13	24	25

ATR analysis was performed to ensure removing the water molecules from crystal structure of the salt and completion of the drying process at 250°C (Fig. 3) on HoNit and the samples oven-dried at 75, 165, 217, and 250°C. The signal appeared at 1650 cm⁻¹ is related to the water hydroxyl groups. Peak intensity is reduced with increasing of temperature and at *ca.* 250 ° is almost vanished.

Conclusion:

the results in this report show thermal drying of commecial HoNitis possibleat 250°C. TGA and ATR-FTIR findings confirm this conclusion. Above this temperature, holmium nitrate begins to decompose and below this temperature all water molecules are not removed.





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Kinetics, Isotherm and Thermodynamic Studies of Adsorption of Blue 56 From Aqueous Solution onto Sea shell Powder

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Key Words: Kinetic, Dyes, Sea shell Powder, Blue 56, Isotherm, Adsorption

Introduction:

Dyes are substances that impart color material. Mankind has used dyes since the dawn of civilization. Hence attempts are made in this study to develop an inexpensive adsorbent for wastewater treatment using sea shell powder. The adsorption of Blue 56 by sea shell powder was investigated by varying the parameters such as agitation time, concentration, adsorbent dosage, pH and Temperature. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. Optimum pH=2. Adsorption kinetics was determined by pseudo first order and pseudo second order models to the experimental data. The results indicated that the pseudo second order model proving the best description of Blue 56 onto sea shell powder the experimental adsorption equilibrium data was analyzed by Langmuir, Freundlich adsorption models. Based on correlation coefficient (r^2) values, equilibrium data found fitted well to the Langmuir isotherm.

Materials and Methods:

Bivalve type sea shells that most commonly wash up on large sandy beaches were used in this study. The sea shells were collected from the sea beaches of Purity, Orissa, India. The shells were first thoroughly washed with double distilled water to remove sand, dirt and any unwanted particles. The shells were then dried at 383 ± 1 K for 24h in an oven drier.



Result and discussion:

Effect of pH on adsorption of Blue 56 by sea shell powder (2g/25 ml).



Adsorption kinetics parameters for the adsorption of blue 56 at temperature $25\pm0.^{0}$ C on condition optimum: SSP amount 2.0g/25ml, contact time 12 min and PH=2. Concentration (60 mg/L)

psudo-	first-order kinetic	model		psudo-first	-order kinetic model	
9rel(m99 ⁻²)	k ₁ (min ⁻¹)	R ⁵	9 ₆₋₂ (m.99 ⁻²) k _i (9	nuo_ouiu_o)	h(gmg ⁻³ min ⁻¹)	R ^t
22.35	0.0514	0.9685	41.28	0.0038	65.11	0.999

 R^2 >0.999 shows that the model can be applied for the entire adsorption process and confirmed that the sorption of Blue 56 onto sea shell powder the pseudo-order kinetic model.

Conclusions:

The results of present investigation show that sea shell powder has considerable potential for the removal of Blue 56 from aqueous solution over a wide range of concentration. Equilibrium and kinetic studies were conducted for the adsorption of blue 56 from aqueous solutions onto sea shell powder.

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Kinetics, Isotherm and Thermodynamic Studies of Adsorption of Blue 56 From Aqueous Solution onto Barley straw

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Key Words:Kinetic,Barley straw, Dyes, Blue 56, Isotherm, Adsorption

Introduction:

Dyes are organic materials with complex structures, toxic, carcinogenic, teratogenic, nonbiodegredable properties and the most important pollutants of textile industrial wastewaters. In general, several methods including biological and physic-chemical technologies have been used for removing colored contaminants from wastewater. The adsorption of Blue 56 by barley straw was investigated by varying the parameters such as agitation time, concentration, adsorbent dosage, pH and Temperature. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. Optimum pH=2. Adsorption kinetics was determined by pseudo first order and pseudo second order models to the experimental data. The results indicated that the pseudo second order model proving the best description of Blue 56 onto barley straw the experimental adsorption equilibrium data was analyzed by Langmuir, Freundlich adsorption models. Based on correlation coefficient (r^2) values, equilibrium data found fitted well to the Langmuir isotherm.

Materials and Methods:

Barley straw used as an adsorbent for the removal of a Blue 56 dye from aqueous solution. To Preparation the adsorbent, washing the adsorbent with tab water for tree time and then washed with distilled water several times. Then let dry for 24 hours in the sun.



Result and discussion:

Effect of pH on adsorption of Blue 56 by Barley straw (0.25g/25 ml).



Adsorption kinetics: Adsorption kinetics parameters for the adsorption of blue 56 at temperature $25\pm0.^{0}$ C on condition optimum: Barley straw amount 0.25g/25ml, contact time 13 min and PH=2. Concentration (60 mg/L)

psudo-first-order kinetic model		psudo-first-o	rder kinetic mo	del	
9.01(m99 ⁻¹)	k2(mm_,)	R ^z	$q_{cal}(mgg^{-1})$ $k_2(gmg^{-1}mins^{-1})$	h(gmg ⁻¹ min ⁻¹)	R ^z
4.85	0.0511	0.96	5.291 0.1641	4.593	0.997

All findings presented in this study suggest that Blue 56 / BS system cannot be described by a first-order reaction model.

Conclusions:

The results of present investigation show that pH solution play an important role on the retention of Blue 56, the basic environment is the most suitable for the removal of Blue 56. The kinetics data of the Blue 56 adsorption onto BS were well described by Pseudo-Second-Order model with a good correlation.

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Efficient removal of phenol using sonicated MCM-41

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Key words: Ultrasound, Surfactant, Template, Phenol

Introduction:

In spite of the considerable efforts that have been made toward making larger and regular pore systems, ordered mesoporous materials still remained indefinable until the discovery of MCM-41 in 1992. Using the spaces available from the pores of MCM-41 can create huge sites and surface area. This space may be partly from the template and partly due to the empty spaces which can be formed by removing part of them. This arrangement of the channels of MCM-41 may provide a suitable sorbent for organic compounds [1].

Materials and methods:

The surfactant-templated MCM-41 was synthesized by our common room temperature synthesis method [2]. Template removal was done using ultrasound waves [3]. We examined the capability of the prepared adsorbents for sorption of phenol.

Apparatus:

A Philips PW1840 diffractometer with CuKa radiation was used to record the powder XRD patterns of the MCM-41 samples within a range of of 1–10°. XRD patterns were recorded using an automatic divergence slit system. Specific surface area of the samples was estimated based on the data provided by a Sibata Surface Area Apparatus 1100. The sample was degassed at 250°C for 2 h prior to nitrogen physisorption measurement.





Result and discussion:

The BET surface area of the as-synthesized MCM-41 was found to be 13 m² g⁻¹ which is very low as compared to the sonicated MCM-41 which is 1195 m²g⁻¹. The XRD patterns for the ultrasound-treated MCM-41 shows that they preserve their structural order upon irradiation. Figure show the XRD patterns for the two as-synthesized and sonicated MCM-41. The crystallite size obtained from XRD data using Scherrer equation is about 33 nm.

The sonicated sample was used for adsorption of phenol. Different pH was tried to find out the highest amount of adsorption. A basic pH close to 9 was found to be suitable for adsorbing phenol. At this pH the phenolate negative species are high enough and both hydrophobic and electrostatic interactions are involved in phenol adsorption onto the sonicated sample. Extended studies were carried out to determine the adsorption capacity and equilibrium constant for PhOH on the MCM-41 samples. The distribution of solute between the liquid phase and the solid phase is a measure of the distribution coefficient in the adsorption process and can be expressed by the Freundlich and Langmuir equations. To determine the equilibrium isotherms, adsorbent dose were varied, while the initial concentration of PhOH was kept constant. The value of K_F and K_L and also n were calculated as shown in the Table. The calculated parameters show that Freundlich isotherm fits our data.

			MCM	-41(AS)	MC	CM-41(US)
			n	1.1178	n	1.404
ŧ		Freundlich	K _F	0.7452	K _F	2.064
8	V		\mathbb{R}^2	0.9299	R^2	0.9902
			Q_0	40	Q ₀	200
	a.	Langmuir	K _L	0.0130	K _L	3.92×10 ⁻³
(0 2 4 6 8 10 2 0 (Degree)		R^2	0.2008	R^2	0.8771

Conclusion:

The present study shows that the MCM-41 is an effective adsorbent for the removal of PhOH from aqueous solution. It was found that MCM-41 shows significant adsorption for PhOH as compared to MCM-41(US), this may be because of the hydrophobicity created by surfactant





template in the MCM-41. It was found that pH play an important role in the removal of PhOH from wastewater. It was observed that the adsorption of PhOH was highly dependent on pH of the aqueous solution. This was also supported by Freundlich adsorption isotherm.

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Preparation and characterization of Fe_3O_4/ZnO core/shell magnetic nanoparticles

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Keywords: Magnetic nanoparticle, Core/Shell, Surface modification, Fe_3O_4/ZnO .

Introduction:

The novel bi functional nanomaterials that exhibit magnetic-optical properties are good candidates for "bioassays" through harnessing of the optical properties as "markers" and magnetic properties as "vehicles".

Nano sized Fe_3O_4 (as magnetite), is an important member of spinel type ferrite, and has been widely used in tissue imaging, drug delivery and information storage.

Zno is an important wide band gap 2-6 semiconductor, which has a wide and direct band gap of 3.37 eV at room temperature with large exciton binding energy of 60 MeV and has great potentiality for being used in preparing gas sensors, chemical absorbent, catalyst for photocatalytic degradation, electrical and optical devices.

The result Nano composites not only have the magnetism of Fe_3O_4 nanoparticles that make the Nano composites easily controlled by an external magnetic field but also have the good photocatalytic of zno nanoparticles.

Material and methods:

 Fe_3O_4/ZnO core/shell nanomaterial were synthesized in three steps involving preparation of core Fe_3O_4 nanoparticles by co-precipitation method and its surface modification by sodium citrate then growth of ZnO shell layers on core Fe_3O_4 nanoparticles by refluxing methods





Result and discussion:

XRD: The X-ray powder diffraction pattern of the as-prepared Fe_3O_4 , ZnO and Fe_3O_4/ZnO are respectively ,shown in fig.1a-c.



Fig 1: XRD Spectrum Of (a) Fe_3O_4 , (b) Zno, (c) Fe_3O_4/ZnO

FT-IR: Fig.2 shows the IR absorption spectrum of Fe_3O_4/ZnO the characteristic absorption of Fe-O bond is at 571.9 Cm^{-1} and the absorption of the Zn-O bond is at 429.9 Cm^{-1} .



Fig2: FT-IR spectrum of Fe304/Zn0 composite





Effect of pH and ionic strength on phosphorus removal from aqueous solution by TiO₂ nanoparticale modified

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Abstract

Effect of pH and ionic strength on Phosphorus (P) removal from aqueous solutions was investigated using TiO₂ modified. The adsorption capacities were calculated to evaluated effectiveness of TiO₂ nanoparticles modified. Sorption capacity for TiO₂ modified by Chitosan (44.41 mg g⁻¹) was greater than other modifications. The result of pH at zero point charge (pH_{ZPC}) showed that the surface charge of the TiO₂ modified was negative. According to obtained results, when ionic strength increased removal of P increased at a constant pH. Finally, the highest percentage of removal P at all of the pHs was in ionic strength equal to 0.1.

Keyworde: Nanopaticles, removal, ionic strength, pH_{ZPC}, phosphorus.

Introduction:

Phosphorus is one of the greatest concerns because it can contribute significantly to eutrophication in aquatic environment [1]. In recent years, in situ soil remediation by direct injection of reactive metal nanoparticles into the contaminated source zone has attracted increasing interest [2-3]. The pH and ionic strength values played important roles in the use of nano-adsorbent as supports in the P adsorption process. In this study, effect of pH and ionic strength on P removal from aqueous solutions using TiO₂ modified was investigated.

Materials and methods:

We prepared TiO_2 nanoparticles modified with Walnut skin, Wheat straw, Chitosan, Sodium Carboxymethyle Cellulose (CMC), Malic acid and Humic acid. We measured the pH_{ZPC} of paticles by Revera et al. [4]. The adsorption isotherms of the P with TiO_2 modified were





determined at different initial P concentrations (0, 5, 10, 20, 40, 60, 100, 150, 200 and 250 mg L⁻¹). The Langmuir equation was used to describe the sorption isotherms P onto TiO₂ modified using the nonlinear procedure with Sigmaplot statistical software package (version 10.0).We also investigated the effect of ionic strength (0, 0.001, 0.01 and 0.1) and pH (2-8) on removal P by TiO₂ modified that had the highest percentage of P removal.

Results and discussions:

Our study showed that P sorption capacity for TiO₂ modified by Chitosan (44.41 mg g^{-1}) was greater than Wheat straw (38.10 mg g^{-1}), CMC (34.27 mg g^{-1}), Malic acid (31.34 mg g^{-1}), Humic acid (29.97 mg g^{-1}) and Walnut skin (29.18 mg g^{-1}). Our study showed that after making modify, amount of pH_{ZPC} increased in order to: TiO₂ modified by Chitosan (4.04) > Wheat straw~ CMC ~ Humic acid (3.98) > Malic acid (2.99) > Walnut skin ~ TiO₂ (2.0). When the solution pH is more basic than the pH_{ZPC}, negative ions and complexes will predominated at the interface and the surface will be negatively charged [5]. Based on the pH_{ZPC} determination, it can be deduced that the TiO₂ nanoparticles modified surface charge is negative, as the solution pH is 5.45. On the contrary, with a solution pH higher than the pH_{ZPC}, the surface is negatively charged and there will be an electrostatic repulsion between P species and the surface of TiO₂ modified. Sorption of P result onto TiO₂ nanoparticales modified was well described by the Langmuir model. According to the Q (mg g⁻¹) parameter, maximum sorption capacity are arranged in the following sequence, Malic acid (165.3 mg g^{-1}) > CMC (156.1 mg g^{-1}) > Humic acid (119.7 mg g^{-1}) ¹) > Chitosan (91.4 mg g⁻¹) > Wheat straw (75.7 mg g⁻¹) > Walnut skin (42.6 mg g⁻¹). Figure 1 shows effect of ionic strength and pH on the removal of P by TiO₂ modified with Chitosan. According to obtained results, when ionic strength increased removal of P increased at a constant pH. Similar result was obtained by Wang et al [6]. In high ionic strength solution, the negative charges on phosphate macromolecules were well screened and consequently the phosphate molecules wounded up like random coils. In this more compact configuration, more phosphate can be sorbed onto adsorbent surface.







Figure 1. Effect of ionic strength and pH on the removal of P by TiO₂ modified with Chitosan

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Adsorption properties of CO on (4,0), (6,0), and (8,0) zigzag single-walled carbon nanotubes: a density functional study

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Keywords : Nanotube , Adsorption , Carbon monoxide, DFT

Introduction:

In the recent years, single-walled carbon nanotubes (SWCNTs) have attracted great interest owing to their physical and chemical properties[1-3] .Because of their size, large surface area and hollow geometry, SWCNTs are being considered as prime materials for gas adsorption [4-8], biological, chemical, electromechanical sensors and nanoelectronic device [9,10]. Gas adsorption on carbon nanotubes is an important issue for both the fundamental research and technical applications of nanotubes. Sensitivity of CNTs to the carbon monoxide (CO) has been indicated by quantum mechanics calculations.The determination of the structure of adsorbed CO on CNT surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena.

Computational details:

In the present work, adsorption behaviors of the CO on SWCNTs were studied by using the representative models of (4,0), (6,0), and (8,0) zigzag single walled CNTs in which the ends of nanotubes are saturated by hydrogen atoms. The hydrogenated (4,0), (6,0), and (8,0) zigzag single-walled CNTs have 48 ($C_{40}H_8$), 72 ($C_{60}H_{12}$), 80 ($C_{64}H_{16}$) atoms, respectively. In all cases, the calculations are carried out with the B3LYP/6-31G** level of theory. The adsorption energy of a CO on the CNT wall was calculated as follows:

 $Ead = (E_{CNT} + E_{CO}) - E_{(CNT-CO)}$.





Results and discussion:

A CO can approach the nanotube walls from outside (out), which is the most common case, and from the inside (in). For the adsorption of the CO (O-down and C-down) on the CNTs, we considered two sites (i.e., the C1, and C2 sites above the carbon atoms). The calculations showed that the obtained adsorption energies depend on orientations and locations of CO, and the interaction becomes rapidly repulsive as the molecule approaches the CNT wall. The notation O-down and C-down denotes a CO perpendicular to the surface via O and C, respectively. In all pathways the potential is attractive, presenting a well of maximum ca. -130 kcal mol⁻¹, which is characteristic of a chemisisorption process. The adsorption energy with the equilibrium distance in each case is summarized in Table 1.

Table1. Adsorption energy (kcal/mol⁻¹) and equilibrium distance (Å) (rd) of a CO molecule on zigzag (4,0), (6,0), and(8,0) CNTs

Model	Mode		site	
			C1	C2
(4,0)	O-down	Adsorption energy	-103.54	-103.72
		rd	1.5	1.5
	C-down	Adsorption energy	-36.27	-38.64
		rd	1.5	1.5
(6,0)	O-down	Adsorption energy	-108.88	-112.81
		rd	1.5	1.5
	C-down	Adsorption energy	-77.88	-75.39
		rd	1.5	1.5
(8,0)	O-down	Adsorption energy	-122.32	-129.09
		rd	1.5	1.5
	C-down	Adsorption energy	-87.66	-89.47
		rd	1.5	1.5

Conclusions:

we theoretically studied the adsorptions of the CO on zigzag (4,0), (6,0), and (8,0) single walled CNTs through DFT calculations. For the CNTs the calculated E_{ad} for CO in O-down is more than that in C-down. We showed that by increasing the nanotube diameter more efficient binding could not be achieved.

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The photocatalytic degradation of methylene blue on the surface of sol-gel prepared nanostructured ZnTiO₃ and Zn₂TiO₄

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Key words: Nanostructure, ZnTiO₃, Zn₂TiO₄, photocatalyst

Introduction:

Semiconductor research has been promising in areas such as dye-sensitized solar cells and photocatalytic remediation of harmful organics from air and water. Among the semiconductors investigated, titanium dioxide (TiO₂) has received attention. On the other hand, zinc oxide (ZnO) has also been promising in the areas of solar cells, gas sensors and photocatalysis. The simultaneous synthesis of a ZnO-TiO₂ composite usually results in the formation of one or more of the three known compounds from the ZnO-TiO₂ system: Zn_2TiO_4 (zinc orthotitanate), with a cubic spinel crystal structure; $Zn_2Ti_3O_8$, with a cubic defect spinel structure; and ZnTiO₃ (zinc metatitanate), with a rhombohedral ilmenite structure. $Zn_2Ti_3O_8$ is the metastableform of ZnTiO₃. Pure ZnTiO₃ is not easily obtained, as it transforms to Zn_2TiO_4 and rutile. Zinc orthotitanate (Zn₂TiO₄) is an inverse spinel [1, 2]. These materials can be used for the photocatalytic compounds, but have a wide band gap (3.1 eV), restricting their photocatalytic activity to ultraviolet (UV) light [3]. In this study, we prepared nanostructured ZnTiO₃ and Zn₂TiO₄ via a modified sol-gel method which has been developed in our laboratory and investigated the kinetics of photocatalytic degradation of methylene blue on their surfaces.





Materials and methods:

Zn(NO₃)2.6H₂O, as the source of Zinc, tetrapropylorthotitanate, TPOT, as the source of Titanium, ethylene glycol, EG, 1-propanol and nitric acid were purchased from the Merck company. To prepare the sols of ZnTiO₃ and Zn₂TiO₄, an appropriate amount of zinc nitrate was dissolved in EG, and then the alcoholic solution of TPOT was gradually added to the solution. The obtained gels were kept at 70°C for 5 hours and were calcinated at 550°C and 700 °C for 3 hours for ZnTiO₃ and Zn₂TiO₄, respectively. The crystal structure and morphology of prepared materials were studied by XRD and TEM analysis. Finally, the catalytic degradation of MB on the surface of samples was measured in Birjand with a mean sea level of 1491 meters ,a longitude of 59° 13' and a latitude of 32° 13', in darkness and again in the presence of sun light at 1:00 P.M. The converted amount of MB was determined by the max absorption peak of MB in visible region using UV-Vis spectroscopy.

Apparatus:

The crystal structure of the obtained materials was investigated by using Bruker, Advane D8 diffractometer with Cu-K radiation (=0.15404 nm). The morphology and particle size of the nanocomposites was studied by Zeiss em10c, TEM. UV-Vis studies were carried out by Shimadzu UV-2501PC, UV-Vis spectrometer. Calcination temperature was determined by a Shimadzu TG-50, thermal gravimetric analyzer

Results and discussion:

The nanostructured ZnTiO₃ and Zn₂TiO₄ can be prepared via a low temperature route by a modified sol-gel method verifying XRD pattern analysis. The kinetics studies of photocatalytic and catalytic degradation of methylene blue is described by the first order rate law. Also, the rate constant of photocatalytic degradation was 100 times that of catalytic degradation emphasizing the formation of hole-electron pairs and a radical formation mechanism for degradation. Finally, the photocatalytic degradation of MB on the surface of Zn_2TiO_4 is carried out ten times faster than ZnTiO₃. Despite the fact that the same band gap values were used, the existence of a very little amount of ZnO in Zn₂TiO₄ has accelerated the rate of this catalyst compared to ZnTiO₃.





Conclusion:

Our studies show that the modified sol-gel method could develop a simple low temperature route for synthesis of nanostructured Meta- and ortho-zinc titanate. These materials work as proper photocatalysts for methylene blue degradation.

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sunflower seed hull adsorbent for removal of reactive red 198:kinetics and isotherm study

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Key words:adsorption isotherml,Reactive red 198,kinetic,Removal.

Introduction

one of the most important factors for the Absorption system design is predict the rate of absorption that controlled by the kinetic system. Kinetics of absorption depends on the chemical and physical properties of the adsorbent that impact on the absorption mechanismThe equilibrium adsorption isotherm is of importance in the design of adsorption systems. In general, the adsorption is other how adsorbates interact with adsorbents. Two commonly used isotherms such as Langmuir and Freundlich were selected for equilibrium absorption of dye Reactive Red 198 by particle shell sun flower seeds. The Langmuir adsorption isotherm is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption takes place at that site. The oretically, the sorbent has a finite capacity to adsorb the sorbate.

Predict the rate of absorption is one of the most important factors for the system design controlled by the kinetic system.

The purpose of this work to find a suitable adsorption isotherm and degree of kinetic for the absorption reactive red 198 by sun flower seed hull [1-3].

Materials and methods:

The raw material, sun flower seed hulls were repeatedly washed with distilled water to remove dirt, dust and other impurities and The washed hulls were then sun dried for 48 h Variable





mixing time and other parameterswere fixed toexamine the effect of contact time.Several kinetic models can be used to express the mechanism of solute sorption onto a sorbent. In this study, pseudo-first-order and pseudo-second-order kinetic models were tested.

Apparatus:

The kinetics studies were carried out using a mechanical stirrer and The samples were with drawn at predetermined time intervals and centrifuged. for separates Particulate from the liquid.The pH of sample solution was adjusted by addition of HCl or NaOH using a pH/Ion meter model-686 (Metrohm) and absorption studies were carried out using Jusco UV-Visible spectrophotometer model 160-shimadzo.

Result and discussion:

Contact time is one of the factor affecting the absorption process and Adsorption process reached equilibrium after 24 minutes.in this study Absorption was rapid in the early stages and gradually decreased with time after reaching equilibrium is almost constant. The kinetics process is can be successfully fitted to pseudo-second-order kinetic model respectively.

Conclusion:

The adsorption isotherm was best defined by the Langmuir isotherm model The kinetic experimental results were fitted with the pseudo-second-order model. The thermodynamic studies showed that the process was endothermic and spontaneous in nature.

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MP2 comparison of the effect of Fluorine and Amine groups on kinetics the of carbocation formation

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Key words; carbocation, MP2, kinetics

Introduction

The alkane which substituted with one or more halogen atoms such as chlorine or fluorine named as haloalkanes. The important type of haloalkanes is CFC compound. The CFCs are chlorofluorocarbons which contain chlorine and fluorine and were used as refrigerants, propellants for aerosols, for generating foamed plastics like expanded polystyrene or polyurethane foam, and as solvents for dry cleaning and for general degreasing purposes in last century. Unfortunately, in high atmosphere, the carbon chlorine bonds break to give chlorine free radicals which destroy ozone and so CFCs are largely responsible for destroying the ozone layer. Studying the chemistry of haloalkanes can be useful for understanding the chemistry of atmosphere[1,2] and many researchers work to know the chemistry which taken place in haloalkane [3,4,5]. In this research effect of the fluorine and amine groups on the kinetic of formation of carbocation from haloalkane and E1 reaction which compete to each others were studied by MP2 Methods.

Methods

The energy surface of the reaction of separation of the halide atoms from alkyle halide and carbocation formation was studied by MP2method, 6-311++G(d,p) basis set and Gaussia03W package. The difference between the used alkyl halides is the type of substitutions attached on them. The energy surface for each reactions were calculated and then the transition state (TS)





and activation energy of them were calculated. Analyzing of the results is the final step of the research.

Results

In the starting point of the research, the energy surfaces of the separation of halogen atom from molecules were calculated by the method and basis set mentioned previously. In Fig.2the energy surfaces for the reaction of separation of chlorine atom from 1-chloro 2-methyl 3-propane amide is shown. The transition state of reaction occurs when the chlorine atom separates from alkyl halide and the cabocation is formed. After formation of carbocation, it may be rearranged. In distance greater than 4.8 angstrom the formed carbocation will rearrange to make more stable (°2 type) carbocation. The carbocation formation and rearrangement of it in alkyl chloride include fluorine atom is the same as alkyl chloride include NH2 group. In Fig1 the carbocation formation from these two alkyl halide are compared. The transition state of reaction occurs when the chlorine atom separates from alkyl halide and the cabocation is formed. After formation state of reaction occurs when the chlorine atom is the same as alkyl chloride include NH2 group. In Fig1 the carbocation formation from these two alkyl halide are compared. The transition state of reaction occurs when the chlorine atom separates from alkyl halide and the cabocation is formed. After formation of carbocation, it may be rearranged. In distance greater than 4.8 angstrom the formed carbocation is formed. After formation of will rearrange to make more stable (°2 type)carbocation.



Fig1.The comparison of energy surfaces for the separation of chlorine atom from1-chloro 2-methyl 3-fluoro propane amide and 1-chloro-2-methyl 3-fluoro propane





In Fig1 it was shown that the kinetics and thermodynamics of reaction depends on the substituent nature so the transition state and products are more stable for NH_2 in comparison to F substitution. It is obvious that the transition state of reaction is in maximum of the graph of energy versus reaction coordinates and has one negative vibrational frequency. In this step, the structures of transition state for the studied reactions were firstly approximated from calculated energy surface and then by method and basis sets mentioned previously were optimized. Additionally the activation energies of the reactions were calculated. In table1 the list of calculated activation energies is presented.

Reaction	Activation Energy of 1 st	Activation Energy of 2 nd
	(kcal.mol ⁻¹)	(kcal.mol ⁻¹)
1-chloro 2-methyl 3-propane amide	90.02	91.93
1-chloro 2-methyl 3-fluoro propane	89.40	60.60

Table1. The list of calculated activation energies for each reactant

As the table1 show the activation energy for separation of halogen from the alkyl halide substituted with fluorine is greater than amine group. This fact can be explained by the relative electronegativity of these substituents. The TS of reaction must have a negative vibrational frequency so to ensuring the structure of TS, the IR spectrum of transition state was calculated and then the negative vibrational mode was looked for. Existence of one negative vibrational mode confirms the structure of TS. The negative mode in every calculated IR frequencies for these transition state shows that these transition states are really exist.

Conclusion

The haloalkanes especially CFCsare very important in industrial process. In this research the kinetics of carbocation formation from 1-chloro 2-methyl 3-propane amide and 1-chloro 2-methyl 3-fluoro propane were studied. As the result of this research, the kinetics of carbocation formation reaction depends on the nature of substitution attached to halo alkane. For instance the





activation energy for the reaction of halo alkane including the fluorine as substitution is greater than the carbocation formation from the halo alkane substituted with NH2 group. This fact can be explained by the electronegativity of substitutions.

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Kinetic study of the catalytic methane dry reforming to synthesis gas over Fe- V_2O_5/ZrO_2 Catalyst

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Key words: Methane reforming, Kinetic, Fe-V₂O₅ catalyst, Syngas, ZrO₂ support

Introduction:

In recent years, the catalytic process of carbon dioxide reforming of methane into synthesis gas, which converts two of the cheapest carbon-containing gases (CH_4 and CO_2) into a useful chemical product, has received considerable attention. This process produces synthesis gas with a low hydrogen-to-carbon monoxide ratio (1:1). The kinetics and the mechanism depend on the type of catalyst, the nature of support and the operating temperature range [1-2].

Materials and methods:

Nano ZrO_2 powder was purchased from East Nano Material Co. Inc. and used as a catalyst support. Fe-V₂O₅ supported nano ZrO₂ catalyst were prepared using coprecipitation method. The procedure is as follows: 0.016 mole of vanadium pentoxide (Sigma Aldrich) was dissolved in 0.5 M sodium hydroxide (Kanto Chemical Co. Inc) solution. Then, 0.01 mole of hydrogen peroxide (Merck) was added to this solvent to complete oxidation. It was acidified slowly with nitric acid (BDH chemical) down to pH equal to 6 (at 25 0 C). Then, 10 grams of nano ZrO₂ was added to the solution. It was stirred for 10 hours using a magnetic stirrer. At the end 0.007 mole Fe(NO₃)₃.9H₂O (Merck) was dissolved in 20 ml distilled water and it was added drop wise to the above Solution. The solution was stirred for 10 hours and filtered. It was washed with distilled water to remove the ionic co-products, and then it was air dried to formation of Fe-V₂O₅/ ZrO₂ catalyst and subsequently calcined at 923 k for 4 h in air.





Apparatus:

A magnetic stirrer (Griffin & George) was used for stirring the solution. A pH meter (Kent Industrial) was used for adjusting the pH of the solution. The prepared catalyst was calcined in furnace (Griffin). The catalyst structure was studied using techniques XRD (Seifret ID 3003), XRF (ARF) and TEM (PHILIPS/ Model CM120).

Result and discussion:

The results of the XRD for the Fe-V₂O₅/ZrO₂ catalyst showed that V₂O₅ at 20= 25.6, 26.5, 31.8, 52.6 and 61.3 was appeared. The Iron, has good distribution at the surface of the catalyst. The results of the XRF showed that 60% Zr wt., with 4% V wt. and 3%Fe wt. there were at the structure of the catalyst and the results of the TEM showed that the average crystals size were ~ 50 nm. According to the Iyer etal's Power-low kinetic model ($r = k[P_{CO_2}]^n[P_{CH_4}]^m$), the values of the power-law rate coefficients of CO₂ and CH₄ was calculated 0.43 and 0.17 respectively. According to the results, the diagram of the reaction rate constant[Ln K] *vs.* reverse absolute temperature [1/T] for Fe-V₂O₅/ZrO₂ and ZrO₂ catalyst, K₀ at Arrhenius equation is equal to 120.9 and 8.7 mol/g Cat. h. bar^{0.6} respectively, and energy of activation (E_a) is equal to 44.23 and 44.71Kj/mol, respectively.(Figures 1and 2)







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Nanochemistry





Linear correlation between thermal conductivity enhancement and fluid adsorption in water nanofluids at different temperatures

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Keywords: Nanofluid, Thermal Conductivity, Nanoparticle.

Introduction:

This is known that addition of nanoparticles can increase thermal conductivity of the base fluid [1]. Between various factors, the layering behavior of the fluid molecules on the nanoparticles surface has a determinant role on increasing the nanofluid thermal conductivity. Temperature, can affect the layering of fluid molecules around a nanoparticle as well as the shape and size of nanoparticle, density, intermolecular and nanoparticle-fluid molecules interactions [2].

Due to the solid-like ordering of the fluid around nanoparticle, the local density of the base fluid close the particle surface is usually greater than the bulk fluid. The number of adsorbed molecules on the nanoparticles surface can be showed by excess adsorption. Excess adsorption around a spherical particle can be calculated by the following equation [3]:

$$\Gamma = \int [\rho(\mathbf{r}) - \rho_b] d\mathbf{r} = 4\pi \int [\rho(r) - \rho_b] r^2 dr$$
(1)

where Γ is excess adsorption, $\rho(r)$ is the local density and r is the nanoparticle-fluid molecule distance. Due to the solid-like ordering, the thermal conductivity coefficient of the adsorbed fluid is greater than the base fluid and fewer than the metallic nanoparticles. Therefore, with increasing the excess adsorption, the thermal conductivity will enhance.

Density Functional Theory (DFT):

In density functional theory, the grand potential energy is related to the Helmholtz free energy functional [3]:

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int d\mathbf{r}\rho(\mathbf{r})\{V_{ext}(\mathbf{r}) - \mu\}$$
(2)





where μ is the chemical potential of the inhomogeneous system and $V_{\text{ext}}(\mathbf{r})$ is the external potential. According to the variational principle, the equilibrium one body distribution function of the fluid can be obtained by minimization of the grand potential [3],

$$\rho(\mathbf{r})\Lambda^{3} = exp\left(\beta\mu - \beta \frac{\partial F_{ex}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} - \beta V_{ext}(\mathbf{r})\right)$$
(3)

In DFT Eq. (3) may be solved using a proper iterative method.

Results and Discussion :

The obtained DFT results in Fig. 1 show that the thermal conductivity enhancement in nanofluids is linearly dependent on the excess adsorption. It can be seen that increasing the adsorption of water molecules around Au and Al_2O_3 nanoparticles leads to linear increasing of the thermal conductivity. An important point that must be noted is that the surface of nanoparticles remains unchanged with increasing the temperature. Therefore, improvement of the thermal conductivity cannot be because of the increasing of the nanoparticles surface. These results clearly confirm that the thermal conductivity enhancement is due to the increasing in adsorption on the nanoparticles surface. In the other hand, the adsorption is dependent on the temperature.



Fig. 1 Linear dependency of the thermal conductivity enhancement to the adsorption at different temperatures for two different water nanofluids, *a*) 0.026% solution of 17 nm Au nanoparticles in water [1] and *b*) 4% solution of 38.4 nm Al_2O_3 nanoparticles in water [1].





Conclusion:

The obtained results in this work show that the adsorption increases with increasing the temperature. Linear correlation between thermal conductivity enhancement and adsorption is obtained in various water nanofluids.

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Growth and characterization of nanocrystallineCdSe thin films deposited By chemical bath deposition method

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Keywords: Nanomaterias, CdSe thin films, Optical properties, Chemical deposition

Introduction:

NanocrystallineCdSe (E_g (bulk) =1.7 eV) thin films have received considerable attention because of their tunable band gap, which can vary their optical response from the infrared region to the ultraviolet [1,2]. Among various methods used for preparing thin films of CdSe, the chemical deposition (CD) is an easy, convenience, fast and economically available method [3]. In this work, we report the preparation of nanocrystallineCdSe thin films in a neutral medium as a new chemical bath deposition route. The resulting films are characterized in terms of composition, nanocrystalline structure, surface morphology and optical properties.

Experimental:

Glass slides were used as the substrate. Cadmium acetate, $Cd(CH_3COO)_2$, 2-(dimethylamino)ethanol (DMAE) and selenium powder of analytical reagent grade all from Merck Chemical Co., were used as received. For deposition of CdSe thin films, 20 ml of 1 M $Cd(CH_3COO)_2$, and 5 ml of 0.2 M DMAE solution were mixed in a beaker. Then 50 ml of freshly prepared Na₂SeSO₃ solution was added slowly with constant stirring and finally 58 ml diluted deionized water was added to the beaker. The pH of the solution was adjusted to 7.0 by addition of HCl solution. About 50 ml of this solution was poured into a glass tank being used as a reaction bath for the film deposition. Substrates were immersed vertically in the bath,





and the glass tank was placed in a thermostat bath set at the desired temperature (50 ± 0.5 °C). The deposition was carried out in controlled time periods up to 6 h. The deposited films were then washed with distilled water and dried in air at room temperature.

Results and discussion:

Figure 1 show the X-ray diffraction patterns of the CdSe films grown on glass substrate. The thickness of the CdSe film was about 380 nm. The XRD patterns of the CdSe film exhibit three distinguished peaks at the angles of 25.6°, 42.7° and 50.8° corresponding to diffraction of the (111), (220) and (311) planes of the cubic phase, respectively [2].

The average nanocrystallites size of the CdSe film deposited on glass substrate is estimated to be about 4.5 nm. The SEM micrograph of the CdSe thin film is shown Fig. 2 (Right). The film show smooth and uniform surface with very low pinholes and well covered to the glass substrate. Small nanosized grains were uniformly distributed over smooth homogenous background. Fig. 2 (Left) shows the optical transmittance and reflectance spectra for CdSe films prepared from a precursor solution at pH 7.0 and 50 °C as a function of depositions times. In this work the band gap energy (E_g) was determined to be in the range of 2.57-2.76 eV for the CdSe films with deposition times varying from1-6 hours. These values are rather larger than the literature value for the bulk CdSe (~ 1.7 eV). The result could be attributed to the quantum size effects as expected from the nanocrystalline nature of the CdSe thin films.



Fig. 1: X-ray diffraction patterns of the CdSe film deposited on glass substrate.



Fig. 2: UV-Vis. transmission and reflection spectra of the CdSe films on glass substrate deposited at pH 7.0 and 50 °C as a function of the deposition times (Left) and SEM image of the CdSe thin film on glass substrate with thickness of about 120 nm (Right).

Conclusions:

NanocrystallineCdSe thin films were chemically deposited at pH 7.0 and 50 °C, from aqueous solution using cadmium acetate as Cd^{2+} and sodium selenosolfate as Se^{2-} ion sources. The CdSe thin films grew with nanocrystalline cubic structure with optical absorption edge at about 550 nm. A blue shift is observed in the spectra comparing to that of the bulk CdSe. Morphology of the CdSe grains in the films and also the structure of CdSenanocrystalline composing the grains were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

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Growth technology, X-ray and optical properties of NanocrystallineCdS:Cu prepared by Chemical Bath Deposition Method

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Keywords: Thin films, Nanostructures, Chemical bath deposition, Optical properties

Introduction:

Cadmium sulfide thin films are widely used as a window material for thin films hetrojunction solar sells such as the highly efficient CdTe and CuInSe₂ devices [1]. Among various chemical methods for deposition of thin films, the chemical bath deposition has been proved to be the most suitable method to produce CdS:Cuthin films for photovoltaic applications because of its efficient, cost effective and large scale capability [2]. In this work, we study the optical properties of nanocrystallineCdS:Cuthin films prepared by a chemical bath deposition route [3-4]. These thin films have been studied as a buffer layer which is an important part of the solar cell. The parameters studied include the optical constants, band gap, reflectance, absorption coefficient, refractive index, extinction coefficient, and thickness.

Experimental:

Glass slides were used as the substrates. The deposition solution was prepared by mixing 5 mL of a 1 M cadmium acetate solution, 20 mL deionised water, 16 mL of a 1 M ammonium acetate solution and optimum of a 0.05 M copper nitrate solution (for 0.2 mL to 3 mL with increase value 0.2 mL in various steps) in a glass beaker and the PH was about 5. In the next step, 40 mL of a 0.3 M thioasetamide (TAA) solution was added and the pH was adjusted





about 5 again. This solution was poured into a glass tank being used as a reaction vessel for the film deposition. Glass substrates were immersed vertically in the reaction vessel, and the glass tank was placed in a thermostat bath set at 50 and 75 °C for 4 hours and at 25 °C for 96 hours.

Results and Discussion:

The NanocrystallineCdS:Cu thin films were characterized by XRD, SEM and UV-Vis spectra.Table 1 shows change in the parameters of the CdS:Cu thin films deposited from a chemical bath at PH=5 and 75 °C. As seen from Table 1, with increasing the deposition time thickness layers and nanocrystal radius increase but their band gap decrease.

Table 1. Changes in the Parameters of the CdS:Cu Thin films deposited from a chemical bath at PH=5 and 75°C.

Deposition	Thicknes	Band gap	Nanocrysta
time (h)	S	(eV)	l
	(nm)		radius
			(<i>nm</i>)
1	30	3.90	4.34
2	65	3.85	8.21
3	85	3.80	13.74
40	130	3.72	20.89

The XRD pattern of CdS show three broad peaks at around 26.5°, 43.8° and 52.3° reveal a cubic lattice structure of CdS. These peaks can be assigned to the planes (111), (220) and (311), respectively, of the cubic zinc blend structure [4]. From the Debeye-Scherrer equation, the average nanocrystallite size in the CdS:Cu film was estimated to be 9.14 nm.

Fig. 1 shows a SEM image of the CdS:Cu film prepared at 75 °C. As can be seen, the surface of film is homogenous with grain size of about 150-300 nm. Fig. 2 shows the transmittance and reflectance spectra of nanocrystallineCdS:Cu thin films deposited onto the glass substrates. Optical transmission spectra of the thin films are observed to be slightly shifted towards the longer wavelength with increasing deposition time. This suggests the decrease in





the band gap energy (E_g) with the increasing thickness. The absorption coefficients (α) of the films have been calculated





(2)

Fig. 1. SEM image of the CdS:Cu thin film **Fig. 2.** Optical transmittanceand reflectancespectra of CdS:Cu thin Preparedat 75°C for 4 h.Films with different Deposition times: (a) 1, (b) 2, (c) 3 and (d) 4 h.

Using the following relation valid for the mean absorption edge [5]:

$$\alpha = \frac{-1}{t} \ln \left\{ \frac{T}{\left(1 - R\right)^2} \right\} \tag{1}$$

Where t is the thickness of the film, T and R are the transmission and reflectivity, respectively. The absorption coefficient (α) is related to the incident photon energy as follows:

 $\alpha h \upsilon = k (h \upsilon - E_g)^m$

Where *k* is a constant, E_g is the separation between the valence and conduction bands and *m* is a value depending on the nature of the transition. The value of mis 1/2 for allowed direct transition. The value of the energy gap were calculate from the transmittance spectra by plotting $(\alpha hv)^2$ versus hv (Fig. 3). α , *h* and v are absorption coefficient, Planck constant, and frequency, respectively. As can be seen $(\alpha hv)^2$ varies linearly with hv above the energy gap. As shown in Fig. 2 and Table 1, the band gap energy slightly shifts to a lower wavelength with decreasing deposition time. These values are somewhat larger than the typical value of the bulk CdS (ca.2.42eV), probably due to the quantum size effect as expected from the nanocrystalline nature of the CdS:Cu thin films [4].







Fig. 3. Plot of $(\alpha h v)^2$ versus hv for CdS:Cu thin films different deposition times: (a) 1, (b) 2, (c) 3 and (d) 4 h.

Conclusions:

NanocrystallineCdS:Cu thin films of different thickness were deposited by a chemical deposition technique. The film thickness was controlled by the deposition time. UV-Vis transmission spectroscopy showed that the prepared films were highly transparent (>80%) in the visible region. Optical study is performed to calculate the refractive index (*n*), extinction coefficient (*k*), absorption coefficient (α), dielectric constant (ϵ) and optical band gap (E_g) using transmission and reflection spectra in the wavelength range 250–800 nm. The band gap measured was found to be in the range of 3.72–3.90eV. The XRD pattern and SEM images showed that the films consisted of small CdS:Cunanocrystallites, 4–21 nm in size, showing quantum size effects.

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Adsorption kinetics models for Cd(II) removal by Thiol-Nanosphere in a single component system: Error analysis

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Key words: Kinetic models, Error analysis, Heavy metal removal, Nanosphere adsorbent

Introduction:

Due to its high chemical and thermal stability, large surface areas, low density, low toxicity and good compatibilities with other materials, hollow silica spheres have wide varieties of applications [1]. Thiol-functionalized nano hollow silica spheres exhibited a highly selectively adsorptive capability for heavy metal ions. The present work is aimed at evaluating the kinetic models for the adsorption of Cd^{2+} onto thiol functionalized silica nano hollow sphere (thiol-SNHS).

Methods:

1. Materials: Thiol-SNHS with the specific surface area of 834 (m² g⁻¹) were synthesized in our laboratory and reported in our previous work [1], (Cd(NO₃)₂.4H₂O, \geq 99.5%, Merck) as a cadmum source and was used without further purification. The Cd⁺² concentrations were determined by using an atomic absorption spectrometer (SpectrAA-220 Varian).

2.Experimental: This kinetic experiment were obtained by employing 40 mg L⁻¹ initial concentration of Cd⁺² with adding 0.01 g of thiol-SNHS and allowed to contact at different contact times. Then the samples were centrifuged at 11000 rpm for 2 min and filtrated. The residual metal concentrations in the solutions were measured using an atomic adsorption spectrometer. The sorption capacity q_t (mg g⁻¹) of thiol-SNHS was calculated using [2]:





$$q_t = \frac{C_0 - C_t}{W} \times V \tag{1}$$

where C_0 is the initial ion concentration (mg L⁻¹) and C_t is the remaining metal concentration (mg L⁻¹) at time t, *V* is the volume of ion solutions (L), and *W* is the adsorbent amount (g). The sorption dynamics presented by thiol-SNHS were tested with the Lagergren pseudo-first order, the chemisorptions pseudo-second order and Elovich kinetic model [2]. In order to confirm the fit model for the adsorption system, it is necessary to analyze the data using five analysis. The seven error functions employed in this study are as follows: R², RMSE and ERRSQ [2].

Results and Discussion:

The experimental data were fitted to the kinetic models using Wolfram Mathematica software and the graphical representations of these models is presented in Figure 1.



Figure 1. The nonlinear fitted curve with different kinetics models applied to Cd²⁺ sorption by thiol-SNHS.

Among three different kinetic models, pseudo-second order kinetic model had very high value of R^2 for kinetic data. The values of RMSE and ERRSQ about pseudo-second order kinetic model were smallest among the three kinetics model, respectively.

Conclusions:

The adsorption kinetic to removal Cd^{2+} using thiol-SNHS was carried and the pseudo-second order kinetic model was found to be applicable for the adsorption kinetic data. The pseudo-





second order kinetic equation was developed for the sorption process and there are 3 consecutive steps taking place in the sorption of an adsorbate by a porous adsorbent: (1) migration of the metal ions from solution to the surface of the adsorbent; (2) migration of the metal ions into the pores of the adsorbent; and (3) adsorption of the metal ions on the interior surface of the adsorbent. The rate of the reaction is mainly controlled by the first two steps.

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On the Binding of Mercaptopurine to Cucurbit[7]uril Host: Density Functional Investigations

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keywords: Cucurbit [7]uril, Mercaptopurine, Adsorption, Binding energy

Introduction:

Interest in pumpkin-shaped molecules being a cyclic oligomer of n units of glycoluril enlaced by methylene groups, namly cucurbit[n]urils, has been increasing in the recent years. Since its discovery, CB[7] as a large-cavity homologue has attracted a great deal of attention as hosts in inclusion complexation, drug delivery and nanotechnology [1]. In this effort, we pay attention to the capability of cucurbit [7]uril (CB[7]) nanocavitand for adsorbing 6-Mercaptopurine (6-MP) as an antitumor agent [2] by means of DFT computations.

Method:

We have employed the generalized gradient approximation (GGA) with the Perdew–Burke– Ernzerhof (PBE) functional [3] in density functional theory and the standard norm-conserving Troullier–Martins pseudo-potentials [4]. The calculations are done using TZ2P as basis set.

Results and discussion:

In order to examine the adsorption behavior between 6-MP and CB[7], we model the interaction of 6-MP with CB[7]. As displayed in Fig. 1 (a, b), two significant approaches, named A and B respectively, were selected which facilitate hydrogen bonding interactions between NH groups of MP and oxygen portals of CB[7].

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Fig. 1. Model for a MP molecule encapsulated in the CB[7] cavity (a) approach A and (b) approach B.

After fully structural optimization binding energies of approaches A and B are found to be - 0.57 and -0.76 eV, respectively, indicating the rather high tendency of MP molecule to be adsorbed

within the related nanocapsule. Fig. 2 illustrates the geometry optimized of approaches A and B for MP@CB[7] systems.



Fig. 2. The optimized geometries of MP@CB[7] complexes (a) approach A and (b) approach B.

The equilibrium distances between hydrogen atoms of NH groups belong to MP molecule and the closet oxygen atoms of portals at the range from 1.944 to 2.505 Å and -0.57 and -0.76 eV as binding energies reveals that stabilization of the MP@CB[7] complex is governed by HBs. 2299





Conclusion:

The calculated results show that cucurbits as nanocapsules have the carrying capability of biological species and vital drugs. From our findings, it could be concluded that hydrogen bond formation between guest and host atoms play significant role in the stable formation of inclusion complexes in bio area.

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Adsorption behavior of 6-Mercaptopurine drug on the C₆₀ fullerene nanocage: a first-principles study

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Keywords: Mercaptopurine, Adsorption, Binding energy, Nanocage

Introduction:

The unique properties of nanocages such as fullerenes made them suitable in the bio-area and very striking for a wide range of applications [1]. On the other hand, 6-Mercaptopurine (6-MP) is a sulfur analogue of adenine which being generally employed as an antitumor agent [2]. Therefore, numerous investigations have been devoted to study the adsorption behavior of 6-MP onto different surfaces [2, 3]. In this study, we have investigated the interaction between MP molecule via its several active groups and C_{60} fullerene by means of calculating the binding energy, density of state and Mulliken charge analyses.

Method:

We have employed the generalized gradient approximation (GGA) with the Perdew–Burke– Ernzerhof (PBE) functional [4] in density functional theory and the standard norm-conserving Troullier–Martins pseudo-potentials [5]. The calculations are done using a split-valence double-zeta plus polarization function (DZP) as basis set.

Results and discussion:

To investigate 6-Mercaptopurine adsorption capability of C_{60} fullerene, we consider several possible adsorption sites on MP approaching on the exterior surface of C_{60} nanocage. After structural optimization, we found that the binding energy value by employing the BSSE corrections for all configurations is negative in the range from - 0.22 eV (-21.05 kJ/mol) to





0.31 eV (-30.06 kJ/mol) indicating physisorption of MP with the exterior surface of C_{60} nanocage. Fig. 1 (a) shows the most stable configuration with binding energy of -0.31 eV (-30.06 kJ/mol) and the equilibrium C-H distance of 2.426 Å. These suggest that the adsorption characteristic is a strong physisorption. Mulliken charge analysis for MP/C₆₀ complex shows that 0.13 e charge transferred from from MP to the C₆₀ fullerene. Furthermore, the density of state (DOS) for MP/C₆₀ was calculated, as depicted in Fig. 1 (b).



Fig. 1. (a) The most stable configuration of MP/C₆₀ and (b) comparison between the density of states for an isolated MP molecule, an isolated C_{60} and the combination of the two at equilibrium geometry (MP/C₆₀).

Considering the results highlight that the MP and C_{60} are interacting rather weakly, and that no significant hybridization between the respective orbitals of the two entities occurs.

Conclusion:

Our first-principles calculations predicted that the MP adsorptive capacity of C_{60} fullerene is at the range of physisorption. Considering the electronic structures suggest that hybridization between the respective orbitals of the two entities is weak.





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Photocatalytic degradation of nonionic surfactant from wastewater using Zinc oxide nanoparticles

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Key words: Zinc oxide nanoparticles, Photocatalytic degradation, Surfactant, Wastewater.

Introduction:

During surfactant production and textile manufacturing processes a large amount of wastewater with toxicity can be introduced into aquatic systems [1]. In recent years an alternative to conventional methods, is "advanced oxidation processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals, that oxidizes a broad range of organic pollutants quickly and non-selectively. AOPs include photocatalysis systems such as a combination of a semiconductor (TiO₂, ZnO, etc.) and UV light [2]. In our research, we selected a nonionic surfactant as a model compound for organic pollutants and ZnO nanoparticles as photocatalyst. The effects of various parameters, such as the concentration of the photocatalyst, illumination time, electron acceptor, initial concentration and pH of the reaction on photocatalytic degradation of NP10EO were studied.

Materials and methods:

Photodegradation studies were carried out with a 400 W Xe arc lamp house as the light source. The experiment was performed by mixing 0.2 g/L ZnO and 1 mM of $K_2S_2O_8$, in 25 mL of the Nonylphenol solution with an initial concentration range of 30-120 g/L. The pH was chemically controlled at 6. The mixtures were mixed by stirring at 80 rpm for 2 h under UV irradiation. The temperature was kept constant at (25±2) °C. Suspended solids were then separated out and concentration of surfactant measured using (Jenway 6405 UV-VIS)





spectrophotometer at λ_{max} =223nm. The degree of photodegradation (X) as a function of time is given by: X=(C_0 -C)/ C_0 where C_0 is the initial concentration of surfactant, and C the concentration of surfactant at time t.

Results and Discussion:

Acceleration in degradation rate of photocatalytic oxidation on ZnO occurs by photogenerated holes. It is well known that oxidation rate increases when recombination process is suppressed. The effect of peroxydisulfate as the electron acceptor was examined and is presented in Fig. 1. The degradation of NP10EO was remarkably accelerated by addition of peroxydisulfate: 30 mg/L NP10EO and in the presence of 0.2 g/L, ZnO was completely degraded under irradiation of 6 to 2 h in the absence and presence of 1 mM K₂S₂O₈ respectively.

The relationship between the photodegradation efficiency of NP10EO and the illumination time was investigated. The result resented that photodegradation efficiency of NP10EO increases with an increase in the illumination time. The degradation of NP10EO was more enhanced in the range of pH 6-7 than the other pH values. The lower rate of degradation at acidic and alkaline pH may be attributed to dissolution of ZnO. the photodegradation efficiency increases with an increase in ZnO concentration up to 0.2g/L, and is then decreased









Fig.2.Effect of catalyst weight Conditions: [NP10EO]₀ =30mg/L; [S₂O₈²⁻] =1mM; pH=6; Irradiation Time: 120 min; V_t: 25mL.





This can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The rate of photodegradation of the surfactant decreased at higher concentrations. With increasing the amounts of NP10EO, more surfactant molecules were adsorbed on the surface of the photocatalyst and the active sites of the catalysts were also reduced. Analysis of kinetic showed that the amount of surfactant photodegradation could be fitted into pseudo-second-order model.

Conclusion:

In this study the surfactant NP10EO was appropriately mineralized by a photocatalytic reaction in using nanoparticles of zinc oxide in the form of slurry. The results are summarized as follows: The optimal degradation conditions of NP10EO were: the dosage of catalyst 0.2 g/L, pH 6-7, the amount of $K_2S_2O_8$ 1mM. Under optimal degradation conditions of NP10EO, the photodegradation of NP10EO was 90% when the solution was irradiated by the 400w high pressure mercury–vapour lamp for 2h. Degradation of NP10EO was remarkably accelerated by addition of proxydisulfate. The kinetics of photocatalytic degradation for surfactant NP10EO follows a pseudo-second order equation.

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Synthesis and investigation the catalytic behavior of Cr₂O₃ nanoparticles

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Key words: Synthesis, catalytic behavior, Cr₂O₃, nanoparticles

Introduction:

Cobalt (II) chloride was used as a precursor to prepare Co_3O_4 nanotube in reverse micelles. In recent years, there has been an increasing interest in developing materials with low dimensional nanostructure. Co_3O_4 is an important functional material for a wide range of technological applications such as heterogeneous catalysts, anode materials in Li-ion rechargeable batteries, solid-state sensors, magnetism, and optical devices [1].

Here in, we describe a simple way to generate Co_3O_4 nanotubes. In our experiments, Co_3O_4 nanotubes are acquired, at nano and micro reverse micelles by using basic cobalt (III) chloride precursor and purified soybean oil as organic phase.

Materials and methods:

CoCl₂, NaOH, purified soybean oil, Tween 80 and distilled water were used in the experiments. Nanotube were synthesized by the following steps: 0.30 g of CoCl₂ in water and 4% Tween 80 were added into 30 mL of purified soybean oil under mechanical stirrer with 2000 rpm until obtaining a nearly clear emulsion. This solution was referred to as solution A. 0.16 g of NaOH was dissolved into 3.5 mL of water was added into solution A. 0.16 g of NaOH was dissolved into 3.5 mL of water was added into solution A under mechanical stirrer with 2000 rpm for 4 h at 20-25°C and then the reaction mixture was filtrated. The precipitates were washed and dried.





Apparatus:

The powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu K α radiation ($\lambda = 1.54056$ Å) with a MINIPROP detector and operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded between 2 $\theta = 5^{\circ}$ and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting Cr₂O₃ powders were collected by using the PC-APD, Diffraction software Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, PHILIP XL-30).

Result and discussion:

Fig. 1. shows the scanning electron microscopy (SEM) images of Co_3O_4 nanotubes indicating the homogeneous size and high purity of the product.

Fig. 1: SEM image of the Co3O4 nanotube.

Conclusion:

In our case, Co_2O_3 formation in this process may proceed through two steps. Firstly, $Co(OH)_2$ is formed in aqueous solution when $CoCl_2$ is dissolved in H₂O, and a fraction of $Co(OH)_2$ is oxidated to $Co(OH)_3$ by the oxygen in the environment. Secondly, $Co(OH)_2$ and $Co(OH)_3$ deposit with each other in the basic conditions and then Co_3O_4 nanostructures are obtained.

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Experimental evaluation of silica nanocontainers and smart coatings for active corrosion protection of aluminum alloy

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Keywords: Corrosion Protection, Nanocapsules, Coatings, AA 2024

Introduction:

The development of active corrosion protection systems for metallic substrates is an issue of prime importance for many industrial applications. Different types of inorganic corrosion inhibitors include chromates, phosphates, molybdates, and nitrites being used in different media [1]. One of the main disadvantages of inorganic inhibitors is their toxicity; for example, chromates are proven to cause several diseases, including cancer, and are recently forbidden for common usage [2]. Different inhibitor encapsulation techniques have been investigated, including polyelectrolyte, sol-gel nanoparticles, nanotubes, and other methods [2, 3]. In this research work, a novel technique was used to investigate the protection of 2024 aluminum alloy against corrosion with self-healing ability composed of paint films doped with nanocontainers that release entrapped corrosion inhibitor by corrosion process. Silica nanoparticles covered layer-by-layer with surfactant layers and layers of inhibitor, salicylaldoxime (SAL) were randomly introduced into the paint films.

Methods:

To produce an inhibitor impregnated polyelectrolyte shell, the LbL deposition followed procedure involving surfactant molecule and SAL ones. The deposition of the positive cetyltrimethylammonium bromide (CTAB) was performed on the first stage. Deposition of the second inhibitor layer was carried out in acidic media solution of SAL. The last deposition





step (CTAB) were repeated once. In order to provide a comparative study of effect of the loaded SiO₂ nanoparticles with corrosion inhibitor on the corrosion protection performance of the paint coatings, two composite coatings were synthesized and doped with SAL loaded nanocapsule and undoped epoxy painting.

Results and discussion:

The change of concentration of inhibitor released from nanocapsule into solution ascertained using UV spectrophotometry at different temperatures is illustrated in Fig. 1. It was observed that the capsules exhibit spontaneous release of the inhibitors. In addition, As the figure shows by increasing solution temperature, SAL concentration increased for nanocapsule.

The main idea of introduction of nanocapsule into paint coatings is the reinforcement of corrosion protection. Fig. 2. presents Polarization curves of the two aluminum samples: the first one was coated by a paint film loaded with nanocapsules-entrapped SAL, and second one was coated without nanocapsules. It is understood that the AA2024 sample coated with the nanocapsule-doped paint film testifies the lower corrosion activity and consequently better corrosion protection.



Fig.2 Polarization curves obtained for AA2024 electrode coated with paint film a-doped with nano capsule b- undoped nano-capsule, determined in 0.5 M NaCl solution containing by time.





b

Conclusion:

a

The obtained results indicate beneficial effect of loaded nanocapsules on paint coat's barrier properties which are evident from the low corrosion current and other electrochemical parameters.

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Benzotriazole Contained in the Holloysite Nanotubes Using Different Metal Ions as Stoppers

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Keywords: Corrosion protection, inhibitor, Nanocapsules, Holloysite nanotubes

Introduction:

Different types of inorganic corrosion inhibitors include chromates, phosphates, molybdates, and nitrites being used in different media [1]. Halloysite is a naturally occurring cylindrical clay mineral with an internal diameter in the nano meter range (50 ± 5 nm) and a length up to several micrometers ($1-15 \mu m$), yielding a high-aspect-ratio hollow tube structure [2]. Halloysite aluminosilicate nanotubes have been developed as an entrapment system for loading, storage, and controlled release of anticorrosion agents and biocides [1-4]. Benzotriazole (BTA) corrosion inhibitor is encapsulated within Holloysite nanotubes by metal ions and releasing it into the solution in a controlled way is investigated.

Methods:

In this research, The use of halloysite as containers are descibed for the loading, storage, and sustained release of benzotriazole. Extended controlled release 0.06 g of halloysite was mixed with 0.5 mL of 20 mg.mL⁻¹ BTA solution (three times). Loaded Holloysite by benzotriazole was mixed with Al³⁺, Na⁺, Mn²⁺ and Mg²⁺ ions ((Al₂(SO₄)₃, Na₂(SO₄), MnSO₄ and MgSO₄), which diffused into the tube openings to form insoluble metal-benzotriazole complexes that act as stoppers for the benzotriazole contained in the tubules. For this purpose, benzotriazole-loaded halloysite samples were exposed for 1 min to the bulk aqueous solution containing metals ions. In addition,the investigation effect of polyelectrolyte shells, Mg-nanocapsule (Mg-NC) was incubated by 3 mL of 4mg.mL⁻¹ poly(ethyleneimine) polyelectrolyte (PEI) for





15min. The processed (Mg+PEI-NC) nanocapsules were separated from solution by centrifugation. The concentration of benzotriazole during release into the solutions was detected using a Varian CARY 50 Conc UV-vis spectrophotometer.

Results and discussion:

The change of concentration of inhibitor released from different nanocapsules into solution ascertained using UV spectrophotometry is illustrated in Fig. 1.

Fig. (1a), shows that release rate from nanocapsules follows the sequence: (Al-NC) > (Na-NC) > (Mn-NC) > (Mg-NC). Fig. (1b), shows concentration of benzotriazole released in solution by the time for (Mg-NC) and (Mg+PEI-NC) nanocontainers. The results indicate that the quantity of corrosion inhibitor taking up and inhibitor releasing rate follows the sequence of (Mg-NC) > (Mg+PEI-NC), which shows by adding polyelectrolyte layer rate of releasing BTA decreased.

Conclusions:

The results indicate that the quantity of corrosion inhibitor taking up and inhibitor releasing rate follows the sequence of (Mg-NC) > (Mg+PEI-NC), which shows by adding polyelectrolyte layer rate of releasing BTA decreased.



Fig.1.a Relation between the concentration of released benzotriazole and time in water containing for four kinds of capsules. b Relation between the concentration of released benzotriazole and time in water containing (Mg-NC) and (Mg+PEI-NC) capsules.





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Molecular Dynamics Simulation of the Melting Behavior of Cs-Na Bimetallic Nanoparticles

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Abstract:

Bimetallic particles have two features not observed in one-component systems: surface segregation and compositional ordering. Molecular dynamics simulations have been performed to study the melting of Cs-Na nanoparticles at different compositions.

Keywords: Bimetallic nanoparticle; Gupta potential function; Melting transition; Molecular dynamics simulation; Thermodynamic properties;

Introduction:

Bimetallic nanoparticles are of wide interest since they lead to many interesting sizedependent electrical, chemical, band optical properties. [1,2]. Theoretical approaches to understanding the phase stability of solid nanoparticles are often based on the analysis of a core–shell configuration. Furthermore a number of molecular dynamics simulations [3,4] have predicted that a core–shell configuration would stabilize clusters in the 1–5 nm diameter range. The present simulations consider two individual Cs-Na nanoparticles including 2664 atoms, whose Na concentrations are 25 and 75% (Cs₃Na and CsNa₃).

Methods:

We used Gupta potential function [5], which is based on the second moment approximation of the tight bonding model, [6] to describe the interaction potential in liquid metals. Classical molecular dynamic simulations on solid and liquid Cs nanoclusters were performed using the





DL-POLY-2.17 program [7]. The initial structures are arranged in a bcc configuration with a random distribution of Na atoms embedded in a Cs matrix. The MD simulations were carried out in a canonical ensemble without periodic boundary conditions. A constant temperature with Berendsen thermostat at relaxation time of 0.5 ps was used. The equation of atom motion was integrated using the Verlet–Velocity algorithm with a time step of 2.4 fs.

Results and discussion:

In heating process, the initial structure was heated up to 400k, higher than the bulk melting temperature, was cool to solid bimetallic structure down to 40K. The melting transition is identified by studying variations in thermodynamic properties such as potential energy and specific heat capacity. Figure 1 shows the temperature dependence of the total potential energy for $(Cs_3Na)_{2664}$ and $(Cs Na_3)_{2664}$. The total potential energy shows a simple jump as a function of temperature at the melting transition from the solid to the liquid state. The melting point of 160K and 225K were estimated for Cs_3Na and $Cs Na_3$ nanoparticle, respectively.

In the case of the Cs-Na system considered in the present investigation, cesium has a much lower surface free energy than sodium. Therefore, Cs atoms tend to migrate to the surface of the cluster, reducing the total free energy.

Figures 2(a-b) illustrates these behavior, which was previously observed for Cs-Na nanoparticle at 300K (a), Cs₃Na and b, Cs Na₃).



Fig.2a

Fig.2b

Fig. 1. Potential energy variation with temperature for CsNa bimetallic nanoparticle.





Conclusions:

The melting point of the cluster increases with the increase of Na composition. Since the proportion of surface atoms in nanoparticles is very high, surface segregation may play a key role in the determination of their structure.

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Study of physical chemistry properties of polystyrene and carbon nanotube as phase change materials using molecular dynamics simulation

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Keywords: Phase Change Material, Simulation, Carbon Nanotube, Polystyrene.

Introduction:

We study phase change material with CNT the saturated with one layer polystyrene phase change material have a high heat of fusion which melting and solidifying at a certainly temperature. This material capable store and release large amount of energy . in this work, we shown that melting transition in monolayer of polystyrene on to the CNT occur and this phenomena studied through use of molecular dynamic (MD) simulations.

Simulation details:

MD simulation performed are different temperature for system containing a CNT (5,5) with length of 50Å and polystyrene monolayer using canonical ensamble Since each simulation is performed in constant temperature many simulation are required at different temperatures. The simulation box dimensions is $130 \text{nm} \times 70 \text{nm} \times 70 \text{nm}$ and their volume is 637000 nm3 Energy minimization was performed to find the thermal stable morphology and achieve a conformation with minimum potential energy for polymer molecules. the velocity form verlet algorithm method and the nose-hoover thermostat algorithm were used to integrated the equations of motion with a time step of 1.0 fs. a cut off distance of 12.5 Å was used for the van der walls potentials and Lorentz-Berthelot mixing rules were used for cross interaction. force field used in this simulation is mm3. the CNT atoms to their initial positions have been fixed.





Results and Discussion:

In this study, we demonstrate on the thermodynamic properties of polystyrene and carbon nanotube (5, 5). polystyrene has been arrangement regular on the CNT. Molecular dynamic simulation performed at 14 temperatures (250, 300, 320, 340, 360, 380, 400, 450, 500, 550, 600, 700, 750, 800).

The values of the potential energy for simulations at various temperatures are given in fig 1a.



Fig 1a. Potential energy andFig1b. interaction energy at simulated temperature points.Results from potential energy plot showed that melting point is started from 50k. in compareto the melting point of polystyrene , this plot is shown that melting point increases about 17k.that increase caused from interaction between polystyrene and CNT.

The values of the intermolecular energy for simulations at various temperatures are given in fig 1b. There is a discontinuous rise in intermolecular energy at the onset of melting in 540k and it increases to 600k, this rang is called phase change zone for this system. We see that interaction energy increases with increase in temperature since system is unstable.

Conclusion:

We investigate the molecular dynamic simulations of carbon nanotube - poly styrene. We result that system (polystyrene + CNT) start the phase change in 540 k and the continue to the 600 k. this indicate that this system can be use as phase change material.

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Ultrasonic-assisted method for preparation nanoparticles of Cu-doped ZnS in water

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Keywords: Cu-doped ZnS, Ultrasonic irradiation, Nanoparticles, Adsorption.

Introduction:

Cu-doped ZnS is an active photocatalyst for hydrogen generation by water splitting under visible light irradiation [1,2]. Recently, Mohamed have prepared thin films of Cu-dopped ZnS by electron beam evaporation on glass substrates at 1000 °C for 2 h and investigated photocatalytic activity of the prepared nanoparticles [3]. In addition, Pouretedal and et al. have prepared nanoparticles of ZnS doped with manganese, nickel and cupper in presence of mercaptoethanol as capping agent and investigated photocatalytic activities [4]. As can be seen, the reported preparation methods mainly have high temperature or long reaction time and most of them involved environmentally malignant chemicals and organic solvents, which are toxic and not easily degraded in the environment. Therefore, searching new methodology to prepare these nanomaterials is of great importance. In the present paper, ultrasonic-assisted method was applied for preparation Cu-doped ZnS in water as a green and template-free method.

Materials and methods:

The chemicals were obtained from Merck, and employed without further purification. The ultrasound radiation was performed using dr. heilscher high intensity ultrasound processor. The X-ray diffraction (XRD) patterns were recorded on Ital Structures MPD3000. Diffuse reflectance spectra (DRS) were recorded by a Scinco 4100 apparatus. Surface morphology of particles was studied *via* LEO 1430VP scanning electron microscopy (SEM). In a typical procedure for preparation of the nanoparticles, zinc acetate dihydrate (4.258 g) and cupper





acetate (0.0599 g) were dissolved in 50 ml of distilled water under stirring at room temperature. Also, 1.50 g of thioacetamide (TAA) was dissolved in 50 ml of distilled water. Then, TAA solution was slowly added into the above mentioned solution under magnetic stirring. The titanium tip of the horn was immersed directly in the reaction solution. The solution imposed to ultrasonic irradiation for 30 minutes in a beaker. The formed suspension was centrifuged to get the precipitate out and washed to remove the unreacted reagents and dried at 60 °C for 48 h.

Results and discussion:

The Zn_{0.985}Cu_{0.015}S, Zn_{0.97}Cu_{0.03}S and Zn_{0.94}Cu_{0.06}S nanoparticles have the XRD patterns similar to that of the ZnS. Therefore, the prepared nanoparticles have the same crystal structure. Zinc and cupper cations have similar ionic radii (0.74 and 0.72 Å, respectively), then Cu⁺² ions can incorporate in the ZnS lattice [5]. The average crystallite sizes obtained for as-prepared ZnS, Zn_{0.985}Cu_{0.015}S, Zn_{0.97}Cu_{0.03}S and Zn_{0.94}Cu_{0.06}S nanoparticles by Scherrer's equation are about 2.48, 3.28, 3.33 and 2.30 nm, respectively. Morphology of the nanoparticles obtained by SEM is nearly spherical with various sizes. Moreover, size of the nanoparticles (3.85 eV) is increased compared to that of bulk ZnS (3.60 eV). Moreover, the visible light absorption for the nanoparticles increases with increasing Cu⁺² ion content.

Adsorption capacity (q_e) of the nanoparticles for methylene blue (MB) molecules increases with cupper content in the nanoparticles. The SEM images demonstrated that size of the nanoparticles decreases with cupper content. Then, increase of the adsorption capacity of the nanoparticles can be attributed to increasing the surface area with decreasing particle sizes.

Conclusions:

A template-free and green method was applied for preparation of Cu-doped ZnS in water and the nanoparticles were characterized with various methods.

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The study effects of Ga and As-doping in Armchair and Zigzag forms of boron phosphide nanotubes

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Key word: Born phosphide nano tube, chemical shielding, DFT, Gap Energy

Introduction:

Nanotubes have been a focus of researches and received increasing attention during the past 10 years, due to their unique and fascinating properties, and wide potential applications. After the discovery of carbon nanotubes in 1991 , the nanotubes composed of other chemical compositions have also been investigated. Among them, the binary materials composed of Group III–V wide band-gap semiconductor BPNTs has attracted extensive interest for applications as electrical substrate and packaging material due to its high thermal conductivity and low coefficient of thermal expansion that closely matches that of silicon (Si), and as reinforcement in structural composites owing to its excellent mechanical strength and chemical stability [1-3]. Recently, the nanotube has been proved to be a very good and useful tool for biomedical, molecular and cellular applications and in techniques, engineering, electronics, optoelectronics, chemistry, and biochemistry too [4-5]. The aim of this work, the study of electronic structures and the effects of Gallium and Arsenic doped on electrical and chemical shielding parameters of armchair and zigzag models of boron phosphide nanotubes (BPNTs).

Computational methods :

The calculations on BPNTs and with Ga and As doped were carried out using density functional theory (DFT) with the BLYP/6-31G(d) using the Gaussian 03 program package .The calculated chemical shielding tensors in principal axes system converted to measurable





NMR parameters: CS^{I} and CS^{A} . The gap energy between HOMO and LUMO orbital is calculated from optimized structures by equation : $E_{gap} = E_{HOMO} - E_{LUMO}$

Results and discussions:

The geometrical results show that bond lengths of B-P are increased with doping As and Ga and the bond angles of are decreased. Due to the donor electron effects of Ga and As doped in stead of boron the E_{gap} between Homo and Lumo orbital in Zigzag model is decrease and the electrical conductance in zigzag model is significant than armchair. The CS^I values of B sites neighbor of As and Ga doped in Zigzag model are increased due to donor electron effect of As. But at the P sites the CS^I values in two modes are decreased so the charge density electrons at these sites are smaller than other sites.



Fig. 1 the optimized structures of Armchair and Zigzag models of BPNTs.

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Preparation, Characterization and Controllable Synthesis of Nano Zero Valent Iron Particles

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Keywords: Nano Zero Valent Iron, Synthesis, Reduction method, Size

Introduction:

Water and soil contamination due to their great environmental concern are among the active areas of research among researchers [1]. Use of micro-Scale Zero valent iron used to be among methods of remediation of soil and underground water and taking zero valent iron from micro scale to nano scale made it much superior [2].

Considering the significant influence of the size of particles on their reactivity [3], other methods, except the liquid phase reduction (LPR), do not suggest a systematic control over the size. Particles synthesized by using the LPR have amorphous structure. This characteristic increases reactivity of particles produced by this method [4]. Several strategies have been proposed for control over the size of the particles in reduction method [5, 6]. Control over the size of the particles from 7 to 70 nm for more than 90 percent of the particles has been achieved by the introduction of ethanol into reaction medium [7].

In this paper, NZVI particles were synthesized by the drop wise addition of the NaBH₄ aqueous solution into Fecl₂.4H₂O aqueous solutions, which contain DI water and ethylene glycol. Using ethylene glycol and water to the best of our knowledge, is a novel solvent for this purpose. Also, the ratio of Ethylene glycol to DI water was changed and new products achieved.





Experiment and Materials:

In our experiment three NZVI samples were synthesized by using different percentages of Ethylene glycol and DI water. In the process of synthesizing NZVI, 0.015M of Fecl₂.4H₂O which is one of our Iron sources were dissolved into a solution that contained 50 mL DI water and 50 mL Ethylene glycol. Then, 0.06 M sodium borohydride was dissolved into the same portion of the solution that was used to dissolve Iron. Next, the aqueous solution that contains NaBH₄ was added slowly to Fecl₂ aqueous solution in N₂ atmosphere and was stirred with a mechanical stirrer for 30 minutes with the speed of 400 rpm. The synthesizing process was carried out in a four open neck 1 L flask. The portion of used Ethylene glycol to DI water in solution was changed from 1:1 to 5:4 and 3:2.

Characterization:

The NZVI was characterized using Scanning Electron Microscopy (SEM) (Hitachi S-4160, Japan) operated on 15KV, Transmission Electron Microscopy (TEM) (Zeiss EM 900). The crystallinity of the particles prepared by different Iron sources was investigated by using XRD patterns (Philips PW 1800 X-Ray Diffraction) results. The size of nanoparticles was determined using Dynamic Light Scattering (DLS) (Malvern, Nano ZS red badge, ZEN 3600). Also, Specific surface area of NZVI particles was analyzed by Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome Autosorb 1).

Result and Discussion:

We synthesized the nanoparticles by the reduction method. However, the portion of ethylene glycol to water was changed from 1:1 to 5:4 and 3:2. For simplicity, we labeled the products as NZVI-A, NZVI-B and NZVI-C respectively. The synthesized NZVI particles were observed by SEM and TEM images. The particles have a spherical morphology and the chain-like structure is maybe due to the magnetic properties and surface tension [8]. Based on the DLS results and the TEM images, by changing the ratio of ethylene glycol to water from 1:1 to 5:4 and 3:2, the size of NZVI particles was changed from 47.05 nm to 34.97 and 19.72 nm





respectively. Also, the BET results show a noticeable increase in the BET of the particles from $39.00 \text{ m}^2/\text{g}$ to 43.26 and $56.86 \text{ m}^2/\text{g}$ respectively.

Conclusion:

In this study the effect of the solvent on the size and BET of NZVI particles were investigated. As the results suggest, the mean size of NZVI-A, NZVI-B and NZVI-C are 47. 05, 34.97 and 19.72 nm, respectively, which indicates a dramatic decrease in the mean size when the percentage of ethylene glycol in the solvent increases. However, the BET of the particles conversely increases from 39.0 to 56.86 m^2/g for the produced samples which, to the best of our knowledge, is a novel result in this field.

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Stabilization study of Photodegradation of acrylonitrile–butadiene–styrene (ABS)/TiO₂ polymeric nanocomposite

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Abstract:

the photodegradation of acrylonitrile–butadiene–styrene (ABS)/TiO₂ nanocomposite investigated under exposure to UV light (90W) in weathering chamber. Stabilization was monitored in terms of changes at four various times by using of Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) patterns, Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC) were also used to assess the stability of nanocomposite. The results suggest that a better performance was achieved for stabilized ABS sample with TiO₂ nanoparticles, which are very important to extend the copolymer lifetime and significantly reduce the rate of degradation of polymer and providing a protective barrier to nanocomposite.

Keywords: ABS Copolymer, Photodegradation, Thermal Stabilization, Polymeric Nanocomposite

Introduction:

Flame retardation is a process by which the ignition or degradation of compounds is delayed by addition of specific material. Some plastics are inherently flame retardant However, for many plastic materials, it is necessary to improve their fire performance by incorporating flame retardants [1–4]. Nanocomposite technology is the next great frontier of materials





science, because by using minimal addition levels, we can achieve excellent mechanical properties, chemical resistance and thermal stability [5]. Nowadays, natural and synthetic polymer materials are used in ever increasing areas. However, one of the main disadvantages of most of these compounds is their inherent flammability, most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Among the major markets where flame retardants are required, the industries dealing with construction, electronics components and transportation are of the greatest importance [6]. ABS is a commercial material because of its desirable properties, which include good mechanical properties, chemical resistance, good processing characteristics and relatively low cost. ABS is a mixture of styrene, butadiene and acrylonitrile. One of the main drawbacks of ABS is its inherent flammability and therefore there is a need to increase its thermal stability and flame retardant properties [7].

Materials and methods:

Titanium dioxide (rutile, fluka) was purchased from TATCO Lab. ABS copolymer (SD-0150, 72%SAN, 28%PB, $\sim \overline{M}_{w} = 175000 \text{ g.mol}^{-1}$) was supplied kindly by T.P.Co. The ABS/TiO₂ nanocmposite prepared as following process: 0.01 g.mol⁻¹ (2% w.w⁻¹) TiO₂ dissolved in 10 ml chloroform (extra pure DAB 9,BP; purity: 99.9%, Merck). For better dispersion of TiO₂ nanoparticles in polymer matrix, solution stirred under ultrasonic bath (D-38678 Clausthal-Zellerfeld, elma) at room temperature via distillated water for 3 hours. Then the solution added to 0.49 g.mol⁻¹ (98% w.w⁻¹) granulous ABS which dissolved in 10 ml chloroform solvent. Thin films of ABS/TiO₂ samples (~35 µm thick), under exposure to UV light (90W) with 50 cm distance from samples in QUV box (110×100×70 cm³) on glass plaques (7×15 cm²) irradiated at four different times (20h, 36h, 52h, 112h) were prepared.

Fourier Transform Infrared Spectroscopy: Fourier transform infrared (FT-IR) spectroscopy (Tensor 27, Bruker) was used to monitor the alteration of surface layer of the photo-irradiated and unirradiated ABS/TiO₂ thin films at various times.





X-ray diffraction patterns: The X-ray diffraction (XRD) patterns were obtained on Siemens D5000 advanced X-ray diffractometer, using Cu K α radiation ($\lambda = 0.1542$ nm) in the range of the diffraction angle of $2\theta = 2.0 - 60.0^{\circ}$ at 25°C temperature.

*Scanning Electron Microscopy (SEM:*Scanning electron microscopy (SEM) was used to analyze the surface morphologies of the polymer nanocomposite using an instrument (SEM; XL30, Philips,) with gold sputtered coater powders. We used the physical vapor deposition (P.V.D) instrument by BAL-TEC, SCDOOS.

Differential Scanning Calorimetry (DSC): Dynamic differential scanning calorimetry (DSC) measurement was performed using a PL-DSC. A sample of the ABS film (approximately 6 mg) was placed in a clean aluminium pan and oxygen atmosphere (flow rate 50 mL/min) was established in the measuring cell. The sample and the reference were heated rapidly (10°C/min) from room temperature (25°C) to 300° C to realize equilibrium conditions.

Result and discussion:

FT-IR analysis: We investigated the selected photo-irradiated unstabilized ABS sample after 112 hours with respect to the ABS/TiO₂ sample. The conversion of peak absorbance at 20, 36 and 52 hours was nominal. In order to obtain a quantitative picture of the structural changes caused by weathering, we determined the relative absorption ratios of the peaks corresponding to the maximum of the carbonyl region (1700-1730 cm⁻¹), trans-1,4 group (967cm⁻¹), and vinyl-1,2 group (911 cm⁻¹) in relation to the height of a reference peak at 702 cm⁻¹ absorption band. According to FT-R results the amount of the carbonyl products (C=O) transmittance percentage at 1719 cm⁻¹ increases with addition of TiO₂ nanoparticles. This result shows the ability of TiO₂ nanoparticles on inhibition of carbonyl products dispersion in polymer matrix after 112 h irradiation time.





X-ray diffraction patterns investigation: The peaks attributed to the basal spacing of the nanocomposite layer were the same for virgin ABS around $2\theta = 1.5 - 1.8^{\circ}$ (broad peak), respectively, in 2 θ scales. These peaks prove an intercalated structure for the nanocomposite with a larger interlayer spacing with respect to TiO₂ itself. After loading TiO₂, at small relative ratio of ABS/TiO₂ (98:2 %w/w), it can be concluded that initial intercalation of polymer molecules between the butadiene layers is a thermodynamically favored process rather than kinetically. By the fact that both the XRD peaks are located around a same value on the 2 θ scale, which in turn results in a same interlayer spacing for the nanocomposite.

SEM analysis of the ABS/TiO₂ nanocomposite: The SEM micrographs showed a good dispersion state of nano-TiO₂ particles with a dimension of $1 \mu m - 500 nm$ in rubbery nanocomposite. It indicates the good chemical bonding and miscibility between nano-TiO₂ particles and PB phase of polymer. The grafting monomers can easily penetrate into the agglomerated nano TiO₂ particles due to their low molecular weight and react with the active sites of inside and outside of the agglomerates. Therefore, the dispersion state of nanoparticles can be improved by the penetrating nature of grafting monomers and steric effect of long polymer chain. The well-distributed nano-TiO₂ particles are beneficial for fire resistance of nanoparticles in polymer.

Differential Scanning Calorimetry (DSC) evaluation: It was seen that the maximum enthalpy of oxidative reaction of PB in unstabilized ABS appears in 152.98 J/g at 230.5°C temperature. The stabilized sample with TiO₂ nanoparticles (Fig. 4(b)) shows a decrease of the oxidative reaction of PB temperature (exotherm temperature) at 206.54°C via maximum enthalpy of 363.74 J/g and a decrease in the height of the exotherm compared to unstabilized ABS sample. These results indicate that the ABS/TiO₂ nanocomposite achieves the most partial energy of decomposition of Polybutadiene segment. In addition the heatflow of onset temperature of





thermal degradation of PB phase increases to 2.7955 mW in comparison of 0.8129 mW, heatflow of virgin ABS copolymer.

Conclusions:

Stabilization of ABS/TiO₂ polymeric nanocomposite was monitored in terms of changes at four various times. The results suggest that a better performance was achieved for stabilized ABS sample with TiO_2 nanoparticles, which are very important to extend the copolymer lifetime and significantly reduce the rate of degradation of polymer and providing a protective barrier to nanocomposite. The combination of nano titanium dioxide in polymer matrix is an important factor lowering the heat release rate (HRR). However, more profound study to support this assertion should be carried out in the future.

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A thermodynamic study and characterizations on Fe₃O₄ nanoparticles and coated with human and bovine serum albumins

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Key words: iron oxide nanoparticles, Fe₃O₄, human serum albumin (HSA), bovine serum albumin (BSA)

Introduction:

The development of a wide of superparamagnetic magnetite nanoparticles has shown great promise for various biomedical and biotechnological applications, for example magnetic resonance imaging contrast enhancement, hyperthermia, drug delivery, bioseparation. A number of preparation methods for MNPs have been developed, such as chemical coprecipitation, microemulsion, thermal decomposition, electrochemistry and sol-gel methods. Bovine serum albumin (BSA) has been one of the most extensively studied proteins and human serum albumin (HSA) is the most abundant protein in blood plasma and it is also the principal factor contributing to the colloid osmotic pressure of the blood[1,2].

Materials and methods:

The chemical reagents used in this work were $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, ammonium hydroxide (NH₃. H₂O), cetyl tri methyl ammonium bromide (CTAB) and cetyl pyridinum chloride (CPC) surfactant. BSA and HSA were purchased from Merck and Sigma-Aldrich. Distilled water was for preparation of the solutions after deoxygenating with dry N₂. In this research, the Magnetite nanoparticles (Fe₃O₄) were prepared by coprecipitation of Fe³⁺and Fe²⁺ solution in alkaline medium. Two kinds of surfactants CTAB and CPC were used in the synthesis. Fe₃O₄Nanoparticles were coated with HSA and BSA. The interactions of colloidal iron oxide





nanoparticles with serum albumins, including BSA and HSA, were investigated by UV-Vis spectroscopy at process different pH and temperatures. The thermodynamic parameters of coating were obtained from Van't Hoof equation.

Apparatus:

Characteristics of coated magnetic nanoparticles and no coated were carried out using scanning electron microscopy (SEM, Philips XL30, SE detector), X-ray diffraction (XRD, Bruker D8 Advance Germany) and FT-IR spectroscopy (MIDAC M1200-SP3 spectrophotometer) The interactions of colloidal iron oxide nanoparticles with serum albumins, including BSA and HSA, were investigated by UV-Vis spectroscopy.

Result and discussion:

The energetic of BSA- nanoparticles or HSA- nanoparticles equilibrium can be conveniently characterized by three thermodynamic parameters, standard Gibbs free energy, ΔG° standard enthalpy, ΔH° and standard entropy change, ΔS° can be calculated from the equilibrium constant, K, of the reaction using the relationship, $\Delta G^{\circ} = -RTLnK$, in which R and T referring the gas constant and the absolute temperature, respectively. With respect Van't Hoff equation.

Conclusion:

Carboxylate groups of BSA or HSA provide excellent ligation for iron oxide NPs. The presence of BSA or HSA on the NP surface was confirmed by FT-IR spectroscopy, SEM and XRD protein coated Fe₃O₄ nanoparticles have excellent biocompatibility and low toxicity. The thermodynamic parameters of coating process represent to that both entropy and enthalpy parameters are driving forces.

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Measurement and Modeling of Volumetric Properties of Nanofluid Containing Fe₃O₄ Nanoparticle, Poly(ethylene glycol) and Water

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Keyword: Magnetic nanofluid, Fe_3O_4 nanoparticle, Poly(ethylene glycol), Volumetric property.

Introduction:

Nanofluids are two phase mixtures consisting of solid nanoparticles with sizes varying generally from 1 to 100 nm dispersed in heat transfer liquids such as water, ethylene glycol, propylene glycol and light oils. Magnetic nanofluids, also called ferrofluids, are stable colloidal solutions consists of magnetic nanoparticle dispersed in a base fluid. Density and viscosity of nanofluids should be well determined for their effects on nanofluid flow and heat transfer characteristics.

Methods:

The nanofluid of Fe₃O₄ nanoparticles (Nanjing High Technology Nano Material Co., Ltd. (HTNano)) dispersed in PEG and nanofluids of Fe₃O₄ nanoparticles dispersed in aqueous solutions of PEG with PEG mole fraction of 0.1528 (type I) and 0.0633 (type II) were prepared by mass using an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. The colloid was then stirred and agitated thoroughly for making homogeneous nanofluids by an ultrasonic generator (Dr. Hielscher UP 200 H ultrasonic processor). Stability of these nanofluids has been verified with UV-Vis spectroscopy (Shimadzu UV-1700-Pharma). The particle size distribution of Fe₃O₄





nanoparticles dispersed in PEG and PEG + H_2O was measured by dynamic light scattering (DLS, Malvern, Nano ZS, ZEN 3600, England). Density and speed of sound data were measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000) with density uncertainty of $\pm 3.0 \cdot 10^{-6}$ g·cm⁻³ and velocity uncertainty of ± 0.1 m·s⁻¹.

Results and discussion :

The particle size distribution of Fe₃O₄ nanoparticles dispersed in PEG and PEG + H₂O was shown in Figure 1; the mean particle size of 307.5 nm and 277 nm was respectively determined for theses nanofluids. This may be because of polymer chains around nanoparticles and also aggregation structure of nanoparticles. UV-Vis spectra recorded with passage of time revealed that the nanofluid of Fe₃O₄ in PEG is stable. Density, *d*, and speed of sound data, *u*, were measured at T = (293.15- 318.15) K. For elucidating the interactions occurred in nanofluids studied, we decided to determine the excess molar volume, V_m^E and isentropic compressibility, κ_s , by the following equations:

$$V_m^E = \sum_{I=1}^3 x_I M_I [\frac{1}{d} - \frac{1}{d_I}]$$
(1), $\kappa_s = \frac{1}{du^2}$ (2)

where x is the mole fraction; M is the molar mass. V_m^E values for nanofluid of Fe₃O₄ in PEG are positive and decrease with increasing of temperature which indicate the van der Waalstype interactions and packing effect [1] (Figure 2). We found that the interactions between molecules of PEG and H₂O are higher than van der Waals-type interactions between molecules of Fe₃O₄ and PEG in the nanofluids of Fe₃O₄ + PEG + H₂O. Compressibility of nanofluids is decreased in the order of $\kappa_{s(Fe_3O_4inPEG)} > \kappa_{s(typel)} > \kappa_{s(typel)}$. The V_m^E values of nanofluid of Fe₃O₄ in PEG were correlated by Ott et al. equation [2]. The performance of Ott et al. equation has also been shown in Figure 2. As can be seen from this Figure the performance of Ott et al. equation in fitting of V_m^E values is good (Figure 2).



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Figure1: Particle size distribution and TEM



Figure2: Experimental and calculated V^E

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Investigation on Rheological Properties of Nanofluid of ZnO Nanoparticles Dispersed in Poly(ethylene glycol)

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Keyword: Nanofluid, ZnO nanoparticles, Poly(ethylene glycol), Rheological properties

Introduction:

Nanofluids, which are dilute colloidal dispersions of nanosized particles in heat transfer liquids such as water, ethylene glycol, propylene glycol and light oils, are a recent matter of interest. Rheological behavior is an important parameter in systems involving fluid flow. This property is required for illustrating the interactions of molecules in solutions and suspensions and also colloid structures. Rheological properties are also important in designing nanofluids for flow and heat transfer applications because the pressure drop and the resulting pumping power depend on this property [1, 2]. In this work, ZnO nanoparticles were dispersed in poly(ethylene glycol), PEG, then the rheological properties of these nanofluids have been measured.

Methods:

The nanofluid of ZnO nanoparticles (Nanostructured & Amorphous Materials, Inc. USA) dispersed in PEG with molar mass of 400 (g.mol⁻¹) (Merck) was prepared by mass using an analytical balance (Sartorius BP analytical balances Model BP301S) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. The colloid was then stirred and agitated thoroughly for making homogeneous nanofluids by an ultrasonic processor UP400S (400 watts, 24kHz). Stability of these nanofluids has been verified with UV-Vis spectroscopy (Shimadzu UV-1700-Pharma). The





particle size distribution of ZnO nanoparticles dispersed in PEG was measured by dynamic light scattering (DLS, Malvern, Nano ZS, ZEN 3600, England). Shear viscosity and stress sweep measurements were conducted in an Anton Paar-Physica MCR 300 rheometer using a concentric-cylinders viscometer (CC 27).

Results and discussion :

The particle size distribution of ZnO nanoparticles dispersed in PEG shows the mean particle size of 545.7 nm. This may be because of polymer chains around nanoparticles and also aggregation structure of nanoparticles. UV-Vis spectra recorded with passage of time revealed that the nanofluid of ZnO in PEG is stable. Shear stress (τ)-shear rate (γ) dependence have been shown in Figure 1 for pure PEG and nanofluid of ZnO-PEG at different concentration and 298.15 K. Variation of nanofluid viscosity with shear rate is shown in Figure 2 at different volume fraction of ZnO. As can be seen from this figure a pseudoplastic (or shear-thinning) behavior was observed for all the suspensions investigated. The shear-thinning behavior have been observed with a little increasing in shear rate levels; this revealed that the ZnO nanoparticle aggregations or network flocs formed between PEG and ZnO in the nanofluid were broken down into smaller flow units by applying small forces, so that the resistance to flow was reduced, leading to the lower viscosity as the shear rate increased. This further confirmed that the suspensions were in fact flocculated, even after the high agitation of nanofluids by an ultrasonic processor. The viscosity of nanofluids appeared to have leveled off at very low shear rate which indicates the low interparticle attraction of ZnO nanoparticles in PEG. The colloid viscosity became minimal at high level of shear rate applied which may revealed the fully existence of liquid base fluid (PEG) between the ZnO nanoparticles.



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Figure1: Shear stress versus shear rate



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Investigation of adsorption CO and O₂ gasses on inside and outside of single-wall carbon 2344anotube surface Using DFT Calculations

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Keywords: adsorption, SWNT, DFT, CO, O₂

Introduction:

Single-wall nanotubes are an important variety of carbon nanotube because they exhibit electric properties that are not shared by the multi-wall carbon nanotube (MWNT) variants. Very high chemical stability and mechanical strength made the carbon nanotube a very important material in nanotechnology. The most active research area using carbon nanotubes includes applications to nanodivices, field emitters, gas sensors, hydrogen storage in fuel cells, and DNA recognition technology [1-4].

Methods:

In this study, First SWNT (6,0), CO and O₂ molecules were separately optimized using GAUSSIAN 03 program and these molecules were passed through single-wall carbon nanotube (6,0) with different intervals and the adsorption energies for SWNT, CO and O₂ molecules were compared and then calculated using B3LYP/6-31G.(Fig.1) In this research, CO gas molecules were approached single-wall carbon nanotube (SWNT) and (6,0) CNT surface from carbon side and oxygen side in three states (top, bridge , centre) and two shapes (vertical, horizontal), then adsorption energies were calculated by B3LYP/6-31G. in order to obtain the most stable adsorption state.(Fig.2) its effect on adsorption energy was investigated by the means of the Equation (1).

Equation:

$$E_{ad} = E_{tot} (CO + CNT) - E_{tot} (CO) - E_{tot} (CNT)$$
 (1)
2344







Fig.1. Adsorption energy of gases inside the SWNT vs. distance (B3LYP/6-31G)





Results and discussion:

After passing CO, O_2 through nanotube with different intervals the Conclusion was that all the calculated adsorption energies of CO molecule were positive. This means that the





adsorption of the CO molecule is endothermic for the tube and there is no adsorption at the room temperature. But O_2 molecule,was adsorped at the distance of 4.5 Å inside the tube (in the centre). This means that the adsorption of the O_2 molecule is endothermic for the tube. In this research, CO gas molecules were approached single-wall carbon nanotube (SWNT) and (6,0) CNT surface from carbon side and oxygen side in three states (top, bridge , centre) and two shapes (vertical, horizontal), then adsorption energies were calculated by B3LYP/6-31G. in order to obtain the most stable adsorption state.it was determined that the most stable state for 6-31G basis set was TOP-V at a distance of 4Å from oxygen side.

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A facile approach for the synthesis of MnFe₂O₄ nanoflakes with low power ultrasonic irradiation

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Keywords: Manganese ferrite, Nanoflack, Ultrasonic irradiation, Reverse precipitation

Introduction:

Spinel magnetic materials, having the general form of AB₂O₄, offer a rich system for the study of complex magnetic order [1]. One of the magnetic spinel materials which have a great attention due to widely application is MnFe₂O₄. There are different methods for the synthesis of MnFe₂O₄. Currently, there is a trend toward simple, low temperature solution method for the preparation of nanoparticle. One of the novel and simple method for the synthesis of nanomaterial is sonochemistry [2]. The aim of current research is the synthesis of manganese ferrite nanocrystal in normal condition with bath sonicator as low power ultrasonic irradiation. As our the best knowledge this is the first time to synthesis this material in such normal condition and nanoflake structure is the new morphology for manganese ferrite nanostructure.

Materials and Methods:

An aqueous solution of 12 mL of $FeSO_4,7H_2O$ (0.1 mol/12mL) and $MnSO_4.H_2O$ (0.05 mol/12mL) was fed to an aqueous solution of containing 18 ml of NaOH (0.13 mol/18mL), dropwise (3.5 ml/h) with syringe pump in the presence of ultrasonic irradiation. After experiment, samples were washed by pure water and ethanol and centrifuged (4500 rpm). The final samples were dried under N₂ atmosphere at room temperature. The temperature was adjusted at 40 °C and the total time was 230 minutes. The synthesis of nanomaterials was carried out with Branson 8510E-DTE bath ultasonic, commonly used for cleaning purposes in





laboratories (40 kHz). Syringe pump (Cole-parmer, dual syringe, 74900 series) was used to dropwise adding of metal solution into the reaction media.

Results and discussion:

Characterizations of MnFe₂O₄ nanoflakes were carried out with X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, High resolution transmission electron microscopies (HRTEM), energy-dispersive spectrum (EDS), and scanning electron microscopy (SEM). As XRD result, diffraction peaks match well with the pattern of cubic MnFe₂O₄ (ICDD no.10-0319). The SEM analysis reveals that the product consists of MnFe₂O₄ nanoflakes. According to the HRTEM results, the size of nanoflakes is about 45nm and the SAED pattern shows the polycrystalline structure. As our best knowledge this is the first time to obtain such morphology for MnFe₂O₄ nanostructure. EDS analysis confirms the presence of Mn, Fe, and O elements on the samples and FTIR analysis reveals that the presence of the band around 500cm⁻¹ corresponds to the stretching vibration due to the interaction produced between the oxygen and the cation occupying the tetrahedral sites for MFe₂O₄.

Conclusion:

We demonstrated the sonochemical preparation of manganese ferrite nanoflake by reverse precipitation in bath ultrasonic at medium temperature. This is the first time that we are reporting formation of nanoflake for manganese ferrite. The wide of nanoflake is up to 500 nm. The appropriate microjet and shock waves provided by low power ultrasonic agitation could activate the liquid-solid boundary layer, and the mass transfer. The oriented attachment of the primary particle is the possible growth mechanism. This sonochemical method provides a new route to fabricate 1D material.

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The Effect of Polymer Conformations on the Heat Flow in Nanoconfined Polymers

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Keywords: nanoscale heat flow, nanoconfined fluids, reverse nonequilibrium molecular dynamics simulation.

Introduction:

The change in polymer conformations beside the surfaces, compared to the bulk polymer, on the anisotropic heat flow in polyamide-6,6 has been calculated using by reverse nonequilibrium molecular dynamics simulation. In this method the heat exchange between polymer layers is done artificially and the coefficient of thermal conductivity is calculated from the slopes of linear temperature profiles in the pore.

Method:

The reverse nonequilibrium molecular dynamics simulation (RNEMD) method is used to investigate the anisotropy of thermal conductivity of polyamide-6,6 in a confined geometry. The simulation box is divided into a number of slabs in the direction of confinement kinetic energies have been exchanged between the hottest and coldest slabs. The thermal conductivity is calculated as:

$$\lambda = -\frac{\sum_{transfers} \frac{m}{2} \left(v_h^2 - v_c^2 \right)}{2t L_x L_y \left\langle \partial T / \partial z \right\rangle}$$
(1)

where t is simulation time, the subscripts h and c refer to the hot and the cold particles of identical mass m whose velocities are interchanged. L_x and L_y , are the box lengths in x and y directions, respectively, and the factor 2 in the denominator arises from the periodicity of the box.





Results:

Thermal conductivity has been calculated in both parallel (λ_{\parallel}) and perpendicular (λ_{\perp}) directions with respect to the confining surfaces [1]. Our results show that heat transport in the parallel direction is much higher than that in the perpendicular direction. In addition anisotropy is defined as the ratio of thermal conductivity in the parallel to the perpendicular directions $(\lambda_{\parallel}/\lambda_{\perp})$. The results show that the anisotropy depends on the pore size. In small pores with well organized polymer layers beside the confining surfaces, the anisotropy gets close to its value in bulk (1). The anisotropy is relates to the change in polymer conformations beside the surfaces (see Figure 1). As the results in Figure 1 show, the chains adopt flattened conformations beside the surfaces, and hence, the heat flow in the parallel direction is facilitated by the skeletal vibrations. The results on the anisotropic heat flow (shown in Figure 2) indicate that the anisotropy depends on the pore width.



Fig.1. Conformation of polyamide-6,6 near the surfaces.



Fig.2. The anisotropy in thermal conductivity of polyamide-6,6 as a function of intersurface separation.





Conclusion:

Our results indicate that the heat conduction in nanoconfined polymers is anisotropic. The thermal conductivities depend on the intersurface separation and on the degree of layering of polymer in the pore. Because of the change in the mechanism of heat flow in the parallel direction with respect to the perpendicular direction; heat flow through skeletal vibrations in the former case compared to the heat flow via molecular collisions in the later one, more flattened polymer conformations show higher anisotropies in the thermal conductivities.

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Thermal Properties and Kinetic Analyses of Novel Highly Energetic Reactive Materials-Nano versus Micron Composites

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Key words: reactive material, thermal properties, kinetic analyses, nanocomposites

Introduction:

Reactive Materials (RMs) are energetic materials consisting of two or more solid-state reactants that together form a thermo-chemical mixture. Typical RMs includes metal-metal and/or metal-metal oxide mixtures with and without polymer binders. RMs have higher predicted energy per unit volume than conventional energetic materials and can provide alternate kill mechanisms besides those obtained for conventional energetic materials. Relatively low rate of energy release in heterogeneous reactions presents the major bottleneck for most applications. Increase of reactive surface or reduction of reactive elements to nanosize results in a quantitative increase in the reaction rate. Reactive Nano-materials have high specific reactive interface area and high energy density. Substantial size reduction of each reactant powder from micro to nano-size leads to increase of reaction front propagation in some systems under unconfined conditions by approximately two to three order of magnitude. This is accomplished when nano-sized fuel and oxidizer particles are mixed. The scaling of these reactants to the nano-scale has allowed for several capabilities and applications that were not previously possible with conventional micro-sized RMs mixtures. A significant size reduction of reactant powders allows more intimate contact. As a consequence of this significant reduction of size, new issues such as dispersion and mixing of reactants, safety, and surface fictionalizations of fuel particles in order to minimize potential undesired reaction with oxygen and water vapor must be addressed. In recent times with advances in materials and





material processing, reactive mixtures of aluminum and TFEF have applications in high energetic materials [1-6]. But this study examines the thermal behavior and Kinetic Analyses of a novel triplet mixture of Tetrafluoroethylene fluorocarbon (TFEF) polymer, CuO and nano-size Al particles compared with micron-scale Al particles.

Materials and methods:

Powder samples were prepared consisting TFEF(Aldrich), CuO(Merck), 100nm Al(Alex) and 1-10µm Al(AEE). Al+TFEF+CuO (50+25+25wt%) samples were mixed by a V-blender mixture 8 hours according to the mass proportion respectively in nano-size and micron of Al. A non-isothermal simultaneous thermal analysis(STA) were performed on both nanometer and micron scale mixtures in a helium atmosphere at liner heating rate of 10 Kmin–1 from room temperature to 1000°C using a thermal analyzer (NETZSCH-Geratebau GmbH STA 409 PC). A high speed camera system (FASTCAM-Ultima, APX-RS, 60-250,000 fps) was used to capture the optical emission from the 25g pressed cylindrical pellet in an open burn setup combustion events of both samples with 50,000 frames per seconds captures images rate. The reaction was initiated by applying a voltage to the nicrome wire.

Result and Discussions:

The exothermic reaction (Eq. (1)), between Al, TFEF and CuO is a heterogeneous reaction. Thermal Analysis methods are the best method for study of these solid state reactions. Fig.1 show the simultaneous DTA/TGA response for 1-10 μ m Al/ TFEF /CuO and 100nm Al/ TFEF /CuO. Fig.1.a and Fig.1.b demonstrate that the thermal behavior patterns for micron and nano sample are very different. The ignition temperature of nano-size sample reaction very lower of micron sample. Ignition temperature of the RMs is very important factor for management of usage these materials. RMs with very high ignition temperature are difficult to start reaction and when ignition temperature is very low that is problem for safety response. As shown in . Fig.1 the major exotherm (611.6°C) for nano-size sample very sharp relative to micron exotherm (763.5°C) that means the energy relays for nano-size sample very rapidly. The minor





exotherm (396.2°C) for nano-size sample donates the preignition reaction (PIR) but this phenomena doesn't occurs in micron sample reaction.

$$6Al + 3CuO + 3(C_2F_2) + 3CuO \rightarrow Al_2O_3 + 3Cu + 4AlF_3 + 6C_{\text{Graphite}}$$
(1)

For kinetic analysis of solid state reaction (Eq. (1)), we used the integral form of the nonisothermal rate law(Eq.(2)) from Coats / Redfern calculation method[7-9]. (Eq.(3)).

$$g(\alpha) = \frac{AE_{\alpha}}{\beta R} \int_{E_{\alpha}/RT}^{\infty} \frac{e^{-E_{\alpha}/RT}}{\left(\frac{E_{\alpha}}{RT}\right)} d\left(\frac{E_{\alpha}}{RT}\right) \quad (2) \qquad \qquad ln \frac{g(\alpha)}{T^{2}} = ln \left(\frac{AR}{\beta E_{\alpha}} \left[1 - \left(\frac{2RT_{exp}}{E_{\alpha}}\right)\right]\right) - \frac{E_{\alpha}}{RT} \quad (3)$$

where α is the fraction of solid reaction progress at time t, $g(\alpha)$ is the integral form of the empirical function $f(\alpha)$ is a function of α depending on the reaction mechanism, k is the rate constant given by the Arrhenius equation, A is the pre-exponential factor (1/min), E α is the activation energy (J/mol), R is the universal gas constant (8.314 J mol-1K-1), T is the temperature of reaction (K), β is constant heating rate β =dT/dt (K/min) and T_{exp} is the mean experimental temperature.

By plotting the left-hand side (including the model, $g(\alpha)$) of Eq. (3) versus 1/T gives the activation energy (E_{α}) and frequency factor (A) from the slope and intercept, respectively. The model that gives us the best linear fit is chosen as the model. For nano-size sample the solid state reaction kinetic model was indicate Order-based models, F_n, $g(\alpha) = (1-\alpha)^{1.3}$, versus to micron sample solid state reaction model the best fit was indicate geometrical contraction model R2, $g(\alpha) = 2(1-\alpha)^{0.5}$, as summarized in table 1.

The corresponding Propagation time data were determined by sequence of images that illustrate the fairly planar flame propagation through the pellet was recorded via the high-speed camera with 50,000 frame per second as summarized in table 1 that donate the propagation rate of nano-size Sample (88μ sec/g) very fast relative to micron sample (404μ sec/g).

Conclusion:

From the results obtained the ignition temperature of nano-size sample reaction very lower of micron sample. The nano-size sample indicate a PIR phenomena donate that there is a




transition at which diffusively-controlled reaction will start to reaction kinetically-controlled. The activation energy and frequency factor is very lower for nano-size versus micron sample. Fn(Order-based) kinetic model for nano-size sample versus R2(geometrical contraction) model for micron sample were confirmed the very high reaction rate and flame propagate for nano-size sample.

High burning rate for nano-size versus micron sample can be concluding from very high flame propagation that was captured by high-speed camera.



Fig.1. TGA/DTA results of, (a) 1-10 μm Al/ TFEF /CuO (b) 100nm Al/ TFEF /CuO heated at 20kpm in helium **Table1.** Results of solid state reaction kinetic parameters of 1-10 μm Al/ TFEF /CuO and 100nm Al/ TFEF /CuO

Characteristics	Samples			
Characteristics	1-10 μm Al/ TFEF /CuO	100nm Al/ TFEF /CuO		
Onset/ignition Temperature(°C)	695.8	554.2		
Peak Temperature(°C)	763.5	611.6		
Propagation Time (µ Sec/g)	404	88		
Activation Energy (kJ/mol)	177.381	44.242		
Log A(-/s)	14.347	1.4113		
$f(\alpha)$	2(1-α) [^] 0.5	(1-α)^1.3		
r	0.9806	0.9914		

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Separation of CO₂, N₂ and CH₄ in Gases Mixtures by Single-walled Silicon Carbide Nanotubes: a GCMC Study

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Keywords: Separation, Adsorption, Storage, GCMC Simulation, SiC nanotube.

Introduction:

In the last years nanotube membrane processes due to their fascinating properties and their well-defined structures with hollow nano-size interiors suggest their potential use as sorbents for gas adsorption and separation which are gaining a larger acceptance in industry and in the market [1]. As far as we concern, a large number of theoretical and experimental studies have been carried out thus far on the adsorption/storage/separation of CO2, N2 and CH4 on various carbon nanotubes, single- or multi-walled, closed- or open-ended [2], but single-walled silicon carbide nanotubes (SWSiCNTs) have being considered rarely, to be characterized by these gases [3]. Therefore in the present work, we evaluate the storage/separation properties of SWSiCNTs by grand canonical Monte-Carlo (GCMC) computing for CO2, N2 and CH4 adsorption. Very recently, Sun et al. have reported the synthesis of silicon carbide (SiC) nanotubes produced via the reaction of Si with carbon nanotubes [4]. Menon et al also investigated the structure and stability of various SiC nanotube structures using the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy and *ab initio* methods [4]. They found the bond lengths of SiC nanotube is about 1.87 Å that is larger than bond length of boron nitride (BNNT) nanotube (1.44 Å) and carbon nanotube (1.42 Å). Therefore, SiCNTs are predicted to have the faster rate gas penetration through the wall of BNNT and CNT.





GCMC simulation details:

We use GCMC simulations [5] to study the separation of CO_2 , N_2 and CH_4 equimolar binary mixtures in (10,10), (20,20) and (40,40) SWSiCNTs. All nanotube length is fixed on 5 nm and the nanotubes have rigid structures, and no geometry variation of the adsorbent is considered, since the induced geometric variation of nanotubes can be neglected by gases at room temperature.

Results and discussion:

We used the GCMC simulations to obtain the weight percentage of CO_2 , N_2 and CH_4 separately and in equimolar binary mixtures while they can be stored in SWSiCNTs under different thermodynamic conditions. Fig. 1 presents the adsorptivity of CO_2 , N_2 and CH_4 inside (10,10) SWSiCNTs at 300 K and varying pressure. Also, Fig. 2 shows the adsorptivity of $CO_2/N_2/CH_4$ in the same SWSiCNTs at 300 K and varying pressure.



Conclusion:

This paper using GCMC simulation explain the optimal thermodynamics conditions to achieve the best remove of CO_2 and CH_4 based on storages inside SWSiCNTs. The energies and the isotherms of CO_2 , N_2 and CH_4 adsorption in SWSiCNTs are plotted. The results indicate that the elimination of CO_2 and CH_4 can take place while they are in mixtures. Also, CO_2





adsorption is more than CH₄. It is should be noted that our simulations have not completed and would be continued.

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Optical and Structural Properties of ZnS Quantum Dots Fabricated by Sonochemical Method

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Keywords : Zinc sulphide, semiconductor, band gap energy, sonochemical method.

Introduction:

Zinc sulfide (ZnS), as an important semiconductor compound with wide band gap energy of 3.7 eV, has attracted much research interest because of its unique properties and potential applications [1]. It has a wide range of applications covering optical devices, ultraviolet sensors, lasers, diodes, and photocatalysts in pollutant treatment [2-4]. In this study, ZnS NPs were fabricated via a sonochemical method. The quantum dots were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), Fourier transform infrared spectroscopy (FTIR), and UV–vis absorption spectroscopy.

Methods :

In a typical synthesis of ZnS NPs, zinc acetate was dissolved in water to make 0.27 M solution. Subsequently, 0.043 mol thioacetamide was added to the solution and the mixture was stirred for 20 min. Then, the ultrasonic irradiation was accomplished to form the precipitate. The obtained powder was centrifuged, washed, and dried in a vacuum oven.

Results and Discussion:

Structural and optical properties of ZnS quantum dots were investigated by different methods. For instance, according to the TEM image and the histogram of particle size distribution (PSD)



of the sample the average particle size of ZnS NPs was ca. 2 nm (Fig. 1 (a)). HRTEM image of sample shown in Fig. 1 (b) reveals that the NPs were uniformly structured and the spacing of the crystallographic planes was 0.29 nm which is confirmed by the values reported in literature [5].



(2)

Fig. 1. (a) The TEM image of ZnS NPs along with the histogram of PSD and (b) The HRTEM image of NPs. The optical band gap of the ZnS quantum dots was estimated from the Tauc equation [7]:

$$(\alpha h v)^2 = C(h v - E_g)$$

where α , $h\nu$, C, and E_g stand for the molar absorption coefficient, the photon energy, an arbitrary constant, and the band gap of the NPs, respectively. The optical band gap of ZnS NPs was 5.77 eV (the inset of Fig. 2) which is fairly large in comparison with the value for the bulk ZnS [8].



Fig. 2. The UV-vis spectrum of ZnS NPs. Plot of $(\alpha hv)^2$ vs. photon energy (inset).

Conclusions :

A novel method for preparation of very small ZnS NPs with high purity and good uniformity using ultrasonic waves was described. The optical band gap energy of ZnS NPs was calculated using UV-vis





spectroscopy. The band gap of ZnS NPs estimated from the absorption peaks is much larger than that of bulk ZnS due to the quantum confinement effect.

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The electrical properties of GDE/DGA/nano-Al₂O₃ system

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Keywords: EIS, Epoxy, Reaction time, Initiator

Introduction:

Epoxy resin is one of the most versatile materials used in a wide range of electric power installations and equipments, including generators, transformers, switchgear and so on. Because their high thermal stability, the epoxy materials broadly employed in electrical insulation [1]. Electrochemical Impedance Spectroscopy (EIS) is used to investigate the electrical behavior of various nanocomposite systems. The main parameters those determined by the EIS technique are the electrical resistance and relaxation times [2]. In this work, electrical resistance of the nanocomposite was investigated with content of nanoalumina, changing the reaction time and temperature and concentration of the initiator.

Experimental:

Glycerol diglycidyle ether (GDE), 3,3-Dimethylglutaric anhydride (DGA) (in stoichiometric ratio), and nanoalumina (0-15 phr) were mixed, and then the initiator (triethyl amine, $X_{TEA} = 0.0188$) added in the last stage. The mixtures were dissolved in tetrahydrofuran (THF) and then ultrasonicated for 60 min to produce homogenous blends. The samples were casted on a Teflon mold and cured at 130 °C for 4 hour. EIS measurements were performed using a Potentiostat / Galvanostate EG&G Model 263 A; USA. Through analyzing the input and output signals, the impedance of the system can be determined according to this equation: Z = Z' + jZ'' Where, Z' and Z'' are the real and imaginary parts of the complex impedance, respectively.





Results and discussion :

The effect of nanoalumina concentration on electrical resistance was clarified by analyzing the compositions involving different amounts of nanoalumina. We observed that the resistant of samples is not affected by nanoalumina concentration (Figure 1). Accordingly, we set our further studies based on the composition having 10 phr of nanoalumina as previously optimized [3].



A few measurements were carried out at different temperatures to obtain more information about the resistance properties of cured samples. The EIS results show (Figure 2) very large increase in the semicircle diameter at the lowest temperature.

Three samples were heated at 130 °C in a vacuum oven and then removed at 0.5, 2, and 4 h to perform EIS analysis. It is observed that the resistance changes during curing reaction. The results indicate that the reaction mainly progresses in the first 30 min, but reaching an endpoint after 4 h, because at higher time resistivity remains constant.

We also studied the effect of initiator concentration on electrical resistance of the samples. Our results showed that there is a direct correlation between the concentration and resistance, i.e. by increasing of TEA concentration the resistance increased as well.

Conclusion:





The results obtained by EIS showed that the nanoalumina content has no effect on the resistance of samples. The decreases in resistance with temperature can be explained due to the decreased flexibility and bond rotations on the polymer chain. Also, it was founded that the resistance increase with initiator concentration and reaction time.

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The nano-Al₂O₃ effect on glass transition temperature of a new nanocomposite based on glycerol diglycidyle ether: An EIS and DMTA study

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Keywords: DMTA, EIS, Glass Transition, Nano-Al₂O₃

Introduction :

Materials derived from epoxy resin have been widely used in polymer industry such as electrical insulating materials because of their remarkable properties for instance moderate mechanical properties, great electrical properties and excellent processability. Dynamic mechanical thermal analysis (DMTA) is one of the ways to estimate changes, which occur for polymeric materials in the broad range of temperature [1]. Several researchers have also studied the relaxation processes in polymeric systems using DMTA and Electrochemical Impedance Spectroscopy (EIS) [2] techniques and found that they are shifted according to the frequency used in the given method.

Experimental:

Glycerol diglycidyle ether (GDE), 3,3-Dimethylglutaric anhydride (DGA) (in stoichiometric ratio), and nanoalumina (10 phr) were mixed, and then the initiator (triethyl amine, $X_{TEA} = 0.0188$) added in the last stage. The mixtures were dissolved in tetrahydrofuran and then ultrasonicated for 60 min to produce homogenous blends. The samples were casted on a Teflon mold and cured at 130 °C for 4 hour. EIS measurements were performed using a Potentiostat / Galvanostate EG&G Model 263 A; USA, and the viscoelastic properties were





measured on a Tritec 2000 DMTA (Triton Technology Co. England) dynamic mechanical thermal analyzer.

Results and discussion :

According to EIS technique, the electrical resistance was studied as a function of temperature from 10 to 30 °C. As it is evidenced in the literatures, the glass transition temperature (T_g) can be taken as that corresponding to the apex of $Tan\delta$ versus temperature peak. Accordingly, we can write this equation [3]: $Tan\delta = Z''/Z'$, Where, Z' and Z'' are the real and imaginary parts of the complex impedance, respectively. Figure 1 shows the curve of $Tan\delta$ versus temperature at which the T_g of the nanocomposite is found to be 23 °C.



The DMTA revealed that the incorporation of filler into a polymer matrix decrease the mechanical damping of the polymer [3]. The damping property, as the ratio of the dynamic loss modulus to the dynamic storage modulus, is related to the molecular motions and phase transitions. The important point is that a very slight change was observed in the position of the glass transition temperature. Strong interactions of nanoalumina and matrix tend to diminish the mobility of the molecular chains at interface and therefore to reduce the damping revealing the increasing trend of rigidity of the nanocomposites (Figure 2). The value of T_g is 15 °C for the nanocomposite and is in reliable agreement to that value found by EIS results.





Conclusion:

Based on the results obtained by EIS, the T_g was calculated and compared with those values measured by DMTA technique. The addition of nano-Al₂O₃ in GDE matrix made its difficult to move the polymer chain. Therefore, the peak *Tan* δ value decreased and glass transition temperature was shifted to higher temperature. Correlations between the results obtained by DMTA and EIS techniques result in interesting conclusions.

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Molecular dynamics simulation of the melting process in Ag₂₇Cu₁₃ core-shell nanoalloy

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Keywords: Nanoalloy, Molecular dynamics, Phase transition

Introduction:

One of the most important characteristic of nanosystems, is their thermal stability and because of this, studying melting of nanoparticles has received great attention both from the point of view of experiment and theory and/or simulation [1]. The melting phenomenon of small finite systems is a complex field, which has some differences with respect to melting of bulk solid systems. Despite bulk systems, melting, doesn't occur in a precise temperature but is over a temperature range [2,3]. Moreover, melting range depends on the size of the system [3,4].

Computational method:

At different temperatures, the MD simulation is done in NVT ensemble, employing Evans thermostat with a time step of 1fs, resulting in long simulation runs of 11ns. To study melting property of the nanoalloy, instant positions and velocities of the atoms are recorded.

I. Result and discussion:

Three kinds of criteria, is used to analyze thermal behavior of the Ag₂₇Cu₁₃ nanoalloy:

1. Thermodynamical criterion :

Two common thermodynamical criteria to monitor the occurrence of phase transitions are the caloric curve and the heat capacity and the results are reported below. 15th Iranian Physical Chemistry Conference University of Tehran, Tehran, September 3-6, 2012

0.012

0.01

600

Fig. 1

T(K)



700 T(K)

Fig. 2

-110

Root mean square bond length fluctuation, δ , has been used as a geometrical criterion and the result is given in Fig.3

3. Dynamical criteria:

Velocity autocorrelation function can be used as a dynamical criterion In Fig. 4, VAF of the atoms is shown at different temperatures.



Conclusion:

In general, different criteria are in a good agreement. From the caloric curve and heat capacity data we see that, the melting transition occurs at about 610K. As it is shown in the Fig. 3, abrupt change of δ values occurs at lower temperature that is less than 610K. Thus we must be





cautious in employing it as a phase change decisive factor because its value changes significantly in response to geometrical isomerization before occurring melting transition. As it is shown in Fig. 4, with increasing temperature, the dynamical behavior of the each kind of atom in the system (Ag and Cu atoms) becomes much more similar and at 840K (that the heat capacity has its maximum value), two different kinds of curves, match for each type of atoms.

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Investigation on electrochemical behavior of poly (o-amino phenol/nano SiO₂) films synthesized by cyclic voltametry

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Key words: Nanocomposite, Poly (*o*-aminophenol), glassy carbon electrode, Electropolymerization

Introduction:

Nanotechnology is a rapidly growing area of nano-structured material science because of its numerous applications in various fields such as catalysis, sensors, electronics and optics as well as in the medical sciences [1-4]. Nanometer silicon dioxide (nano-SiO₂) is one of the most popular nanomaterials that are being used in different areas.

In present work, o-aminophenol (OA) monomer is electropolymerized in the presence of an aqueous emulsion containing nano-SiO₂ particles as attractive building blocks for development of novel polymer-based composite with enhanced functionality onto glassy carbon electrode (GCE).

Materials and methods:

The monomer, o-amino phenol (OAP) was purchased from Merck. Sulfuric acid (Merck) 0.5M was used as the supporting electrolyte. Di hydrogen phosphate and di sodium hydrogen phosphate (Fluka) were also used as electrolyte solutions. Silica nanoparticles have an average size of 50 nm and surface area of $35-43 \text{ m}^2/\text{g}$ were purchased from Aldrich.

Apparatuse:

All the experiments were performed using a Potentiostat/Galvanostat (SOLARTON SI 1287). A three-electrode cell system was employed with glassy carbon as working, platinum as





counter and Ag/AgCl(KCl : 3M) as refrence electrod. Electrods were rinsed with distilled water. Glassy- carbon was polished with alumina slurry on emery paper. Phosphate buffer solution (PBS) was prepared by 0.1M NaH₂PO₄-Na₂HPO₄. POAP/ SiO₂ films were grown potentiodynamically in a conventional three-electrode cell system, at a sweep rate (ν) of 50 mV s⁻¹, in a solution of OAP+SiO₂+sulfuric acid 0.1 M. The polymer disposited by CV from - 0.2 to 0.6 v.

Results and discussion:

Figure.1 show, cyclic voltammetry behaviors of POA/MGCE and POA/nano-SiO₂/MGCE in phosphate solution. The electrodes demonstrated their electrochemical activities, which are characterized by typical oxidation and reduction responses. Poly (*o*-aminophenol)/nano-SiO₂ films have considerably higher redox current than the neat poly (*o*-aminophenol) film.



Fig.1 Cyclic voltammogram of (a) POA-nano SiO₂/GCE and (b) POA/GCE in phosphate solution (pH =3), (polymers were formed by potentiodynamic method at potential scan rate of 0.05 v/s between -1.2-0.6 V).

Conclusion:

The differences in redox currents reflect the effective active surface areas that are accessible to the electrolytes at POA/nano-SiO₂/MGCE. Apparently, the porous POA/nano-SiO₂/MGCE films have higher effective surface areas. This improvement of doping-undoping rate is a result from the increase of surface area and porous structure, which are benefit to the ion diffusion and migration.





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Synthesis and Characterization of Polyvinyl Acetate/Montmorillonite Nanocomposite

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Keywords: Nanocomposite, Emulsion polymerization, Montmorillonite, Exfoliation

Polymer-inorganic nanocomposites are an attractive set of organic-inorganic materials which have emerged as a new class of advanced materials containing a low inorganic filler concentration [1]. The most important advantage of synthesis polymer-inorganic nanocomposites is related to combination of the properties of inorganic material (e.g., rigidity and thermal stability) with the organic polymer (e.g., flexibility, ductility, and process ability). The basic feature of polymer nanocomposites is that the nano- size fillers lead to increase in interfacial area as compared with traditional composites [3]. Actually, nano-sized fillers have high potential for use in polymer-inorganic nanocomposites in which enhanced thermal and mechanical properties are required. A significant amount of work has been focused on the synthesis and characterization of these nanocomposites for better understanding of the mechanism of intercalating polymers in layered inorganic hosts to fabricate modified polymerinorganic nanocomposites. In this work, exfoliated Polyvinyl Acetate /montmorillonite, PVAc/MMT nanocomposite was prepared via in situ emulsion polymerization. For preparation of the PVAc/MMT nanocomposite, MMT was dispersed in deionized water, the mixture and the aqueous emulsified solution containing SLS, N₂₀ were added to a 500 ml glass three-neck reactor with a water jacket to maintain a constant temperature $(\pm 0.1 C)$. The glass reactor was fitted with a reflux condenser; funnel and mechanical stirrer, then the initiator (APS) were added. Then monomer poured into the dropping funnel. The mixture was stirred at





300 rpm and heated up to $75^{\circ}C$. After addition of the monomer, the polymerization was carried out for 4 h.

Figure 1 compares the XRD patterns of the exfoliated and non-exfoliated PVAc/MMT nanocomposite sample, in this figure the non-exfoliated sample exhibits a single peak at an angle 2θ of 4.92°. For PVAc/MMT nanocomposites, the characteristic diffraction peak disappeared for samples of the PVAc/MMT nanocomposite, indicating that the MMT has been fully exfoliated in the samples. This shows that polymer chains have exfoliated into the interlayer of MMT. It is found that in all systems the interlayer spacing increases due to the intercalation of polymer into the layers of MMT. Enhanced interlayer distance indicates that the layered structure is retained.



Figure 1. XRD of (a) MMT (b) PVAc/MMT nanocomposite.

Figure 2 shows the results of SEM analysis of PVAc/MMT nanocomposite. According to this figure, the spherical molecules homogeneously dispersed and distributed randomly in surface.



Figure 2. SEM of PVAc/MMT nanocomposite

We synthesized the exfoliated PVAc/MMA nanocomposites and XRD results showed a disorder layer structure due to intercalation of polymer into the layered silicate. The exfoliated





PVAC/ MMA nanocomposite was prepared by emulsion polymerization in the presence of the MMA-modified montmorillonite

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Adsorption of Ethane on Pristine and Ni-doped Single Walled Aluminium Nitride Nanotube

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Keywords: Ethane, AlN Nanotube, Nickel, Binding Energy, Adsorption.

Abstract:

Aluminum Nitride nanotubes show many similarities to the BN nanotubes due to electronic properties, geometers, and stability [1]. A hexagonal AlN nanotubes has been synthesized which are actually nano-rods with a hallow center [2]. On the framework of AlN nanotubes, the Pauling electronegativity of the nitrogen atom is 3.04 which is much larger than that of aluminum atom and leads to a significant charge transfer from aluminum to nitrogen [3]. The interaction of AlN single walled nanotubes with gases, excepting hydrogen, ammonia, and carbon dioxide [4] has seldom been investigated and remains largely an unexplored area. In this research work, we investigate the ability of the ALN nanotube to adsorb the ethane gas.

Method:

We using Density Functional Theory (DFT) and employed CEP-121G for Ni and 6-31G basis set for nanotube and C_2H_6 .

Results and discussion:

The (4, 4) AlNNT with 40 Al atoms and 40 N atoms was selected. Two possible adsorption sites for C_2H_6 on AlN nanotube can be considered, as shown in figure 1: H (Horizontal) and V (Vertical).Firstly, the interaction of C_2H_6 with AlN was examined and secondly, the AlN functionalized with Ni atom was investigated. Results show that the Ni-doped AlN nanotubes





are highly sensitive toward C_2H_6 , which greatly improve the sensivity and broaden the range of detected gases compared with pristine AlN nanotube.



Figure 1: Two possible adsorption sites for C_2H_6 (a) V site and (b) H site.

To examine the adsorption properties of C_2H_6 on nanotubes, adsorption energy, E_{ads} , was calculated using the expression

$$E_{ads} = E_{(tube-Ni-C2H6)} - (E_{tube-Ni} + E_{C2H6})$$
(1)

where E $_{(tube-Ni- C2H6)}$ is the total energy of the Ni-tube with C₂H₆ adsorbed, E_{tube-Ni} and E $_{C2H6}$ are the total energy of Ni doping tube and ethane respectively.

Conclusion:

We found out that the introduction of hetero atom onto nanotubes significantly enhances ethane adsorption.

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Theoretical approach in the study of the adsorption processe of Carbon monoxide on Aluminium Nitride nanotube

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Introduction:

With the discovery of carbon nanotubes[1], experimental and theoretical research interest on similar nanoscale tubular structures is steadily increasing. Recently aluminium nitride nanotubes, structures that show great resemblance to the BN nanotubes, have been studied theoretically with regard to geometries, electronic properties, and stability [2]. Chemical gases such as CO is highly toxic to human beings and animals as it inhibit the consumption of oxygen by body tissues. Therefore, gas sensors with high sensitivity to this gas are highly desired [3].

Method:

The adsorption of CO on (4, 4) AlN nanotube was studied using DFT calculation at the pbepbe/6-31G level of theory. Periodic boundary condition in the tube axis direction was employed. In this case, the length of the cell is 6.34 Å. The interaction between molecule and the surface of the nanotube was fitted to the Morse potential, and the form is expressed as

$$U_i = 2D[x^2 - 2x], \quad x = exp\left(-\frac{\gamma}{2}\left(\frac{r_i}{r_e} - 1\right)\right) \tag{1}$$

Where r_i is the distance between CO and tube surface (Å). The constants D, γ and r_e for CO adsorption the nanotube are given in Table 1.





Result and discussion:

In this work, two configuration of CO molecule (O-down, and C-down) are considered relative to the three possible sites of AlNNT : the top of the Al and N, the center of hexagonal ring (H).

All adsorption energy curves for outside of the tubes were fitted with Morse potential equation, to obtain the parameters of this equation (Table 1). Figure 2 show the fitted potential energy curve with Morse potential equation.

Configuration	site	D (ev)	γ
C down	Al	0.40	7.75
C-down	Ν	0.05	8.89
0.1	Al	0.24	6.74
O-down	Ν	0.08	7.93
	Н	0.17	5.45
0.4			
0.3 -		$\rightarrow \Delta E(ev)$	
0.2 -		Morse	
0.1			
	1 1		
-0.1 1 5	2.5 3.5		5.5
-0.2			
-0.3 -			
-0.4		(Å)	

Figur 2: Typically Fitted potential energy curves with Morse potential

The adsorption energy of single molecular CO on tube is defined

$$E_{\text{ads}} = E_{\text{NTs+CO}} - E_{\text{NTs}} - E_{\text{CO}}$$

(2)

where $E_{\text{NTs+CO}}$ is the total energy of the system, E_{NTs} is the energy of nanotube prior to CO adsorption, and. E_{CO} is the total energy of a CO molecule in free space. Negative adsorption energy, E_{ads}< 0, means that the adsorption process is suitable. Obtained data show that the physisorption was occurred when the CO adsorbed through H site of AlN nanotube. Table 1





summarize results on the equilibrium tube-molecule distance, adsorption energy, HOMO, LUMO, and gap energy for adsorption of CO molecules on the AlN nanotube.

Configuration	site	r _e (Å)	E _{ads} (ev)	HOMO(ev)	LUMO(ev)	Band gap (ev)
C-down	Al	2.16	-0.57	-4.876	-4.358	0.518
	Ν	3.42	-0.17	-4.887	-4.381	0.505
0 down	Al	2.51	-0.26	-4.877	-4.360	0.516
O-down	Ν	3.58	-0.14	-4.887	-4.377	0.510
	Н	3.65	-0.58	-4.875	-4.358	0.516

Conclusion:

The results indicate that CO molecule can be adsorbed at the H site in the AlNNTs and aluminum nitride can serve as efficient sensors for detecting the presence of CO molecules.

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Synthesis and investigation the catalytic behavior of ZnO nanoparticles

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Key words: Synthesis, Catalytic behavior, ZnO, Nanoparticles

Introduction:

Among inorganic nanoparticles, ZnO nanoparticles have received great attention because of their unique catalytic, electrical, electronic and optical properties as well as their low cost and extensive applications in diverse areas. The direct wide band gap (3.3 eV at 300 K) makes ZnO one of the most promising candidates for application in ultraviolet optoelectronics devices, and also has been applied in the fields of gas sensors, varistors, piezoelectric devices, and photodiodes [1]. Normally, ZnO is prepared by techniques, such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) [2], spray pyrolysis [3], pulsed laser deposition (PLD), and hydrothermal synthesis [4]. These ZnO processes are complicated; they not only have huge energy consumption, but also bring serious environmental pollutions.

In this study, we have developed a simple and green method for synthesis of nano-sized ZnO particles using emulsion route, we report the synthesis of ZnO particles using some alter-Native materials, which were different from those used in literatures. The products are characterized with SEM and XRD.

Materials and methods:

Nanoparticles were synthesized by the following steps: 0.30 g of nitrate salt in 1 mL of water and 4% Tween 80 were added into 30 mL of purified soybean oil under mechanical stirrer with 2000 RPM until obtaining a nearly clear emulsion. this solution was referred to





as solution A. 0.16 g of NaOH was dissolved into 3.5 mL of water was added into solution A under mechanical stirrer with 2000 RPM for 4 h at 20-25 °C and then the reaction mixture was filtrated. The precipitates were washed and dried under vacuum at 120 °C for 16 h.

Apparatus:

The powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu K α radiation ($\lambda = 1.54056$ Å) with a MINIPROP detector and operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded between 2 $\theta = 5^{\circ}$ and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting ZnO powders were collected by using the PC-APD, Diffraction software Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, PHILIP XL-30).

Result and discussion:

Fig. 1 shows SEM images of ZnO powders calcined at 120 C° with diameters ranging from 40 nm to 70 nm.



Fig. 1: SEM image of the ZnO nanoparticles.

Conclusion:

The synthesis of nano ZnO were carried out with the concurrent addition of sodium hydroxide and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. This is a multi-step process that involves the transformation of





the nitrate salt of metal to an metal hydroxide M(OH)n followed by the dehydration to form an oxo-hydroxide intermediate, that will constitute the precursor in the sol–gel process.

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Correlation between the theoretical chemical concept of electrophilicity index for fullerene derivatives as acceptors and open-circuit voltage in polymer-fullerene solar cells

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Keywords: Organic solar cells, Fullerene, Electrophylicity, LUMO, DFT, Open-circuit voltage.

Introduction:

Fullerene derivatives with inherent high electron affinity and being able to transport charges effectively introduce an intriguing acceptor for organic solar cells. The power conversion efficiency (PCE) of the PSCs based on a blend of poly(3-hexylthiophene) (P3HT) as an electron donor and PCBM, the most popular fullerene derivatives as acceptors , has reached over 4% [1]. To further improve the PCE, designing new fullerene acceptors has been in priority of many researchers' surveys. PCE is directly proportional to the short-circuit current (I_{SC}) and the open-circuit voltage (V_{OC}) [2]. In a polymer-fullerene solar cell, merely a little improvement of I_{SC} is possible while there are still several considerable paths for improving the V_{OC}. Meanwhile, according to surveys, the efficiency of fullerene as an acceptor in solar cell depends not only on its electron affinity in order to effectively absorb the electron from the adjacent donor molecule, but also on its resistance against electron back transfer to donor molecule (to prevent the losing process of the resulted electron–hole pairs). In this respect, we propose a linear relationship based on electrophilicity index, which has been examined on three series of fullerene derivatives already used in fabrication of polymer-fullerene solar cells.

Computational Aspects:

All density functional theory (DFT) calculations are performed using Gaussian 98 program package at the level of B3LYP/6-31G*. The energies of ionic states ($E(M^+)$ and $E(M^-)$) by





adding/removing one electron to/from the neutral molecule are also calculated at the same level, using the optimized geometry of the neutral form.

Result and Discussion:

A global index for the electrophilicity strength of a system have been already defined by Parr et al. in terms of quantitative chemical concepts in DFT, including the electronic chemical potential (μ) and hardness (η) [5]. Such quantity can be assigned as the electrophilic competence of a system by applying μ as reliable factor for measuring propensity of the system to acquire an additional electron from adjacent electron-rich species, and simultaneously using η for describing the resistance of the system to exchange electron with the environment. Therefore ω is calculated for the molecules using $\omega = \mu^2/2\eta$; $\mu = -(IP+EA)/2$; $\eta = IP - EA$, and the corresponding V_{OC} [2-4] is plotted vs. the calculated ω . Minor deviations from linearity may be referred to the fact that the electrophilicity is calculated for isolated molecules in gas phase while the V_{OC} is measured in solid state devices. These empirical equations also may be applied to predict the possible open-circuit voltage of a BHJ solar cell based on a new acceptor fullerene. Altogether, ω values seem to yield better linear correlation with V_{OC} compared to the relation obtained for LUMO energy levels or EA values.



Fig.1. Optimized structures



Fig. 2. Calculated ω vs. experimentally reported V_{OC}





Conclusion:

The key point of the present survey is achieving a significant linear correlation between the electrophilicity index calculated for the fullerene derivatives and the corresponding opencircuit voltage of the photovoltaic device. This index is a prominent feature in determining tendency of the fullerene derivative towards acquiring an additional electron from the adjacent electron-rich donor molecule, and also its resistance to the electron back transfer.

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Osteoinduction of Mesenchymal Stem Cell in nano bioactive glass scaffold implanted over rat Calvaria

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Key words: Mesenchymal stem cells, nano bioactive glass, scaffold, rat Calvaria

Introduction:

The repair of large segmental bone defects due to trauma, inflammation and tumor surgery remains a major clinical problem. There have been several attempts to combine bioactive glasses (BaGs) with biodegradable polymers to create a scaffold material with excellent biocompatibility, bioactivity, biodegradability and toughness .Mesenchymal stem cells (MSCs) are defined as non-hematopoietic cells that are able to replicate for a long time while maintaining their multilineage differentiation potential[1-3].

Materials & Methods:

Rat MSCs were isolated from the femurs of rats. The bone marrow suspensions were cultured in the DMEM medium. BG Nano-powders were synthesized and Gelatin / Bioactive glass nano-composite scaffold was made through Sol-Gel and crosslinked by glutaraldehide treatment. The BG scaffolds were sterilized, to observe the cytotoxic effects of the BG scaffolds on rMSCs in vitro. The proliferation medium of the cultures will be replaced by osteogenic medium. Occurrence of differentiation will be examined by alizarin red staining. Differentiated rMSCs seeded into scaffolds. Two bilateral full thickness defects created in the calvarium of rats. The defects will be filled by nano bioglass scaffolds enhanced with differentiated rMSCs. Evaluation will be performed using histology.





Results:

Cellular toxicity test results revealed that BG scaffolds has no toxicity. Following alizarin red staining, red mineralizing areas of cultures appeared and revealed that those cells differentiated to osteogenic cells.

Conclusion:

This research studies have been shown that Nano bioglass scaffold could support MSC proliferation and differentiation in vitro. The present study demonstrates that rMSCs enable bone reconstruction of Calvarial defects in an allogenic transplantation model by nano bioglass scaffolds.

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Biocompatibility and Antibacterial Activity of Nanosilver enhanced PLGA Conduits for Peripheral Nerve Repair

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Keywords: PLGA, Biocompatibility, Antibacterial Activity, Nanosilver, Nerve repair.

Introduction:

Peripheral nerve injuries are frequently caused by trauma and may lead to a significant loss of sensory or motor functions. The proximal end of the nerve fiber sends out sprouts toward the distal end [1-3]. Conduits made of different polymers have been developed to regenerate a nerve gap wider than 10 mm [4, 5]. Polyester scaffolds for tissue-engineering be either manufactured aseptically or sterilized must after processing. Biodegradable and suitable mechanical property of PLGA due to its excellent biocompatibility, have been extensively used in tissue engineering [6]. For it was considered to promote cell proliferation and tissue healing. Silver nanoparticles exert their antibacterial activity by interacting with the sulfur containing proteins present in bacterial cell membrane as well as with phosphorus containing DNA [7].

Materials and Methods:

PLGA solution was pepared in 1,4-dioxane. The tootings were dipped in polymer solution and immersed in 2-propanol as a nonsolvent. After washing with deionised water, conduits were soaked in colloidal nanosilver for enriching the conduit surface.





Result and discussion:

SEM in combination with EDX (Energy Dispersive X-Ray spectroscopy) was used to describe the distribution of porosities and also find out which elements. Fourier Transform Infrared Spectroscopy (FT- IR) was carried out to get information about the binding groups between the compositions. MTT [3-(4, 5-Dimethylthiazole-2-yl)-2, 5-diphenyl tetrazolium] assay was used to quantify the live cells.

Conclusion:

This survey is for fabricating a channel that is bridging the gaps for making contact between two ends of nerve.Using PLGA with nanosilver for making a porous channel is not only for repairing the injured nerve but because of nanosilver can make a good place without bacteria for growing axons along.

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Preparation and characterisation of nickel nanoparticles grow on bee wax

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Key words: Bee wax; Nickel nanoparticle; Phosphoric acid fuel cell; Electrocatalyst.

Introduction:

Selecting of suitable electrocatalyst as electrode, increases fuel cell performance [1]. We have studied possibility of use of nickel nanoparticles (NNP) as anode, in phosphoric acid fuel cell (PAFC); this can affect on decreasing fuel cell construction and maintenance prices [2-4]. In this work, we describe NNP production due to electroless plating on activated nonconductive substrate (natural Bee-Wax). We used bee wax due to it could be locally activated; this points can act as nucleation centres. Another reason to use of bee wax confuse to its easily thermal removal from NNP [5, 6].

Materials and methods:

The main compound in bee wax, palmitate melissiyl ($C_{15}H_{31}CO-OC_{30}H_{61}$), purified by multistage fusion, precipitation and freezing. FT-IR spectrum denote to purification also presence of esteric functional group. This sample of bee wax melts at 70°C. A mixture of HNO₃/H₂SO₄ (1:2.5) at room temperature for a 10 minute delay activates the bee wax surface.

Result and discussion:

We chose alkaline electroless deposition baths, because they act at lower temperatures and product impurities.We examined much bathes based on Hydrazine, Diborane and Hypophosphite. Finally, hypophosphite based bath accepted. Produced NNPs separated and





characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM showed that NNPs grow cluster shape. XRD spectrum determined grain size using scherrer equation equal to 3.14 nm. XRD spectrum also showed that produced NNP included crystalline structures. This can express to that soft layer of bee wax don't forced to growing NNP and it can freely crystallized.





Conclusion:

Our studies on cell performance and its behaviors show that Ni nanoparticles can substitute on platinum as anode in fuel cells. These particles increased power efficiency up to1473%.

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Voltammetric Determination of Phenol Based on Ni-Cr-Al LDH Film Modified Glassy Carbon Electrode

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Keywords: sensor, phenol, LDH, Cyclic voltammetry

Introduction:

The Ni-Cr-Al LDH film modified glassy carbon electrode (GCE) was fabricated and used to determine phenol. Ni–Cr-Al layered double hydroxide was synthesized by the co-precipitation method.[1] Layered double hydroxides (LDHs) constitute a family of lamellar solids characterized [2-3] by the general formula $[M_{1_x}^{II}M_x^{III}(OH)_2][A_{x/n}^{n}-.mH_2O]$.

Experimental:

For the synthesis of Ni-Cr-Al-Cl LDH a solution of 0.45 m mol NiCl₂ .6 H₂o and 0.09 m mol CrCl₃ .9 H₂O and 0.06 AlCl₃ with a Ni²⁺/Cr³⁺/Al³⁺molar ratio of 3:0.6:0.4 in 50 ml mixture of H₂O and 2-propanol and Ethylene glycol. This reaction was carried out in hydrothermal conditions in the furnace for 24 hours at 120 °.The pure Ni-Cr-Al-Cl LDH powder was obtained by washing the precipitate with distilled water and drying in vacuum for 2 days at 40° C. After a pretreated GC electrode of 2 mm diameter was rinsed with carbondioxide- free water, and dried at room temperature. The Ni/Cr/Al-LDH suspension was prepared by dispersing powder in deionized water at a concentration with 2 mg.ml⁻¹ by stirring for 24 h. A defined amount of the aqueous mixture was spread on the surface of the GCE. The coating was then dried at 4°C in a refrigerator.





Results and discussion:

The powder X-ray diffraction (XRD) patterns were recorded(Fig.1). The Transmission electron microscopy (TEM) images were taken(Fig.2). To design a convenient approach for routine analysis, electrochemical methods have been employed for phenol sensing because of fast response, safer procedure and simple use.



Fig. 1. XRD patterns of samples prepared

Fig. 2. TEM images for the Ni-Cr-Al-LDH

Figure 3 gives the typical CVs of LDH/GC electrode in0.1 M NaOH with scan rates of 50–240 mV s⁻¹. As shown in Fig. 4, when phenol was added to 0.1 M NaOH, an increase in the I_a .





Fig.3. Cyclic voltammograms of LDH/GC electrode in 0.1 mol L-1 NaOH at different scan rates. The selected scan rates are a 50, b 100, c 140, d 160, e 180, f 200, g 240

Fig. 4. Cyclic voltammograms of LDH/GC electrode in 0.1 M NaOH containing a 0 mM, b 0.01mM ,c 0.05 mM and d 0.1 mM phenol. Scan rate, 50 mV s-1

Conclusions:

The prepared film was characterized by means of CV, and the results indicated that the Ni centers in the LDHs had high electroactivity in 0.1 M NaOH., the LDH/GC electrode could be used for electrochemical nonenzymatic phenol concentration determination and exhibited





many desirable properties such as high sensitivity, low detection limit, good reproducibility, long-term stability, fast current response, and low interference.

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Electrochemical detection of Glucose on a Ni/Cr LDH modified electrode

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Keywords: sensor, glucose, LDH, Cyclic voltammetry

Introduction:

In this paper a Ni/Cr layered double hydroxide (LDH) was first synthesized and was used to modify a GC electrode. The LDH/GC modified electrode can be directly used as the working electrode of a nonenzymatic glucose sensor. The electrochemical response of the electrodes was characterized in solution. Cyclic voltammetry (CV) technique was employed. The LDH/GC electrode could be used for electrochemical nonenzymatic glucose low detection limit, good reproducibility, long-term stability, fast current response, and low interference. In recent years, layered double hydroxides (LDH), also known as anionic or hydrotalcite-like clays, have growing interest for using in the wide fields owing to their attracted desirable properties, which include good biocompatibility[1], intense adsorbability [2], high catalytic activity, low cost, and high chemical stability [3].

Experimental:

The Ni- Cr LDH were prepared by co-precipitation method. For the synthesis of Ni-Cr-Cl LDH a solution of 0.45 m mol NiCl₂ .6 H₂o and 0.15 m mol CrCl₃ .9 H₂O with a Ni²⁺/Cr³⁺ molar ratio of 3:1 in 50 ml mixture of H₂O and 2-propanol and Ethylene glycol. Resulting solution was added drop wise to a solution of 0.01 N NaOH for adjusting pH=9.5. After keeping stirring the solution at 60 \degree C for 24 h, the pure Ni-Cr-Cl LDH powder was obtained by washing the precipitate with distilled water and drying in vacuum for 2 days at 40 \degree C. The





Ni/Cr-LDH suspension was prepared by dispersing powder in deionized water at a concentration with 2 mg.ml⁻¹ by stirring for 24 h. A defined amount of the aqueous mixture was spread on the surface of the GCE. The coating was then dried at 4 $^{\circ}$ C in a refrigerator.

Results and discussion:

The powder X-ray diffraction (XRD) patterns were recorded(Figure 1). The Transmission electron microscopy (TEM) images were taken(Figure 2).



Fig. 1. XRD patterns of samples prepared



Fig. 2. TEM images for the Ni-Cr -LDH

After a pretreated GC electrode of 2 mm diameter was rinsed with carbondioxide- free water, and dried at room temperature. Figure 3 gives the typical CVs of LDH/GC electrode in0.1 M NaOH with scan rates of $50-240 \text{ mV s}^{-1}$.





Fig.3. Cyclic voltammograms of LDH/GC electrode in 0.1 mol L-1 NaOH at different scan rates. The selected scan rates are a 50, b 100, c 140, d 160, e 180, f 200, g 240

Fig. 4. Cyclic voltammograms of LDH/GC electrode in 0.1 M NaOH containing a 0 mM, b 0.05mM ,c 0.1 mM d 0.5 and e 1 mM glucose. Scan rate, 50 mV s-1

As shown in Fig. 4, when glucose was added to 0.1 M NaOH, an increase in the Ia.





Conclusions:

In this work, a novel nonenzymatic glucose sensor based on Ni/Cr LDH modified electrode was fabricated. Electro- chemical behaviors of glucose on the LDH/GC were investigated by cyclic voltammetry. The low-cost electrode possesses many desirable properties such as high sensitivity, fast response, wide linear concentration range.

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SnSNanocrystalline Thin Films:Compositional, Structuraland Opticalproperties

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Keywords :Nanostructures, SnS Thin films, CBD

Introduction:

The recent investigations in the field of photovoltaic are directed towards the development of cost effective and nontoxic materials that can be synthesized by a simple technology for solar cell fabrication [1]. Tin sulphide (SnS) has a near optimum energy band gap, additionally SnS has the advantage of its constituent elements being abundant in nature and not posing any health and environmental hazards. Therefore, SnS can be potentially used as a solar absorber in a thin film solar cell and near-infrared detector, as photovoltaic materials [2,3]. In this paper we report the successful deposition of nanostructured SnS thin films at 25 and 50 °C and investigate the principal characteristics of these films.

Experimental:

The deposition bath was prepared by transferring 10 ml of 0.1M Sn(II) to a 100 ml beaker, followed by the sequential addition of 15 ml 3.7 M triethanolamine, 16 ml 15 M ammonia, 10 ml 0.1 M thioacetamide and distilled water. The glass slides were immersed in bath solution. The deposition was carried out at 25 and 50 °C for 6 h and 2:30 h, respectively. Five consecutive deposits were made to achieve the nanostructured SnS thin films that these films had high thickness and absorbance.





Results and discussion:

Considering the fact that the CBD method is usually carried out at near ambient temperatures (~25-80 °C), so the two temperatures of 25 and 50 °C are chosen to investigate the effect of temperature on structure, thickness and absorbance of nanostructured SnS thin films. Fig.1 shows the transmittance and reflectance spectra for the films grew at 25 and 50 °C. The band gap energy of these films were calculated using the procedure given by plotting $(ahv)^2$ against hv. These results show that, with an increase in deposition temperature, the thickness of films increases but the band gap energy decreases.



Fig. 1: Optical transmittance and reflectance spectra of SnS thin films deposited at various temperatures: (Left) 25, and (Right) 50 °C as a function of the deposition times.

Despite the high thickness of nanostructured SnS thin films; these films had the band gap energy more than the previous works. The films grown at 25 and 50 °C had high transmittance about of 78% and 35%, respectively.X-ray diffraction (XRD) data obtained by scanning 20 in the range 20-80°, with a grazing angle equal to 1.5° for the deposited SnS film on the glass substrate. The thickness of the film was about 420 nm. The four broad peaks observed in the diffractogram at around 26.2°, 31.45°, 51.25°, and 64.4° reveal an orthorhombic lattice structure of SnS. These peaks can be assigned to the planes (120), (111), (151), and (251), respectively, of the orthorhombic phase.

Figs. 2 show SEM images of the SnS thin films on the glass substrate at two different temperatures of 25 (Left) and 50 °C (Right). From Fig. 2 for the thin films deposited at 25 and 50 °C the following points are observable: (i) The grains formed at 25 °C are small of about 50-150 nm in size and are uniform. (ii) The SnS grains at 50 °C reveal some size categories of





100, and 250 nm; larger clusters of about 350 nm in size are formed; the clusters themselves are aggregate of grains.



Fig. 2: SEM images of SnS thin films deposited at 25 °C (Left) and at 50 °C (Right), respectively.

Conclusions:

Nanocrystalline tin sulfide (SnS) thin films were deposited on glass substrate at two deferent temperatures of 25 and 50 °C by a chemical solution deposition technique. Optical study is performed to calculate optical band gap (E_g) using transmission and reflection spectra in the wavelength range 300-900 nm. The band gap measured was found to be in the range of 2.2 - 3.15 eV. These SnS thin films possess a nanocrystalline structure, exhibit quantum size effects due to the small crystal size and produce a blue shift in the optical spectra. This blue shift was attributed to a decrease in crystal size by using X-ray diffraction and scanning electron microscopy.

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Study of Electrochemical Properties and Free Energies of Electron Transfer and Reduction Potential for fullerenes of C₂₀–C₃₆

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Abstract:

Since the discovery of the fullerene in 1985 [1] and up to now, spherical carbon clusters have been the focus of attention for a large number of scien_ tific groups performing experimental and theoretical investigations of these clusters. Already several tens of different fullerenes (including C_{70} , C_{36} , etc.) have been known to date. In 2000, Prinzbach et al. [2] revealed the smallest possible fullerene, namely, the C_{20} cluster in which the C–C bonds form only pentagons and which does not contain hexagons (unlike fullerenes with a larger size). At this stage, the C_{20} and C_{36} fullerenes transform into meta stable defect configurations with two adjacent "windows" on their surface, whereas a similar configuration of the C_{60} fullerene is unstable and corresponds to a saddle stationary point of the potential energy of the cluster. Calculations are 15 presented for the four reduction potentials (^{Red}.E) of fullerenes. The results were extended to calculate ΔG_{et} of ^{Red}.E for fullerenes C_{20} to C_{36} .

Keywords: Fullerenes, electrochemical behaviors, molecular modeling.

Introduction:

The unique stability of molecular allotropes, such as C_{20} - C_{36} , was demonstrated in 1985 (3, 4).

The main body of the paper the electrochemical properties of the C_{60} fullerene have been studied since the early 1990s when these materials first became available in macroscopic quantities (5, 6).





This study elaborates upon the relationship between the number of carbon atoms, the reduction potentials of fullerenes C_n , as assessed by applying the Rehm-Weller equation. The results were extended to calculate the free energies of electron transfer of the other supramolecular complexes and the reduction potentials for fullerenes C_{20} to C_{36} . This study calculated values for E_{red} for C_{20} to C_{36} and for the free energies of electron transfer. The electrochemical properties of the C60 fullerene have been studied since the early 1990s when these materials first became available in macroscopic quantities. Reduction of these films induces a morphological change; that is, they re-structure into conductive nanoclusters~100 nm in diameter (7, 8).

Graph theory has been a useful tool in assessing the (Quantitative Structure Activity 70 Relationship (QSAR) and Quantitative Structure Property Relationship (QSPR) (9, 10).

Numerous studies in these areas have used topological indices (TI) It is important to use effective mathematical methods to make good correlations between several properties of chemicals. In 1993 and 1997, several complex applications of the Wiener and Harary indices in fullerene science were reported. The numbers of carbon atoms in the fullerenes were utilized here.

Experimental (Modeling):

All graphs were generated using Microsoft Office Excel 2003. By knowing the amount of carbon atoms contained

Within the Cn fullerenes, several valuable properties of the fullerenes can be calculated. The values were used to calculate reduction potentials (E_{red}) and the free energies of electron transfer (ΔG_{et}), according to the Rehm-Weller equation for supramolecular Cn complexes.

Both linear (Multiple Linear Regressions, MLR) and nonlinear (Artificial Neural Network, ANN) models were used in this study. Equations 1 (presented below) were utilized to calculate the remaining values E_{Red} and ΔG_{et} that have 100 not been reported in the literature. Some of the other indices were examined, and the best results and equations for extending the physicochemical data were chosen.





The ET equation estimates the free energy change between an electron donor (D) and an acceptor (A) as:

$$\Delta G_{et} = -0.0234 (n)^2 + 2.9098(n) - 48.130$$
(1)
$$\Delta G_{et} = -nFE$$
(2)

By using equations (1–2), it is possible to calculate the values of Δ Get of C₂₀ to C₃₆.

Table 1 contains the calculated values of the free energies of electron transfer (Δ Get in kcal mol⁻¹) between the selected unsaturated Cn compounds supramolecular complexes. The Δ Get for C₂₀, C₂₄, C₃₆ predicted by using equations (1-2) and the Rehm-Weller equation (see Table 1). By utilizing these results and the Rehm-Weller equation, the reduction potentials (.E_{Red}) of fullerenes (C₂₀, C₂₄, C₃₆) were approximated (Table 1). The calculated values of the free electron transfer of Δ Get and the reduction potentials (E_{Red}) of the fullerenes considered in the ET equation and equations (1–2) are compared in Table 1. There was good agreement between the calculated and predicted values. Instead of the number of carbons atoms in the fullerene structure increasing, the values of Δ Get decreased. It seems that electron transfer increases as the electron population in the *Cn* structures increases. Table 1 indicates that the reduction potentials (E_{Red}) increased by increasing the number of carbon atoms in the fullerenes. Table 1 also shows that all of the free energy electron transfer values (Δ Get) of C₂₀ to C₃₆ are negative. Some of the supramolecular complex structures discussed here, the calculated values of Δ Get corresponding to these supramolecular complexes and the reduction potentials (^{Red}.E) for some of the fullerenes were neither synthesized nor reported previously.

Table1-Physical parameters calculated using the potential with the parameters represented by polynomials for C_{20} to C_{36} fullerites:

C _n	ΔG	Ev, eV
C ₂₀	0.706	-0.073
C ₂₄	8.2268	-0.85
C ₃₆	26.2964	-2.725





Results and Discussion:

The relative data of C_{20} - C_{36} are shown in Tables 1. Table 1show the calculated values of the free energies of electron transfer ΔG_{et} that were determined using the ET equation for C_{20} to C_{36} . The values are based on the reduction potentials E_{red} of fullerenes C_n and the reduction potentials (E_{red}) of the C_{20} to C_{36} .

The reduction potential values for C_{20} is -0.073 Volts, respectively. The reported reduction Potentials (E_{red}) of fullerenes C_n for C_{20} is -0. 073 V, The value of E_{red} for C_{24} is -0.85 V, respectively The value of E_{red} for C_{30} is V, respectively value of E_{red} for C_{36} is -2.752 V.

Conclusions:

These include the reduction potentials (E_{red}) of fullerenes C_n and the free energies of electron transfer (ΔG_{et}) calculated using the Rehm-Weller equation for C_{20} to C_{36} .

The Rehm-Weller equation was used to calculate the values of (ΔG_{et}) for fullerens. Using the number of carbon atoms (n) along with the equations of the model, one can derive sound structural relationships between the aforementioned physicochemical data.

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Coarse-grained computer simulation of nanoconfined water

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Introduction:

Investigating the properties of water confined between closely spaced surfaces is crucial in many physical situations, ranging from soil sciences to biology. In this respect, theoretical investigations have been performed to provide a molecular picture for explanation of the wide range of physical, chemical, biological, and geological processes. Among these, molecular dynamics (MD) simulations have extensively been used to study the properties of bulk as well as the confined water.

However, a severe limitation of the atomistic simulations is the computational cost in the case of relatively huge systems. A possible solution is the development of coarse grained (CG) models, in which several water molecules form a single super-molecule (bead), and thus decreasing the computational cost. In this work, we have employed the CG model of Riniker and van Gunsteren [1], in which five water molecules are grouped together to form a CG bead. The CG model of graphene surfaces is adopted from our previous simulation [2].

Method:

The method applied for the construction of CG potentials is the so-called iterative Boltzmann inversion method. Adopting a proper mapping scheme, in this method a reference simulation is done and all possible distributions are extracted from the results of such a reference simulation. Attempt is done to match the CG distributions to the corresponding reference ones by iteratively adjusting the CG potentials.

Results and Discussions:

In this work several nanoconined systems with various pore sizes are simulated. This enables us to study the effect of pore size on the properties of nanoconfined water. Moreover, the





transferability (with respect to the pore size) of the force field can be checked. To be able to compare the effect of confinement on the properties of nanoconfined water, we have further simulated a bulk sample of water. Finally we compare results such as water structure in the pore, solvation force, water diffusion in the pore, and local density fluctuations for reference and CG simulations of water confined between graphene surfaces. To have an example on the tuning of Cg and reference simulations, we have shown in Figure 1 a comparison of the reference and CG distributions (water-water and graphene-water radial distribution functions, RDFs). The perfect match of RDFs in Figure 1 shows that the developed CG potentials are able to generate a correct structure of water in the pore. The same force-field is applied in this work to simulate a number of confined systems with varieties of pore sizes. In all cases a perfect match of reference and CG RDFs is seen, verifying the construction of pore-size transferable CG potentials. The CG potentials are used to calculate a number of physical properties of confined water and the results are compared with the corresponding bulk properties (not shown here). A considerable slow down in water dynamics in the pore, compared to bulk water, is observed.



Figure 1. A comparison of water-water and water-graphene RDFs generated using reference (solid curve) and CG (dashed curves) simulations. Water-graphene RDFs are offset by 2.





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Complexation of C60 derivative as a carbonic anhydrase nanoscale enzyme inhibitor

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Keywords: Carbonic Anhydrase, Fullerene, Inhibitor, Complexation energy, QM calculation.

Introduction:

Several carbonic anhydrase (CA, EC 4.2.1.1) isoforms, Figure 1: A, are known to be present in the vertebrate central nervous system (CNS), being located in various cell populations, where they play a variety of functions. CAs are important targets for the design of novel pharmacological agents useful in the treatment or prevention of a variety of disorders, such as epilepsy and obesity. The inhibition and activation of CAs are also well understood processes, with most classes of inhibitors binding to the metal center [1, 2]. In recent years the nanomaterial fullerene C60 and its derivatives have been chosen to be investigated for their interactions with CAs as an inhibitor. presented study is an investigation of the complexes formed between active site of CA enzyme and the phenylalanine derivative of fullerene as a nanoscale inhibitor from three different positions, 1:N5, 2:N13 and 3:O12, Figure 1: B, by using of quantum mechanical calculations.



Figure 1. A: Chemical structure of carbonic anhydrase (CA) enzyme active site, B: phenylalanine derivative of fullerene as a nanoscale inhibitor.





Computational method:

Ab initio calculations were carried out with the Gaussian program series 2003. The optimization of the all geometries were fully optimized employing B3LYP methods using 6-31G* basis set. the binding energy (BE) and complexation energy (CE) are evaluated.

Results and discussion:

The results of calculations indicate that this special fullerene derivative could be deprotonated from three different positions and interacts with CA active site to form three CA-C60-Inh complexes. As the results indicates, substitution of anionic form of inhibitor in place of water molecule at the active center of CA enzyme is energetically exothermic, and binding of the inhibitor from N13 atom to the active center of CA is more favorable energetically, Figure 2.





Conclusion:

The nano scale inhibitor interacts from three positions with CA active center and tetrahedrally coordinated to the zinc ion of the enzyme. The results indicate that the CA-C60-Inh(N13), is the most favorable complex energetically.

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$Synthesis \ and \ characterization \ of \ nano \ powders \ of \\ Li_{(1-y)} \ Co_{(0/3)} Ni_{(0/4-x)} Mn_{(0/3)} Zn_{(x)} Mg_{(y)} O_2 \ cathode \ materials \ via \ sol-gel \ and \\ Freeze \ drying \ methods$

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Key words: Lithium-ion battery, Cathode materials, nano powders, Zn and Mg doped, Sol-Gel, Freeze drying.

Introduction:

Synthesis of positive active materials plays a major role in battery performance, especially with respect to capacity and shelf life. One approach to improve the electrochemical performance is to dope manganese cobalt nickel oxides for other metals, which may stabilize the layered structure with or without participating in the redox processes. In this study, nano powders of Mg and Zn-doped $Li_{(1-y)}Co_{0/3}Ni_{0/4-x}Mn_{0/3}Zn_xMg_yO_2(0/01 \le x \le 0/05 , 0/1 \le y \le 0/3)$ cathode materials were synthesized via for lithium batteries. Nano structure electrode materials have a stable cycling behavior during charge-discharge processing and also these materials have a better electrochemical property than micropowders. Zn-doping increase electronic conductivity and improve the high rate discharge capability and thermal stability. Mg stabilizes the layered structure and enhances the cycling stability. Various synthesis parameters such as calcinations time, temperature and acid to metal ions ratio were studied to determine the optimized condition for processing the cathode nano materials. Different techniques such as XRD, SEM were employed to characterize crystal structure, size and morphology and optimal condition of the powder. [1, 2]

Materials and Methods:





Stoichiometric amounts of lithium/cobalt/nickel/manganese/zinc/magnesium nitrate were dissolved in distilled water for starting solution. In Freeze drying method the solution was sprayed into liquid nitrogen. The frozen solution was placed in freeze dryer and the water was removed by sublimation. Then the powder was calcined. In Sol-Gel method citric acid play the role of chelating agent during the synthesis. Nitric acid was slowly added until PH=2. The dissolved solution was evaporated until a vicious transparent gel was obtained. The sol was heated until a gel was formed and subjected to further heat treatment.

Results and discussion:

X-Rey diffraction patterns showed a clear splitting of the hexagonal characteristic doublets (006)/(102) and (008)/(110). This indicated that the products possessed typical layered characteristics [1]. Results show that the best condition for synthesizing is at 800°c for 12 hours in sol-gel method and 800°c for 6 hours in Freeze drying. The ratio of the intensity of the (003) reflection to that of the (104) reflection for products was calculated. The maximum in the value for the ratio showed that at a x value of 0.04 and a y value of 0.1, the system exhibited the maximum hexagonal ordering [1]. The Reimers factor[3] (the (006/102) reflection to that of the (101) reflection) was calculated for the compounds synthesized using different acid to metal ion ratio (R), and was found to be the lowest for the compound synthesized with a ratio R=2. The Reimers factor decreases again with a further increase in the ratio R to 3. The SEM pictures demonstrate clearly different nanostructure of powders obtained from different precursors: particle size varies from 36-68 to 91-149.

Conclusion:

The powders had stable layered structure with a-NaFeO₂ type assuming a hexagonal lattice setting and the compounds of x=0/04, y=0/1 had the best layered structure. The hexagonal ordering of the synthesized compounds depends on the calcinations temperature and calcinations time and greatly depends on the acid to metal ion ratio. Solution-based synthesis methods are sensitive to PH which determines the formation of the compound as well as its





electrochemical performance. SEM indicated a homogeneous distribution of nano particles and these nanopowders have a better electrochemical property than micropowders.

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Synthesis of nano SBA-16 using extracted silica source of stem cane ash and its application for electrocatalytic oxidation of methanol

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Keywords: Mesoporous SBA-16, Electrooxidation, Methanol, Modified electrode, Stem cane ash

Introduction:

Among all SBA-type silica materials, silica-SBA-16 is recognized as one of the recently important mesomaterials for potential applications in various fields such as adsorption and catalysis applications [1]. In this work, SBA-16 nano structure was synthesized and characterized via applying pure SiO_2 powders extracted from stem cane as natural sources. Also, we prepared nickel-modified siliceous (SBA-16) carbon paste electrode to study the electrooxidation of methanol in alkaline solution.

Materials and methods:

SiO₂ powder was extracted from stem cane using Kalapathy et al method [2]. Nano SBA-16 was synthesized under hydrothermal treatment. Mesoporous silica (SBA-16) can be modified with Ni(II) ions. The modified electrode was prepared by incorporation of Ni(II)- mesoporous silica in carbon paste.

Apparatus:

X-ray diffraction (XRD) patterns were recorded on an Advance Bruker D8 X-ray diffractometer (Germany) using Cu K_{α} radiation (λ =1.5418°A). Electrochemical studies were performing by Dropsens, Bipotentiostat/Galvanostat (μ STAT 400).





Result and discussion:

All samples were prepared under hydrothermal synthesis at 100 °C for 24 h. The XRD pattern of the calcined SBA-16 powder was showed in Fig. 1. The average particle size was calculated to be 46.26 nm according to Scherer equation. Cyclic voltammetry of methanol on Ni/SBACPE was investigated. Results specified that the oxidation current of methanol on Ni/SBACPE was increased compared to the nickel modified carbon paste electrode (Ni/CPE) (Fig. 2).



Fig.1.XRD pattern of calcined SBA-16

Fig.2.Cyclic voltammogram of Ni/SBACPE (a) and Ni/CPE (b)

Conclusion:

In present work we have developed a facile approach to the synthesis of SBA-16 nanoparticles using low-cost prepared silica source of stem cane. The nickel modified SBA-16 was used to investigate the electro catalytic oxidation of methanol. Cyclic voltammetry of methanol on Ni/SBACPE showed that incorporation of Ni (II) on nano-sized mesoporous silica gives rise to increase oxidation current of methanol.

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Design and Measurement of novel Nanotube(6,6) and Calix[n]arene derivatives Thermodynamic Function as drug delivery by DFT

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Keywords: Calixarene, Drug delivery, Nanotube, Anticancer, DFT.

Introduction:

Calixarenes are a group of organic macrocyclic agents that have cup like shape which are easily available through the cyclocondensation of para-substituted phenols with formaldehyde. One way to increase the aqueous solubility of drugs is to use complexing agents to form hast- guest complexes [1-2]. Single-walled carbon nanotube (SWCNTs) is allotropes of carbon with a cylindrical nanostructure. The covalent attachment of chemical group to SWCNTs is very promising for the applications of drug delivery and gas sensing properties [3, 4]. Calixarenes are promising materials for nanomedicine application in drug delivery systems. For example hydrophilic derivatives have shown interesting levels of activity against bacteria, fungi, cancerous cells and enveloped viruses, but also against thrombosis or fibrosic diseases. These applications can be obtained from Natotubes, too. Because of the safe delivery of drugs in human body, in this paper ability of Calixarenes and Nanotube in transporting skin anticancer is compared.

Computational Method:

This investigation is carried out by a pc computer which has Intel (R) Pentium (R) Dual CPU with 2GB RAM. A Nanotube (6, 6)(composit1) Calix[6]arene(different sit, C-O, N-O; 2,3) Calix[4]arene (4) and p-sulfonato-calix[4]arene (5) including different atom number which





reacts with Fluorouracil drug. The drug delivery properties are investigation. Nanotube is formed by Nanotub Modeler package [5]. The DFT Calculations have been performed using the Gauss view [6] and Gaussian 09 [7] by B3LYP method and 6-31G (d) standard basis set. Then complex between Nanotube and derivations Calix[n]arenes with Fluorouracil drug are formed, optimized ΔG° and ΔH° by B3LYP/6-31G (d) method.

Result and discussion:

The ΔG° , ΔH° , gap energies and formation constant, ΣE^2 for five composites calculated with B3LYP method and 6-31G (d) basis set. For optimized and frequencies (1-5) composites were calculated. The obtained results are shown in undergo table.

Agent	ΔG°/	ΔH° /	Δ E °/	Formation	Gap of	$\sum E^2$
	KJmol ⁻¹	KJmol ⁻¹	KJmol-1	constant	energy/	
				(log K)	KJmol ⁻¹	
Composite1	-1.8185	-13.2804	-13.2752	0.3187	0.2923	47.55
Composite2	-141974.54	-141976.76	-141976.75	24869.76	0.6485	16.27
Composite3	-141990.62	-141992.92	-142115.78	24872.98	0.5545	23.53
Composit4	-141980.38	-141981.64	-141981.63	2471.01	0.6846	20.8
Composite5	-5.09166	-38.9006	-38.8979	0.8919	0.7874	53.63

Conclusion:

The composite (3) is more stable than other complexes. The ΔG° , ΔH° , ΔE° , in composite is more negative and it can be well reasonable for stability in it. The composite (3) are batter transport for drug delivery than other them. The different drugs delivery is shown in below.



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Preparation and Investigation of Nanostructured Zirconia

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Keywords: Nanostructure, Zirconia, Methylene blue, carbon paste electrode.

Introduction:

Today, zirconium oxide has found a wide range of applications from solid oxide fuel cells to catalysts and catalyst support to sensor and to ceramic biomaterials [1, 2]. Recent researches have focused on the making of the nanostructured zirconium oxide to improve its properties [3]. The objective of this work is the synthesis of nanostructured zirconia.

Materials and methods:

ZrOCl₂.8H₂O, ethylene glycol and NaOH purchased from Merck Company and used without any further purification. All solutions prepared using deionized water. Hydrated nanostructured zirconia was precipitated by adding a solution of NaOH to a solution of ZrOCl₂.8H₂O. The size of nanostructured zirconium oxide particles was optimized by controlling the temperature of solution and dielectric constant of solvent, which is set by adding ethylene glycol to the solution. Then, as-deposited materials dried at 100°C and calcinated at 600°C for 6 hours. Finally, the electrochemical behaviour of methylene blue on the surface of naostructured zirconia investigated using carbon paste electrode containing of paraffin, graphite and prepared nanozirconia.

Apparatus:





All electrochemical experiments were carried out via a standard three electrodes cell containing of an Ag/AgCl electrode, a platinum grid and a carbon paste electrode containing the appropriate amount of graphite and nanostructured zirconia as reference, auxiliary and working electrodes, respectively and using a Solartron Electrochemical interface SI1287 and Solartron Phase Gain Analyzer SI 1260. Surface morphological studies were carried out with scanning electron micrographs, obtained with a S4160 SEM (Hitachi, Japan). The crystal structure of the obtained materials was investigated by using of a Bruker, Advane D8 diffractometer with Cu-K radiation (=0.15404 nm).

Results and discussion:

The XRD pattern analysis showed that two different phases, tetragonal and monoclinic zirconia, obtained by changing the electrolyte from water to mixture of water and ethylene glycol, Fig 1.



Fig 1: XRD patterns of nanostructured ZrO₂ prepared in a) water (tetragonal) and b) water+ethylene glycol (monoclinic).

SEM results verified the existence of nanparticulate structure for prepared zirconia. The cyclic voltammetry studies showed a couple redox peaks with the same height emphasizing on the good reversibility of reduction methylene blue on the surface of nanozirconia. Also, comparing the cyclic voltammograms in different potential scan rates corroborated a diffusion nature for this phenomenon.

Conclusion:





The precipitation method is a useful and controllable method for making nanostructured zirconia and factors like precipitation temperature and dielectric constant of the electrolyte have a key role in this manner. Also, the oxidation/reduction of methylene blue on the surface nanozirconia is reversible.

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Synthesis of mesoporous SBA-15 nanoparticles using stem sweep ash silica for adsorption kinetics of the cationic dye, Azure B, from aqueous solution

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Key words: SBA-15 nanoparticles, stem sweep, silica, cationic dye, Azure B

Introduction:

In this study, the application of Synthesized mesoporous SBA-15 nanoparticles from stem sweep ash (SSA) silica for adsorption kinetics of the cationic dye from aqueous solution were inverstigated. silica was extracted from SSA with approximately 80% purity. The present study used stem sweep, which is an agricultural waste, as silica source for mesoporous SBA-15 nanoparticles. The synthesized SBA-15 nanoparticles are rod-like shapes with average diameter of 82 nm and length in the range of 50-250 nm. Finally in this work, adsorption kinetics of a cationic dye, Azure B, from aqueous solution were evaluated with respect to initial dye concentration, temperature, pH, mixing rate and sorbent dosage .

Materials and methods:

phosphoric acid, silica gel, sodium hydroxide, Stem Sweep Ash as source silica, Triblock copolymer P123 and Azure B dye was supplied .In a typical synthesis, Copolymer p123 was dissolved in acidic solution. Alkaline sodium silicate solution was quickly added to this mixture added to the above solution and excess water was added to make up the solution to 80 ml. synthesized gel was in an oil. products were filtrated, washed with distilled water, and dried in an oven. Subsequently the sample was calcined. After the process, SBA-15 nanoparticles which was a white powder was obtained. The dye solution was prepared from Azure B with wavelengths of maximum absorbance was 648nm.





Apparatus:

The physical properties of synthesized mesoporous SBA-15 nanoparticles were characterized by XRD, SEM, TEM, FT-IR, BET/BJH and TGA.

Result and discussion:

adsorption kinetics of a cationic dye, Azure B, from aqueous solution were evaluated with respect to initial dye concentration, temperature, pH, mixing rate and sorbent dosage.. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. The Langmuir model agreed very well with experimental data (R^2 > 0.92). The kinetics of adsorption, the Azure B color value and decolorization efficiency for different initial dye concentrations were evaluated by the pseudo first-order and second-order models. The data agreed very well with the pseudo second-order kinetic model. Kinetic studies indicate that adsorption is an endothermic process.

Conclusions:

In this work, mesoporous SBA-15 nanoparticles was prepared from SSA with sol-gel method. The Langmuir and Freundlich adsorption models were applied to the adsorption data of Azure B onto mesoporous SBA-15 nanoparticles. It was found that the amount adsorbed of Azure B increases with decreasing temperature and also with increasing both sorbent dosage and increasing initial dye concentration. The adsorption capacity increased with increasing solution pH The Langmuir isotherm was the best model to describe the experimental data. Sorption kinetic data revealed that the adsorption kinetics followed the pseudo second order equation for Azure B dyes investigated in this work. Thermodynamic analysis shows that the adsorption of dye is an endothermic process.

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Hand Henrichten





Phosphatide adsorption from the neutralized soybean oil by bleaching earth modified whit nanoclay

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Keywords: Nanoclay, Bleaching earth, Phosphatide, Adsorption, Soybean oil

Introduction:

Clays are widely applied in many fields such as polymernano-composites , adsorbents for heavy metal ions ,catalysts, photochemical reaction fields , ceramics ,paper filling and coating , sensors and biosensors , due to their high specific surface area, chemical and mechanical stabilities, and a variety of surface and structural properties [1-3]. The nanoclay could easily have a sorption capacity of more than 600 mg sorbate per gram of sorbent at a liquor-to-sorbent ratio of 100:1. Furthermore, it could have a sorption of 90% at an initial dye concentration of 6 g/L, or 60% based on the weight of the sorbent, indicating an extremely high dye affinity [4]. In this study; the effect of nanoclay particles on practical properties of vegetable oil bleaching was investigated.

Method:

Bleaching procedure carried out by AOCS method (Cc-8f-91). The PH and acidity of earth samples carried out by AOCS method (Cc-8f-91). Dye analysis of vegetable oil carried out by AOCS method (Cc-13c-50) and Lovibond PFX-j. The content of phosphatide in vegetable oil mastered by AOCS method (Ca12-55). The content of soap in oil mastered by Analysis British Standard.





Result and discussion:

Whit increasing concentration of nanoparticles in bleaching earth the density of this composite (nanoclay and bleaching earth) reduce and adsorption of red dye and phosphatide in bleaching presses of soybean oil will better. Phosphatide, soap, heavy metals and dye in vegetable oil for adsorption on the bleaching earth surface rival together as if one of this compounds adsorbed to bleaching earth surface the capacity of earth for adsorption of other will reduce. The result obtained show when that Phosphatide, soap adsorped other compound adsorpe poorly. In this study the bleaching earth modified whit nanoclay Closite Na+ have better effect on the phosphatide adsorption. The result in 4 formulations was dramatically because that phosphatide content in oil reduces to zero.

Conclusion:

This work establishes nano particles may prove useful for bleaching stage of vegetable oil . We consider two different nanoclay structures for bleaching soybean oil .the result show that adsorption of phosphatide red dye improved by using nanoclay Comparison of the values of phosphatide red dye in bleached oil obtained using nanoparticles shows superiority of the nanoclay composite whit bleaching earth over the bleaching earth. We have shown that nanoclay, are able to decrees the phosphatide of naturalized soybean oil dramatically .Obtained result indicated that PH, moisture and acidity of bleaching earth have important role in bleaching presses. By focusing on the role of the PH, we realized that the selection optimum PH is important in the performance of the bleaching presses. The main conclusion of this study is that nanoparticles are a reliable material for the adsorption of compounds in vegetable oil.

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Effect of the Au Catalyst on Growth of Carbon Nanostructures with Methanol via HFCVD

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Keywords: HFCVD, CNT, CNW, Methanol, Ethanol, Propanol.

Introduction:

Since their first discovery in 1991 carbon nanotubes (CNTs) have been synthesized by three main methods: arc discharge, laser ablation and chemical vapor deposition (CVD) [1]. Excellent mechanical, electrical and surface properties of CNTs make them ideal candidates for a wide range of applications such as structural materials [2], sensors [3], field emission displays [4] and hydrogen storage materials [5]. The influence of the process parameters by HFCVD on the growth of CNTs having specific properties that being the process strongly influenced by the system geometry (local kinetic, gas flow and gas temperature). Using alcohol sources is one of the most attractive methods for the SWCNTs growth by HFCVD.

Materials and methods:

In this research, Si p-type used as substrates and coated with Au thin film as catalyst . Methanol was used as carbon sources to growth of carbon nanostructures by HFCVD system. Analysis of nanostructures was characterized by field emission scanning electron microscopy (FESEM) and Raman spectroscopy. In this manner, Au nanolayer was deposited on the substrates as a catalyst by a direct current sputtering system. Thicknesses of the Au nanolayer that were deposited on the substrates was 13 nm. The surface morphologies of the Au thin films were observed by using the AFM (AFM Park scientific Instruments Auto Probe CP).





Thin film thicknesses were measured by using the Rutherford Back Scattering (RBS) technique. AFM micrographs of these thin films were shown in the Figure 1. Ar gas was bubbled into the alcohol chamber with 100 standard cubic centimeters per minute (sccm) flow rate. Then Ar gas with the alcohol vapor was introduced from the top of the chamber. Therefore, a combination of H_2/CH_3OH was fed into the reaction chamber and the pressure of the reaction chamber set at 15 torr. The carbon nanostructures obtained by using this technique that were analyzed using FESEM (Hitachi model S4160) and Raman spectroscopy (Thermo Nicolet-sccond harmonic with 532 nm of a Nd:YLF laser).

Result and discussion:

The carbon nanowalls were obtained by using the Au nanolayer as the catalyst. It can be noticed that agglomeration takes place during the CNWs growth. Based on the analysis of a series of FESEM images, it can be concluded that near 100% of the catalyst coated surface give rise to CNWs growth. Also, it is clear that the thickness of CNWs that were grown on the substrate is less than 60 nm. In addition, these CNWs have low length and the carbon nanowalls are not well crystallized. Finally, as clearly seen from the FESEM image at the Figure 2. The some of the CNWs collected and obtained a colony on CNWs and were distributed on the surface. But on other place of the substrate surface CNWs were located on the Au nanolayer.

Additionally, the microscopic evidence of the formation of CNWs is supported by their Raman spectra in which the G band at 1596 cm⁻¹ with D band around 1300 cm⁻¹. IG/ID ratio in this Raman spectrum for these CNWs was 0.7. In the other hand, both of the bands (G and D bands) have a wide FWHM that is shown the growth of the multilayer carbon nanowalls and with a low crystallic in this method. Calculation of the crystallite size by L_a 44/(ID/IG) formula is calculated that L_a was 28.9.







Figure 1. AFM micrograph of Au nanolayer as a catalyst after etching.Figure 2. FESEM images of the carbon nanotubes from alcohol source by HFCVD technique.

Conclusion:

We propose new carbon source for the growth of CNWs and CNTs. In this study methanol were used as a carbon source to growth of carbon nanostructures on the Au coated substrates by HFCVD. In the other hand, H_2 gas was used as etching gas. Using methanol as carbon source caused to growth of the CNWs is non-uniformly and low crystallite. Thicknesses of these CNWs are less than 60 nm and it can be noticed that agglomeration takes place during the CNWs growth.

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Photocatalytic degradation of congored under UV and Visible light using Mo and S codoped TiO₂ nanoparticles.

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Keywords : Codoped TiO₂, Photocatalytic activity, Nanoparticle, Mo doped TiO₂

Introduction:

Dyes are one of main sources of water pollutants existing in our environment. For water purification treatment various technologies are in use[3]. Titanium dioxide is a very active photocatalyst, physical and chemical stability, inexpensive and of low biological toxicity[1,2]. The different morphologies of TiO_2 nanoparticles is used as photocatalyst. Heterogeneous photocatalysis by TiO_2 semiconductors is promising for elimination of hazardous environmental pollutants in air and water [3,4]. In recent years, many experimental and research studied have been conducted to improve the photocatalytic activity of TiO_2 , this paper follows this purpose.

Materials and method:

In this expremental have been applied TTIP as precursors of TiO2 nano particle and Ammunium hepta molibdate tetra hydrate as precursors of Mo and Thiourea as precursors of S. Mo by photochemical method and S by sol-gel method codoped TiO_2 and improve photocatalytic activity of TiO_2 .

Apparatus:





Uv and Vis lamp have been applied for degradation of Congored and centrifuge have been applied for filtering nanoparticles from dye solution for spectroscopy ,UV/VIS spectrometer hav been applied for determinating percent of degradation,ulterasonic have been applied for dispersing of nanoparticles in dye solution.

Result and discussion:

The samples are fabricated with different percents of Mo and S. Degradation of congored as a pollution was investigated by this samples and selected the best sample based on the time of degradation and this sample had the better results than pure TiO_2 . The samples characterized by X-ray diffraction (XRD),UV-visible spectroscopy and scanning electron microscopy (SEM).

Conclusion:

The Band Gap (\approx 3.2 eV)) of pure TiO₂ nanoparticles for transition of electron is more supplied by UV light rather than visible light, Many techniques have been examined to achieve the extend of the absorption wavelength range of TiO₂ in visible region[4],for this work,up to now only,Mo doped TiO₂ for decreasing of this distance[1,2],but we did Mo and S codoped TiO₂, doping of various transitional metal ions into TiO₂ could shift its optical absorption edge from UV to visible light range, but a prominent change in TiO₂ band gap was not observed. This red shift in metaldoped TiO₂ was attributed to the charge-transfer transition between the d electrons of the dopant and the CB (or VB) of TiO₂, and recently, C, N, S, F, B anion-doped TiO₂ photocatalysts which show a relatively high level of activity under visible-light irradiation have been reported [4]. Therefore this distance decreases and is provided by visible light.

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Synthesis and characterization of polyaniline/HMS nanocomposite and study of its activity for sorption of Ni²⁺ from wastewater

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Key words: sorption, polyaniline-HMS, nickel, kinetic.

Introduction:

Since mesoporous materials possess high surface areas and the size of pores can be tuned within 20–100 Å in a very narrow distribution by varying the preparation conditions, a large number of potential applications of these materials are expected to emerge in the areas of catalysis, separation, adsorption and advanced materials [1-3]. In this paper the nanocomposite including polyaniline conductive polymer supported on hexagonal mesoporous silicate (HMS) was synthesized and characterized. Then the kinetic study of adsorption of Ni²⁺ cations on the composite was investigated.

Method:

The HMS materials were synthesized by sol–gel method similar to Pinnavaia and coworkers [4], used TEOS as the silica source and dodecylamine as the surfactant. Coating of polymer on HMS was performed by aniline as the monomer, APS as an initiator in 100 cc of sulfuric acid (1M). The Characterization of nanocomposite was performed by FE-SEM microscopy, FTIR and BET measurements. Adsorption experiments were done for the study the effect of experimental conditions on Ni²⁺ adsorption and determining the conditions that achieve the maximum amount of removal. Kinetic evaluation were also conducted in this study.

Results and discussion:





Our results by FE-SEM showed that the synthesized nanocomposite of polyaniline/HMS was Nearly spherical and uniform in morphology with the average particle size of 50-80 nm. The initial pH range of 4 to 11 was used to study the effect of pH of the solution on removing Ni^{2+} by nanocomposite. The efficiency of Ni^{2+} removal increased as the pH was raised. Kinetic adsorption experiments were done in order to calculate the adsorption equilibrium time. The results indicated that Ni^{2+} sorption equilibrium time occurred in the 5 min.



Figure 1. FE-SEM micrograph of nanocomposite

Conclusion:

Polyaniline-HMS nanocomposite was prepared successfully in aqueous media by the chemical polymerization and the sorption of the Ni²⁺ on the producted adsorbent was studied in the aqueous media. Optimum condition for Ni²⁺ sorption occurred at pH 11 and time 5 min. The kinetics studies of Ni²⁺ on nanocomposite were based Pseudo-second-order and Morris-Weber equations. The data indicate that the adsorption kinetic of Ni²⁺ on nanocomposite followed the Pseudo-second-order equation. These studies have also shown that Polyaniline-HMS nanocomposite was an high effective adsorbent for removal of Ni²⁺ cations from water. It is a good alternative for more expensive adsorbents such as activated carbon in removing heavy metals from effluents and wastewaters.





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Study of photocatalytic activity of CoO nanoparticles in photodegradation of 2- nitrophenol.

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Abstract:

Cobalt Oxide nanoparticles were prepared by controlled preciption method and calcined at 300 oC. X-ray diffraction pattern show the cubic structure for prepared nanoparticles that the average size of estimated from the broadening of XRD peak using Scherrer's equation is 10 nm. The photocatalytic activity of CoO nanoparticles was studied in photodegaradation of 2-nitrophenol. The optimum conditions were obtained pH of 10 and photocatalyst dosage of 1.3 mg/L. The apparent rate constant of degradation is obtained 0.745 min⁻¹ at initial concentration of 30 ppm of pollutant.

Keywords: CoO, Photocatalyst, 2-Nitrophenol, Photodegradation.

Introduction:

Preparation, characterization and application of some transition metal oxides, such as cobalt oxide, have attracted an increasing interest due to their physical properties as well as rich technological applications [1]. Cobalt oxides, due to their magnetic and catalytic properties, are used in a wide range of applications in various fields of industry, including catalyst, pH sensors, gas sensors and magnetic materials [2–5].

Materials and methods:

NaOH solution is added drop by drop to 0.05 M $Co(NO_3)_2.6$ H₂O solution while the solution was stirred vigorously. The obtained nanoparticles was removed and washed with distilled water and ethanol. The residue was calcined at 300 °C for 150 min. The XRD pattern used to





characterize of CoO particles. The photodegradation reaction was done in a photoreactor contain 25 ml of 10-40 ppm of 2-nitrophenol at presence of 0.1-1.5 mg/L of nanosized CoO under irradiation a 40 w mercury lamp at time 1-4 h. The degradation efficiency of pollutant is calculated with measurement of absorbance of solution before and after degradation process.

Result and discussion:

Cobalt(II) oxide nanoparticles were prepared by controlled precipitation method and characterized by using X-ray diffraction pattern (XRD) and transmission electron microscopy (TEM) method. XRD pattern of CoO nanoparticles that calcined at temperatures 300 °C show a cubic structure. The average size of nanoparticles was about 10 nm.

CoO nanoparticles were used as photocatalyst in photodegradation process of 2-nitrophenol as a pollutant. The maximum of degradation efficiency was obtained in conditions 1.3 mg/l of CoO, 30 ppm of 2-nitrophenol and at pH 10 in duration of 150 min.

It was observed that rate of reaction increases on increasing the pH, and after a certain pH, further increase in pH decreases the rate of reaction. Initially, when the pH is slightly acidic the rate increases to availability of OH ions in a concentration which is required for increasing the rate of reaction. These OH⁻ ions generate [•]OH radicals which are effective oxidizing species and responsible for photocatalytic degradation of 2-nitrophenol.

Conclusion:

Cobalt oxide nanoparticles were synthesized in good yield with the help of soft chemical approach with controlled size distribution and phase purity. The preparation of pure nano-size Substance is very important not only for the study of their properties but also for their applications.

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Density Functional Theory Study of Sulfur Dioxide Adsorption on the Internal and External of the Single-Wall Carbon Nanotubes

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Key words: Sulfur Dioxide (SO₂), Single-wall carbon nanotube (SWCNT), Adsorption energy, Density functional theory (DFT)

Introduction:

Experimentally the electronic properties of SWCNTs can be appreciably altered by the presence of adsorbed molecules [1]. The interaction of various gas molecules with carbon nanotubes has been investigated in several recent theoretical studies [2, 3].

Method:

In the present study the interaction of sulfur dioxide with single-wall carbon nanotube of (5,0) and (5,5) were investigated using the B3LYP/6-31G(d) density functional theory (DFT) level. Computational calculations were performed in the gaseous phase by the Linux version of Gaussian 09 with 32 processors via shared memory. Fig. 1 shows the optimized geometry of the combined systems.



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Figure 1 Molecular geometry and interaction between (5,0)SWCNT-SO₂ (a, b) and (5,5)SWCNT-SO₂ (c, d). The harmonic frequencies were computed from analytical derivatives for all species in order to define the minimum-energy structures. The geometry of all molecules under investigation was determined by optimizing all geometrical variables without any symmetry constraints. For both the external and internal cases, the effect of molecular orientation on the adsorption process was studied. The adsorption energies, the thermodynamic properties, HOMO-LUMO energy gaps and partial charges of the interacting atoms were also studied.

Results and Discussion:

The (5, 0) SWCNT containing 50 carbon atoms of length 8.5 Å and diameter 4 Å, saturated with 10 hydrogen atoms, and the (5, 5) SWCNT containing 100 carbon atoms of length 9.8 Å and diameter of nanotube is 6.85 Å saturated with 20 hydrogen atoms were selected for this purpose. The parameters calculated in this study are the energy interaction, E_{ads} , of SO₂ with inside wall of SWCNT of (5,0) and (5,5) through the following formula:

 $E_{ads} = E_{tot}(SO_2 - nanotube) - E_{tot}(nanotube) - E_{tot}(SO_2)$ (1)

The adsorption energy increases with the angle of interaction, reaching a maximum at 90° and that the most favorable adsorption distance between the molecule and external wall nanotubes of the (5,0) and (5,5) was 3.0, and 3.4 Å, respectively. SO₂-SWCNT total Gibbs free energy were calculated for inside of (5,0) SWCNT, outside of (5,0) SWCNT, inside of (5,5) SWCNT and outside of (5,5) SWCNT, and they are 426.6009, -96.2428, -62.4802 and -94.3001 kcal/mol, respectively. The lowest energy gap is achieved in the process of SO₂ adsorption on the internal wall of (5,0) nanotube, and the energy gap in nanotube- SO₂ adsorption process is reduced compared to before the interaction.

Conclusion:

According to the results, adsorption of SO_2 molecule on the external wall of the nanotube is more effective than the internal wall, and adsorption of SO_2 on the external wall of the (5,0) nanotube is more effective than external wall of the (5,5) nanotube. The adsorption of SO_2 on





the internal wall of the (5,5) nanotube is more effective than internal wall of the (5,0) nanotube.

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Synthesis and characterization of CdS quantum dots capped with the different amino acids and thioglicolic acid (TGA).

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Keywords: Quantum Dots, Cadmium sulfide, Amino acids, Photoluminescence.

Introduction:

The luminescent semiconductor quantum dots including II–IV and III–V semiconductor Nano crystals. They use such as fluorescent markers in molecular and cellular labeling, imaging, sensing and diagnostics [1–3]. CdS quantum dots (QDs) have attracted considerable attention over the past decades due to their unique properties and potential applications [4, 5]. In this paper, the simple route for synthesis of CdS QDs in aqueous solution was introduced.We studied the effects of the different amino acids and TGA, initial molar ratio and pH on the photoluminescence intensity, emission and absorption wavelength of CdS QDs.

Materials and methods:

In this work for synthesis of CdS QDs, $CdCl_2$ (Merck), two different amino acids as a Serine /Histidine (Merck) and TGA (Fluka) as well as thioacetamide (Fluka) such as source of sulfide were used. These CdS QDs synthesizedwith facile hydrothermal method and following with the different refluxing time [6].

Apparatus:

The UV–Vis absorption and photoluminescence (PL) spectra were recorded on CECILCE 5501 UV–Vis and PERKIN-ELMER LS-3Bfluorescence spectrophotometers, respectively. The FT-IR spectra were recorded on TENSOR 27 infrared spectrometer.X-ray diffraction





(XRD) patterns were recorded on an Advance Bruker D8 X-ray diffractometer(Germany) using Cu K_{α} radiation (λ =1.5418°A).

Result and discussion:

The optical properties of the synthesized CdS QDs, including the UV–visible absorption and photoluminescence (PL) spectra, were studied.Fig 1 displays UV–Vis spectra of the CdS QDs exhibited absorption band from 200 to 500 nm for TGA-CdS and 200-800 for Ser-CdS/His-CdS.The PL spectra showed strong emission band with maximum wavelength at 480 and 518 nm for TGA-CdSand for Ser-CdS QDs respectively. The FT-IR spectra of the bulk CdS, Ser-CdS and His-CdS were studied. In Comparison FT-IR spectra of the bulk CdS with CdS QDs, the stretching bending band of the carbonyl group of the amino acids can be found at 1550–1580 cm⁻¹.



Fig 1. UV-Vis spectra of TGA -CdS, His-CdS and Ser-CdS.

Conclusions:

In summary, the stable CdS QDs with good optical properties were successfully prepared using Ser, His and TGA as the stabilizing agents. This method is facile and low toxic. The CdS QDs exhibited strong absorption and photoluminescence signals. This suggested that the CdS QDs prepared in this work might be used as the potential photocatalyst to effectively treat the organic pollutants under visible light irradiation.

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Preparation, cracteractise and compare thin film of nano particle Lanthanum yttrate with temperature variations

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Key words: Lanthanum yttrate, Fuel cell, Solid electrolyte, Sol-gel

Introduction:

The sol-gel synthesis of metal oxides offers new possibilities in the field of solid state ionic's. The chemical design of molecular precursors allows a better control of the polymerization process so that Taylor-made materials could be obtained. New hybrid organic-inorganic compounds exhibit high ionic conductivities and could be used as electrolytes. Oxide gels are actually particle hydrates. Water adsorption and dissociation at the oxide-water interface are responsible for their properties as ion exchangers or fast proton conductors. Colloidal particles are very small so that the large solid-liquid interface provides improved electrochemical properties which can be used for making reversible cathodes or electro chromic devices. The sol-gel deposition of thin coatings of large area could open the possibility to make multilayer micro-ionic devices [1]. Some aspects of the simultaneous optimization of material properties of proton conductors which are relevant for their use in electrochemical cells such as fuel cells, electrochemical reactors and sensors (high proton conductivity, chemical, electrochemical and morphological stability) are discussed [2, 3]. Conductivity measurements show that doped-LaYO₃ is a p-type semiconductor at high oxygen partial pressures, but becomes a pure oxide-ion conductor at low oxygen partial pressures [4, 5].





Materials and synthesis methods:

Sol-gel has prepared with 0.0288 gr La(NO3)3.6H2O(99%), 0.0084 gr Y(NO3)3.5H2O,11. 5ml Toluene, 13ml Butanol and 3ml water at two temperatures 298K and 320K.This solution is probability contain nano particles Lanthanum yttrate and other materials. We expect with this materials ratio, $La_{0.8}Y_{0.2}O_3$ compound was formed. Then we coat this Sol-gel on glass. Substrate temperature select 300°K. Thin films had nano particle

Apparatus:

The FT-IR (8400S) tool has been applied for determining vibration site and SEM (Hitachi Japan S4160), AFM (solver next model) tool has been applied for determining size nano particles on thin films.

Result and discussion:

The thin films structure was analyzed by FT-IR spectrum. As can be seen in Fig. 1, the 8 peaks FT-IR spectrum shows at (3600/2000-2400/1300-1600/1100-850/600-400 cm-1). The up and down curve relate with high and low temperature respectively that different between those are corresponding to vibrations intermolecular. Scanning Electron Microscopy (SEM) shows in Fig 2 and Atomic Force Microscope (AFM) shows in Fig 3. The particle size of thin films was compared with images obtained from SEM and AFM. The particle size of thin films was increase with increase temperature (25 nm to 200nm).



Fig1: FT-IR spectrum for high and low temperature.Fig2: SEM picture at 298K.Fig 3: AFM picture at 320K.

Conclusion:

The FT-IR spectrum of thin films show that curve peaks in samples that prepare in $T=320^{\circ}K$ are bigger, but this peaks are wider. This can be because particle size distribution at 320K. Of course, these points are confirmed by dates in SEM and AFM pictures.





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A comparative study on structure and microstructure of zinc ferrite nanopowders prepared using different fuels

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Keywords: Zinc Ferrite; Auto Combustion; Fuel; Morphology; XRD; SEM.

Introduction:

Zinc ferrite (ZnFe₂O₄) has a normal spinel structure; it is a commercially important material and has been widely used in magnetic applications, gas sensors, catalysts, photocatalyst, and absorbent materials due to its excellent electrical and magnetic properties [1]. Currently, more attention has been paid to the auto-combustion method for synthesizing nanocrystalline ferrites. Sol-gel auto combustion synthesis induced by a self-sustained exothermic reaction of a fuel mixed to the reactants [2]. The different fuels enhance the efficacy and efficiency of the sol-gel auto combustion process. The experimental investigation showed that, the fuel type, in other words nature of the organic complexing agent has direct influence on the final characteristics of the resultant powders, namely, on the crystallite phase formation process, structural characteristics, morphology of zinc ferrite powders and the produced crystallite size; i.e., with the changing fuel type, would be change these fundamental parameters of crystallites. The ratio of the fuel to metal nitrates (molar ratio of Zn²⁺: Fe³⁺: fuel) could influence the amount of heat release and agglomeration tendency of particles; hence, the varying zinc ferrite crystallites size.

Preparation of Zinc Ferrite :

Zinc Ferrite composites were synthesized using sol-gel auto combustion method. For the preparation of Zinc Ferrite nanoparticles, the detailed process can be described as follows:





Initially, an appropriate amount of metal nitrates as starting materials was dissolved in a small amount of de-ionized water. Glycine, urea and thiourea were added separately to the mixed nitrate solution (molar ratio of Zn^{2+} : Fe⁺³: fuel was fixed 1:1:2). The next stage was the neutralization of the solution by dropwise adding small ammonia with constant stirring until the pH reached 7. The solution was heated on a hot plate at 60-80°C for approximately 5 hours, after which the solution turned to viscous brown gel followed by foaming of the gel. The foamy gel was kept on an electric plate at 300°C which caused its spontaneous ignition. At this temperature, the exothermic decomposition of the fuel took place, leading to an enhancement of the temperature and the reaction between the precursors. Finally, the combustion reaction was completed within a few seconds and loose powder was formed.

Results and Discussion:

The samples produced with glycine, urea, and thiourea fuels at molar ratios 2 will be hereafter called G2, U2, and T2, respectively. The calculated average crystallite sizes for samples G2, U2, and T2 are 23, 25, and 17 nm, respectively.

The produced Zinc Ferrite using the thiourea fuel additive with the molar ratio of (2:1), yield the smallest particle size in comparison to the glycine and urea fuels, at the same molar ratio. Perhaps, this is due to the formation of good and advanced complex which, results in homogenous cations and the heat release; therefore, the smaller particle sizes. A high quality fuel in a combustion process should act as a complexant for metal cations [3].

The thiourea displayed good complexing ability in low temperature ignition and performed controlled combustion reaction with nitrates. This complex increases the solubility of metal cations $(Zn^{2+} \text{ and } Fe^{3+})$ thereby preventing preferential crystallization as the water in the precursor solution evaporates. It is worth mentioning that, the composition of phases and microstructures are affected by changing fuel type in the combustion process. The phase analysis of diffraction peaks U2, and G2 samples presented the formation of $ZnFe_2O_4$, ZnO with FCC spinel and Tetragonal structured systems. Additionally, the XRD patterns of T2 sample presented the formation of $ZnFe_2O_4$ single phase composition with spinel structure.





The SEM images of samples G2, U2 and T2 are presented, that with the changing fuel type, the morphology of crystallites changes.

Conclusions :

The fuels play an important role in the sol-gel auto combustion process, i.e., the rate of combustion is influenced by the nature of the organic complexing agent. In turn, the auto iginition temperature is affected by the formation of homogeneous gel through the stability of the metal ion complex in the auto-combustion reaction. In this paper, with the thiourea's lower auto ignition point (Flash point) and due to the early formation of homogeneous gel, the product temperature decreases; consequently, the smaller crystallite size are formed when compared to the other fuel additives.

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Investigation Effect of pH Variation in preparation and controlling of Zn spinel ferrite nanocrystallites size

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Keywords: Sol–Gel Auto-Combustion, Zinc Ferrite, pH Value, Agglomeration, Crystallite.

Introduction:

Different spinel ferrite compounds can be prepared by almost all the existing techniques of solid state chemistry. Nowadays a considerable attention is attracted to applications of nanoparticles, which leads to the development of different chemical synthesis technique, which common feature- all reagents are mixed in atomic or molecular level [1]. Different methods can be used to prepare such as ferrites, Co-precipitation, mechanical milling, reverse micelle, Hydrothermal, precursor, sol-gel and sol-gel combustion. Various typical have drawbacks. For example in a result of reaction one could obtain products with wide particle size distribution or obtained ferrite compounds could be low crystallinity and high inhomogeneity. The influence of pH values from 2 to 7 in preparation and controlling of Zn spinel ferrite nanocrystallites size by sol-gel auto combustion method with the aid of ultrasonic irradiation have been investigated. The results showed that, the starting pH could have an important effect on size and shape of nanoparticles. Sol–gel auto combustion synthesis is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials.

Materials and Preparation Method:





For the preparation of ferrite nanoparticles Initially, $Zn(NO_3)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ and $C_2H_5NO_2$) were taken in the required ratio and dissolved into a minimum amount of di-ionized water. Small ammonia solution is added dropwise to mixture solution. The pH of sols was changing from 2 to 7. The mixtures were stirred in order to obtain homogeneous sols. The sols were heated on a water bath at 80°C/5h until the gels formed. The foaming of the gels resulting was transformed into voluminous ashes by a self-propagation combustion process when ignited at $\leq 400^{\circ}C$. At this temperature, the exothermic decomposition of the fuel took place, leading to an enhancement of the temperature and the reaction between the precursors. The combustion reaction completed within only a few minutes and fine particle ashes were formed. Finally, the particle ashes were calcined at $500^{\circ}C/3h$ with a heating rate of $10^{\circ}Cmin^{-1}$ and a cooling rate of $5^{\circ}Cmin^{-1}$. After dispersion of the powders, at room temperature, for 20 min in an ultrasonic irradiation bath (HF-35 kHz, Made in Germany). It has some advantages, namely, uniformity of mixing, reduction in crystal growth, morphological control, and reduction in agglomeration.

Characterization:

Studies on the obtained composites carried out using X-Ray Diffraction (XRD: Philips, XPERT- MPD), Scanning Electron Microscopy (SEM: Phillips XL30) and Fourier Transformed Infrared Spectrum (FT-IR, NICOLET-NEXU-870) techniques.

Results and discussion:

The particles size distribution of the calcined powders was determined from the broadening effect of the most intense peak by the Debye-Scherrer formula (1). The average particles size of the synthesized zinc ferrite samples were estimated from X-ray peak broadening of the {227} peak using the Scherrer equation, $D=0.9 \lambda/\beta \cos \theta$ (1) Where β is the full width at half maximum (rad), λ the wavelength of X-ray radiation (0.15405 nm for Cu K_a), θ the angle between the incident and diffracted beams (degree) and D the average particles size of the sample (nm) using Cu K_a radiation, in 20 range from 10 to 90° by 0.01 step size. The samples produced with pH 2, 3, 4, 5, 6 and 7 will be called, respectively





G2, G3,G4, G5, G6 and G7 hereafter. The calculated crystallite sizes for all of samples prepared by this method are 60.12, 57, 48.82, 58 and 60 nm for G2, G3, G4, G5, G6 and G7 samples, respectively. The XRD patterns of the synthesized powders are confirmed the formation of phases $ZnFe_2O_4$ with face centered cubic spinel structure and Fd3m (227) space group and ZnO with tetragonal system and P63 mc (186) space group.

The SEM micrographs of calcined ferrite powders is shown that, in some cases, the powders located in loosely packed agglomerates with the highly porous nature. It can be concluded that the pH control as an efficient factor exerts direct influence on change the morphology.

Formation of spinel structure is confirmed using Fourier transform infrared spectroscopy (FTIR). As magnetic of a ferrite depends not only on the chemical composition but also on various factors such as porosity, size and shape of the pores of the crystals. Thus, the magnetic properties would be affected by the external molecular force which can lead to little shift in the vibration band. Data analysis on the FTIR spectra of ferrite powders indicates that the characteristic band peaking at about 550-660 cm⁻¹ originates from absorption corresponding to the stretching vibrating band of M-O (M= Fe, Zn).

Conclustion:

The dispersed ZnFe₂O₄ powders were synthesized by sol-gel auto combustion technique. The results revealed that, different pH would regulate the proton concentration resulting in the control of nanoparticles morphology. It was also found the pH of the solution affect the crystallite size distribution, stability of nanoparticles and agglomeration degree of the particles. The average particles size as determined by X-ray diffraction in the range 48-60nm, irrespectively of the pH values. SEM micrographs of the samples presented remarkable differences concerning to the agglomeration degree. Also, particle size, in turn, will affect on the magnetic properties.

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Hand Henrichten





Treatment of carbon nanotubes by KOH for removal of fluoride from waste water

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Key words: chemical vapor deposition, carbon nanotubes, Boehm titration, Fluoride, KOH

Introduction:

Since discovery of the carbon nanotubes (CNTs) in 1991, intensive researches have been done to investigate their unique physical and chemical properties, and various production methods have been developed [1]. Synthesis of the CNTs via chemical vapor deposition (CVD) method has shown to be more controllable and cost-efficient when compared with other synthetic high temperature methods such as arc discharge [2] or laser vaporization [3]. The chronic toxic effects on human health of excessive intake of fluoride have been studied intensively and the fluoride concentration in the range 0.5-1.5 mg/l is generally considered to be beneficial to human being. So it is imperative and significant for removing excessive fluorides from water [4].

Materials and methods:

The substrates were prepared as small disc (diameter 2.5cm). 0.01g of CNT was deposited on the surface of each disc and the size of nanostructure was about 70nm (Fig 1). The FT-IR spectra of the treated sample showed that the hydroxyl and carboxyl groups were produced on the carbon nanotubes surfaces at 3426cm⁻¹ and 1639cm⁻¹ respectively. The surface functional was 1.5mmol/g for carboxylic group, 8.5mmol/g for lactonic group and 7mmol/g for phenolic group. The point of zero charge (pH_{pzc}) of the treated sample was 6.02.






Fig. 1- SEM image of carbon nano-structure .

Apparatus:

In this study, chemical vapor deposition (CVD) method was used for synthesis of carbon nanotube (CNT) films on macroporous kaolin substrates using cyclohexanol and ferrocene, respectively as carbon source and catalyst. To examine the adsorption behavior of the disc, chemical surface treatment was carried out with 1M KOH at reflux conditions for 3 h. The surface functional groups were determined according to the Boehm titration with 25 ml of 0.1 N of the following solutions: sodium hydroxide, sodium carbonate and sodium bicarbonate. The point of zero charge (pH_{pzc}) of the treated sample was measured by acid–base titration. The amount of fluoride adsorbed on the carbon nanotubes was determined by ion-selective electrode.

Result and discussion:

Fig. 1 shows that the SEM images of the nanostructure. It is evident that "sword like" nanostructure are synthesized on the surface of kaolin disk. The pH value plays an important role with respect to the adsorption of different ions on nanostructures. According to the results the presence of different functional groups increased after base-treatment. The experimental results indicated that carbon nanotubes are promising candidate materials for fluoride removal.

Conclusion:

Chemical vapor deposition was used for synthesis of carbon nanstructures. The results demonstrated that the adsorption capacity of the carbon nanstructures increases significantly after treatment. The structure of carbon surface were changed after treatment including the





increase in surface functional groups, When the pH of the solution is lower than the pH_{PZC} of the oxidized CNT, the positive charge on the surface provides electrostatic attractions that are favourable for adsorbing anions such as F.

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Co₃S₄ Nanocrystals: Hydrothermal Synthesis, Characterization, and Formation Mechanism

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Key words: Co₃S₄, Nanocrystals, Hydrothermal, Thioglycolic acid

Introduction:

Metal sulfides nanomaterials have been the focus of considerable interest due to their unique optical and electrical properties and their wide variety of potential applications in nanoscale devices such as electroluminescence and nonlinear optical devices [1]. Cobalt usually forms a variety of binary sulfides with the general formula of CoS_x such as Co_9S_8 , CoS, Co_3S_4 , $Co_{1-x}S$, Co_2S_3 and CoS_2 , which have attracted great attention in virtue of their excellent properties and potential application for hydrodesulfurization and hydrodearomatization in many industrial fields [2]. CoS nanoparticles are used in electrochemical capacitors (ECs) or rechargeable lithium batteries [3]. Relatively low cost, high purity of products, and controlling of morphology are the main advantages of hydrothermal method.

Materials and methods:

Appropriate of Co(CH₃COO)₂.4H₂O and thioglycolic acid were mixed in distilled water under stirring and then the solution was sealed into a 250ml Teflon-lined stainless steel autoclave, and heated at 120-180°C for different times in an electric oven. The autoclave was cooled to room temperature naturally when it is up to the required reaction time. The product was separated and some parameters such as reaction time and temperature and concentrations of reactants in growth and morphology of the nano-structures have been studied.





Apparatus:

X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III. The electronic spectrum of the sample was taken on Perkin-Elmer LS-55 luminescence spectrometer. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. (FESEM) images were obtained on HITACHI S-4160.

Result and discussion:

All of the diffraction peaks in XRD pattern were indexed to the face-centered cubic of Co_3S_4 (JCPDS No.73-1703). Photoluminescence spectrum of Co_3S_4 nanoparticles showed a sharp and strong peak centered at about 460.1nm. The blue emission can be assigned to cobalt vacancies. FESEM and SEM images revealed that Co_3S_4 nanocrystals were obtained when temperature, time, and reactant ratio ($Co^{2+}:TGA$) were $150^{\circ}C$, 48h, and 1:1 respectively. Below this temperature products were composed of bulk particles while upper this temperature small particles have agglomerated. At constant condition when reactants ratio was 1:3 cauliflower-like Co_3S_4 microspheres composed of nanoparticles obtained. Large particles obtained at 24h would have broken at 48h under hydrothermal condition and produced small particles which fused to each other due to the free thiol groups which result from something excessive TGA molecule absorbed on surface of the Co_3S_4 nanoparticles, and then hydrogen bonds and S-S bond interactions, so more concentration of TGA may lead to increase in spheres size.

Conclusion:

Nanocrystalline Co_3S_4 has been successfully synthesized. This study has confirmed that reaction time and temperature and concentrations of reactants have great effect on the morphology and size distribution of samples. In comparison to other similar works, current method is simple and has low cost and scale-up route. Also, nontoxic precursor and solvent were used.





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Investigation of the interaction of carbon dioxide fluid with internal and external single-wall carbon nanotubes by DFT

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Keywords: Adsorption energy, Carbon Nanotube, DFT, Carbon dioxide fluid

Introduction:

The special geometry and unique properties of carbon nanotubes offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and sensors, field emission displays, etc. [1]. The electronic properties of single-wall carbon nanotubes (SWNTs) can be considerably affected by the presence of adsorbed molecules. This has important consequences for device applications that use SWNTs as the bases of chemical sensors. Advantages of carbon nanotubes (CNTs) over other materials as good sensors are due to their small size, high strength, high electrical and thermal conductivity, and high specific area. The effects of absorbance of gas on SWNTs were studied theoretically and experimentally [2–6].

In the present study, density functional calculation at the B3LYP/6-311G level of theory is used to determine effective parameters of (5, 0) and (5, 5) SWNT as carbon dioxide sensors. Adsorption on both inner and outer surfaces of nanotubes and CO₂ rotation are examined.

Computational Method

The CO₂-nanotube interactions were studied using Gaussian 03 coding [12] by DFT at the B3LYP/6-311G level of theory [13–18]. The basis set superposition errors (BSSE) were estimated for the counterpoise correction [19]. The (5, 0) and (5, 5) SWNTs were selected for this purpose. CO₂ molecule on the internal and external walls of the SWNTs was fully





optimized without any symmetrical constraints in the parameters, such as the height above the surfaces or CO_2 location and orientation. The adsorption energies were determined according to the expression:

 $E_{ads} = E_{tot}(CO_2 - nanotube) - E_{tot}(nanotube) - E_{tot}(CO_2)$

 E_{ads} <0 corresponds to exothermic adsorption, which leads to a stable structure. The rotation of carbon dioxide molecule in different directions on the internal and external walls of the carbon nanotubes was investigated.

Results and Discussion:

 CO_2 adsorption on (5, 0) and (5, 5) SWNTs has been studied at various sites and tubedistances by DFT. The CO_2 molecule is weakly bound to nanotubes, and the tube-molecule interactions can be identified as physisorption. In the case of external walls, CO_2 adsorption is exothermic and is stronger for (5, 0) than for (5, 5), at -0.8884 and -0.0528 kcal/mol, respectively. The rotation energy barrier for (5, 5) is lower than for (5, 0) in all rotations, therefore (5, 5) is more active in these interactions. The energy gap changes significantly in the presence of carbon dioxide molecules on the inside surface of (5, 0) and conductivity is affected, but no remarkable change is observed in the electronic structure of (5, 5).

Conclusion:

The CO_2 molecule is weakly bound to (5, 0) and (5, 5) SWNTs and the tube-molecule interactions can be identified as physisorption. It is predicted that CO_2 adsorption in bundle interstitial and groove sites may be stronger, and (5, 0) and (5, 5) SWNTs would be good sensors.

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Synthesis of Ni-Al-Fe ternary layered double hydroxides Prepared By Coprecipitation Method

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Key words: layered double hydroxides, Termal, LDH Ternary Ni-Al-Fe, coprecipitation

Introduction:

Nanostructured materials have Important groups scientific and technological and have generated diverse scientific and technological interest in many potential areas of applications such as energy conversion, electronics layered double hydroxides (LDHs) are a class of anionic clays with the structure based on brucite $(Mg(OH)_2)$ -like layers in which some of the divalent cations have been replaced by trivalent cations yielding positively charged sheets. LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]x+(A_{n-})x/n\cdot yH_2O$, where M^{II} and M^{III} cations occupy octahedral holes in a brucite-like layer and A^{-n} anion is located in the hydrated interlayer galleries

Materials and methods:

The Ni-Al-Fe(NO₃) LDH was prepared using a coprecipitation method. The synthesis was carried out under a N₂ atmosphere, and all the solutions were prepared using deionized water to avoid contamination. In this work, the Ni²+(Al³⁺ + Fe²⁺) and Al³⁺:Fe²⁺ molar ratios chosen for the synthesis of the LDH precursors were 3: 1 and 0.7:0.3, respectively.

For this purpose, 1.28g Ni(NO₃)₂·6H₂O, 0.37.85g Al(NO₃)₃·9H₂O, and 0.108g Fe(NO₃)₂·9H₂O were added into 50.0mL deionized water under vigorous stirring at room temperature. Then, 25mL basic solution containing 0.5molL–1 NaOH was added dropwise to





the salt solution, and pH of the solution was maintained at 8.30 under continuous stirring at room temperature. After aging, the Ni-Al-Fe The mixed-metal oxide obtained by heating at 400 K for 48h The precipitate was washed with distilled water until The pH of The Filtrate was around 7. Thoroughly with distilled water and dried at 60°C

Apparatus:

in order to structural study of the LDH, XRD measurements were performed on a Bruker AXS X-ray powder diffractometer The pH valueswere measured with a Metrohm pH meter (model 827), supplied with a glass-combined electrode FT-IR spectra (4000–400cm–1)were recorded on a Vector 22 (Bruker, Germany) Fourier transform infrared spectrometer using the KBr disk method with a ratio sample/KBr of 1:100.

Result and dixcussion:

the X-ray diffraction (XRD) patterns of as-synthesized dried hydrotalcite samples with different Ni/(Al+Fe) and Al/Fe molar ratios. They show sharp and intense reflections at around 2è 11°, 23°, 60°, and 62° attributed to (0 0 3), (0 0 6), (1 1 0), and (1 1 3) planes characteristic of hydrotalcite-like materials with hexagonal crystal system. The positions of the remaining peaks are in agreement with the results reported by other researchers Fig 2 shows the FT-IR spectrum of Ni-Al-Fe (No)₃LDH. The absorption band around 3483 cm⁻¹ is attributed to O-H stretching mode, caused by hydroxyl groups in the brucite-like layers and the interlayer water molecules. The band with maximum peak at 1384cm⁻¹ can be assigned to stretching vibration of (NO₃)⁻







Conclusion :

in the conditions Can be successfully synthesized layers double hydroxide ternary Ni-Al-Fe(NO₃)

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Synthesis of Ni-Al layered double hydroxide as a nano-sorbent and its application for extraction of Para amino benzoic acid from pharmaceutical and healthy products

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Keywords: "Nickel-Aluminum Layered Double Hydroxide, Nanosorbent, Solid Phase Extraction, Spectrofluorometry, PABA"

Introduction:

Layered Double Hydroxides (LDHs), well known as a large class of anionic clays, consist of structures based on brucite type Layers of Mg(OH)₂ sheets, LDHs have the general formula $[M^{II}_{-x}M^{III}_{x}(OH)_{2}] [x^{q-}_{x/q}.n(H_{2}O)] (X^{q-} = SO_{4}^{-2}, CO_{3}^{-2} \text{ or } CI^{-})$

Materials and methods:

[Ni-Al (NO³⁻] LDH The synthesis was carried out Under N2 atmosphere, and all solutions were prepared using deionized water to avoid contamination. obtain stable Layered for this purpose, 0.581 g Ni(NO₃)₂ • 6H2O and 0.375 g Al(NO₃)₃ • 9H2O were added Into 30 mL deionized water under vigorous stirring at room temp. The pH of The reaction mixture was adjusted to 9.6 By The addition Of 1 M NaOH Solution. Then, The obtained slurry was Subjected to thermal treatment at a constant temperature of 90^{-c} in vessel oil for about 24 h. The resulting precipitate was separated by centrifuge Then washed three times with Deionized Water and Dried at $60^{\circ C}$ For 6 h.(Fig. 2 Shown XRD Pattern of Ni–Al (NO³⁻) LDH)





The column was prepared by introducing 200 mg of Ni-Al (NO³⁻) LDH into an empty 2 ml polypropylene cartridge using The dry packing method. before loading The sample, 2 mL of 3

mol L⁻¹ NaOH or NaCl solution were passed through the column to clean It. then, The column was conditioned by passing only 3 mL of Deionized water through it prior to each Use, after loading, The retained analyte in the column was eluted with a 2.5 mL of 1M Nacl as desorbing and ion-exchanger solution. sample analyte inclusive being para amino banzoic acid 100mg portion of freshly weighted willow leaves was transferred into a mortar and complete crushing was carried out in The with deionized water, axtraction of analyte Is based on The adsorption of PABA ions on the Ni–A1 (NO₃.) LDH and/or their exchanging with LDH interlayer NO₃.

Apparatus:

In order to structural study of the LDH, XRD measurements were performed on a BrukerAXS X-ray powder diffractometer The pH valueswere measured with a Metrohm pH meter (model 827), supplied with a glass-combined electrode FT-IR spectra (4000–400cm⁻¹)were recorded on a Vector 22 (Bruker, Germany) Fourier transform infrared spectrometer using the KBr disk method with a ratio sample/KBr of 1:100 by massbetween 5 and 70° generated at 40kV and 35mA at room temperature

Result and dixcussion:

sample volume and vatrix in the optimum experimental conditions the calibration graph using the pre-concentration system Was Linear in The Range of 1_17ppm with a correlation coefficient of 0.9994(Fig_2)whence follow action endow top tender the optimized method was successfully applied to the determination of PABA in samples medication and sanitary and creams sunscreen (For example determine PABA in drug's weelmen and Samples sanitary for example drug's vitamin's for the hair with determinate successfully)



2

1.5





Figure1:Patern XRD LDH (Ni-Al)



Figure2: Diagram Calibration for PABA

diagram calibration

y = 0.092x + 0.011

 $R^2 = 0.999$

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Improvement of photocatalytic activity and stability by immobilization of TiO₂ on the hexagonal mesoporous silicate

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Introduction:

Photocatalytic purification of wastewater treatment as a method of AOP processes has been widely used for remove of organic pollutants of water in the libratory scale. Many literatures have been published about the good photoefficiency of TiO_2 in anatase phase for degradation and mineralization of organic compounds such as textile dyes [1-2].

One of the main problems of using TiO_2 is the deactivation of photocatalyst during the reaction [3]. It has been found that the absorption of organic dyes on the external surface of photocatalyst prevents the UV absorption and excitation of TiO_2 for electron donation and photocatalytic reactions. In this work the dispersion of photocatalyst on the hexagonal mesoporous silicate (HMS) and study of its effect on the stability of the photocatalyst were investigated.

Method:

The HMS materials were synthesized by sol-gel method similar to Pinnavaia and coworkers [4], used TEOS as the silica source and dodecylamine as the surfactant. Immobilization of TiO_2 on HMS was performed by hydrolysis of titanium isoproposide in ethanol at the presence of acetic acid.

The photocatalytic degradation of RB was performed by use of a suspension of 0.1 gr of photocatalyst powder into the aqueous solution of 100 ppm of reactive red. The activity and stability of the photocatalyst was performed by determination of decoloration of solution using of the UV-Vis spectrophotometer.





Results and discussion:

Immobilization of TiO_2 on the HMS enhanced the photodegradation of aqueous solution of dye.

The results showed that the use of TiO_2 + HMS combination was an efficient photocatalytic system to work.



Figure 1. Comparison of stability of TiO_2 (P25) and TiO_2/HMS for decoloration of reactive red. It was found that TiO_2 was deposited on the external surface of HMS channels and the substrate was adsorbed on HMS in active form could reach the TiO_2 [3].

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wand





Physical Chemistry Study of L_nE_mL_n Block Copolymeric Micelles for Protein Delivery

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Keywords: Triblock copolymer, Nanoparticle, Biodegradable, Insulin.

Introduction:

Biodegradable, polymer-based micro-/nanoparticles are attractive drug delivery systems for therapeutics with high pharmacological potential [1-4]. We have previously studied polymeric vesicles of a biodegradable triblock copolymer composed of polyethylene glycol and poly(fumaric acid- co- sebacoyl chloride) (PEG-co-P(FA/SC)-co-PEG) and reported its inertness against insulin [5]. Here a series of biodegradable triblock copolymers made of PEG and poly (L-lactide) ($L_nE_mL_n$), with new and different molecular weights are used to prepare micro-/nanoparticles. The aim is to investigate on the physicochemical properties of the copolymers as well as of the resulting micelles. Then, the effect of the $L_{37}E_{136}L_{37}$ copolymer on the structure of bovine insulin will be evaluated in details.

Methods:

A series of $L_n E_m L_n$ triblock copolymers were synthesized from L-lactide and PEGs of various molecular weights by ring-opening polymerization process. Chemical compositions of the synthesized copolymers were characterized by ¹H-NMR spectroscopy. The molecular weights as well as the polydispersities of the polymers were determined using GPC.





To prepare micelles, a given amount of the copolymer was directly dispersed in PBS, pH 7.4, at RT under vortex mixing. The critical association concentration (CAC) of the copolymers was estimated by fluorescence spectroscopy. Titration of bovine insulin with the $L_{37}E_{136}L_{37}$ copolymer dispersion was studied by UV-vis spectroscopy to determine binding parameters, such as K'_d for the apparent dissociation constant, and n for the number of binding sites for copolymer per protein molecule.

Results and discussion:

Fig. 1 shows the logarithmic CAC values at 25 °C plotted against the total L monomer units in a polymer chain. The longer the L block length, the smaller the CAC would be. Extensive studies on bovine insulin-polymer interactions by UV-vis spectroscopy have led to the calculation of binding parameters, such as $K_d'= 29.17 \mu M$, and n= 3.4.







Fig. 2. Far-UV CD spectra of bovine insulin at various v. (v: the average number of bound copolymers to one protein molecule)





Fig. 2 shows the far-UV CD spectra of the protein at 25 °C up on interaction with different concentrations of the copolymer (v= 0, 1, 2, 3). Analysis of the spectra shows that upon increasing the copolymer concentration, the helical content of insulin decreases, while that of β - structure as well as random coil content of insulin increases.

Conclusions:

The block length of $L_nE_mL_n$ copolymers plays an important role in determining the micellization behavior of the copolymers in aqueous solution. Results indicate that the length of the hydrophobic end L blocks is the dominant factor on the CAC values. Furthermore, comprehensive analysis of binding data led to the fact that in the case of $L_{37}E_{136}L_{37}$ bovine insulin has approximately 3 identical binding sites. Far-UV CD spectra of the protein upon addition of the copolymer demonstrate that the helical content of the protein decreases.

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Study of thermal decomposition kinetics of multi-walled carbon nanotubes functionalized by acidic groups using thermogravimetric analysis (TGA)

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Key words: Carbon nanotubes, Thermogravimetric analysis, Thermal decomposition, Kinetics study.

Introduction:

Carbon nanotubes are one of the most studied nanomaterials in the last fifteen years. Due to their extraordinary chemical and physical properties that this carbon allotrope posseses has emerged as novel nanometric material, promising in most areas of science and engineering. However, research on thermal properties and decomposition reaction for CNTs has been slim [1]. Our aim was to evaluate thermal experimental data of MWCNTs via thermogravimetric analysis (TGA) by applying well known kinetic equations such as the Coats-Redfern kinetic equation and also Friedman, Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose kinetic equation at various scanning rates. Some parameters such as activation energy, frequency factor and also model of degradation were determined and compare with those models [2].

Materials and methods:

Multi-walled carbon nanotubes (MWCNTs) with high purity and bulk yield were achieved on a CaCO₃ substrate and Ni - Co as catalysts under acetylene gas by chemical vapor deposition. Multiwalled carbon nanotubes (MWCNTs) were functionalized by acidic groups via the Fischer- Esterification method. Nitric acid and sulfuric acid treatment was first used to remove the catalyst from MWCNTs and introduce carboxylic acid groups onto the surface of MWCNTs.





Apparatus:

The kinetic study of degradation was performed on a TGA thermal analyzer (STA-PT 1000) at several heating rates (5, 10, 15, 20, 25 and 30 °C/min) from room temperature to 1000 ° C. The thermal analyzer was temperature calibrated between experiments using the Curie point of Pb as a reference.

Results and discussion:

The morphology, surface quality and structure of MWCNTs were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM).

Thermogravimetric analyses were done at six different heating rates. Then based on Coats-Redfern kinetic equation, kinetics' models and also activation energy were calculated. Fig. 1 shows calculated models.



Fig. 1 shows relation between Coats-Redfern kinetic equation and regression's of models in different heating rates; red, purple, green, yellow, blue and orange show 5, 10, 15, 20, 25 and 30°C/min respectively.

Then by use of Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) kinetic equations, activation energy and model of thermal decomposition in each alpha were calculated and compare with Coats-Redfern equation.

Method	E, (kJ mol ⁻¹), for conversion degree, α									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Main value
FR	185.04	195.70	207.67	210.34	208.67	196.00	176.03	151.79	122.98	183.80
FWO	119.66	147.91	168.94	184.84	195.29	199.37	193.72	181.836	166.73	173.14

Table1. Shows comparison of activation energy between FR, FWO and KAS kinetic equations.





KAS 107.59 125.91 145.74 160.72 170.55 174.32 168.85 157.43 142.90 150.45 Conclusion:

Multi-walled carbon nanotubes were synthesized by CVD method and functionalized by acidic groups. Then thermogravimetric analyses were done in different scanning rates. Based on Coats-Redfern kinetic equation, and also by utilize of Friedman equation, kinetics' models and activation energy were calculated and shows same amounts. Then by use of FR, FWO and KAS kinetic equations, activation energy and model of thermal decomposition were calculated.

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Preconcentration and speciation of chromium species in environmental water and food samples using a novel magnetic activated carbon nanocomposite coupled with FAAS

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Key words: Chromium speciation, Magnetic nanocomposite, Preconcentration, Flame atomic absorption spectrometry, Ultrasonic irradiation

Introduction:

Chromium is mainly present as Cr(III) and Cr(VI) oxidation states. The properties of these species are very different from a chemical and toxicological points of view [1]. Determination of chromium species is preferred by AAS due to its simplicity and its lower cost compare to other instrumental techniques, but due to its low detection limit, a preconcentration step for trace levels of element would be needed. Among various methods, SPE has found very important place in speciation studies of metal ions due to its simplicity, selectivity, flexibility and rapid phase separation. In SPE procedures, the choice of the sorbent is a key point because it can control the analytical parameters such as selectivity, affinity and capacity [2]. Magnetic nanocomposites, have gained more attention in analytical atomic spectrometry for trace analysis and speciation research owing to its suitability for bulk solution, easy control and fast magnetic separation under an extra magnetic field [3].

Materials and methods:

Stock standard solutions of 1000 mgL⁻¹ Cr(III) and Cr(IV) were prepared from chromium nitrate and potassium dichromate, respectively. Magnetic activated carbon nanocomposite (MAC) was prepared by ultrasonic waves. A known amounts of Iron (III) chloride and Iron





(II) chloride with mole ratio of Fe(II)/Fe(III) of 1:2 was dissolved in 70 mL of milli-Q and then poured in a rosette cell. Immediately the sonicator was turned on followed by addition of 10 mL of ammonia solution (25%) and then 7 g of rice husk AC to the solution and left aside for 30 minutes.

Apparatus:

The measurements were performed with a Shimadzu model AA-670 atomic absorption spectrometer equipped with an air-acetylene burner and a Cr hollow cathode lamp. The synthesis of nanocomposite was carried out by Sonics and material, 750 watt, 20 kHz.

Result and discussion:

Magnetic activated carbon nanocomposite (MAC) was simply prepared using ultrasonic wave. Cr(III) cations could be absorbed on the surface of MAC (30 mg) at pH 5.0 in batch mode, whereas Cr(IV) oxyanions would pass through MAC without retention. Total Cr and hence indirectly Cr(IV) were determined after reduction of Cr(IV) to Cr(III) with 10%(m/v) hydroxylamin hydrochloride. At the optimum experimental conditions, Cr(III) was eluted with 1.0 ml of 3.0 mol L⁻¹ HCl followed by magnetic decantation. A preconcentration factor and adsorption capacity of 100 and 40 mg g⁻¹ were obtained respectively. The relative standard deviation (R.S.D.) was 4.3% (C=10 μ gL⁻¹ Cr(III), n = 10) and limit of detection (LOD) was 0.4 μ gL⁻¹. Verification of the accuracy was carried out by the analysis of a standard reference material (NSD DC NO. 73301) and satisfactory results was obtained. This procedure was applied to determine Cr(III) and Cr(IV) species in environmental water and food samples.

Conclusion:

The results show that MAC has high and reproducible retention capacity for Cr(III) species. Comparison of the presented method with other procedures reported in the literature reveals that the RSD and LOD of the presented method are comparable or better than others.





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Excitation of particle plasmons in metal nanoalloy

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Key words: Metal Nanoalloy, Extinction cross section, Generalized Lorenz-Mie theory, Particle plasmon

Introduction:

Nanostructures have got lots of properties such as optical, magnetic and electronic properties. These properties can reveal in different science such as chemistry [1], biology [2], physics [3] and medicine [4]. Extinction of electromagnetic (EM) waves is the most important property in optical viewpoint in nanooptics, nanophysics and nanochemistry. Understanding of extinguished energy in nanostructures should help to physicists and chemists for producing modern tools for sensing and spectroscopy [5]. Therefore, we decided to calculate some optical response of Gold-Silver ($Ag_X Au_{1-X}$) spherical nanoalloy by changes of radius, alloy percentages and refractive indices of medium, numerically. This research should be applied in producing alloy nanosensors in biochemistry, nanochemistry, biotechnology and so on.

Material and methods:

In 19th century, Rayleigh's scattering theory was proposed to describe scattering and absorption of EM wave; but more applicable theory is Lorenz-Mie Theory (LMT). LMT can explain optical response of nanoparticles with isotropic, homogeneous and spherical structures when nanoparticles are against the plane waves.[6] After invention of "LASER" and other EM sources, LMT did not be able to calculate Maxwell's equations with incident non-plane waves such as Gauss-Hermite beams, Gaussian beams and so on.[7] Finally, new version of LMT was presented and named Generalized Lorenz-Mie Theory (GLMT).[7] New theory was able to calculate extinction cross sections for different types of incident EM waves and





different morphologies such as ellipsoids, spheroids and etc.[7] By applying GLMT; optical extinction of nanostructures should be calculated , numerically.[7]

Apparatus:

Extinction of EM waves in metal nanoalloy was derived by straightforward calculations of extinction cross section when single nanoalloy is located against the Spherical Gaussian Beams (SGB), numerically. Computational methods were used in "FORTRAN 90".

Result and discussions:

In this work, spherical nanoalloy is made out of gold and silver. Atomic percentages of these metals are characterized by alloy percentage (x). To increase its value gradually, properties of silver reveal more and more. In this calculation, we employed the measured bulk dielectric functions for silver and gold by Johnson and Christy [8]. To use these dielectric functions, we could achieve alloy dielectric functions for each "x", separately. Nanoalloy in calculations was into water ($\varepsilon_{water} = 1.78$) and located against the SGB. After exact calculations of extinction cross section in far-field regions for different alloy percentages, radiuses and refractive indices of surrounding medium, numerically; results of excitation of particle plasmons in gold-silver nanoalloy by incident spherical Gaussian beams (SGB) are as follow:

- a) To increase alloy percentages of nanoalloy, blue shift and increase of the height of plasmon peaks were observed due to disclosing silver properties.[9]
- b) To increase radius of spherical nanoalloy, red shift, increase of the height of plasmon peaks and increase of the number of peaks were observed due to de-polarized fields, increase of the number of free electrons and involvement of multipolar modes in large nanoalloys, respectively.[10]
- c) To increase the refractive indices of surrounding medium (or dielectric constants), red shift and increase of the height of plasmon peaks were observed as well, due to properties of complex dielectric function of metals and their alloys. [6]





Conclusion:

Extinction cross section was considered for Gold-Silver spherical nanoalloy in different alloy percentages in visible region. Particle plasmon resonances are the main reason for observation of peaks in spectrum. Cross sections of small nanoalloys did have one peak in visible and near infra-red wavelength spectrum due to disclosing dipolar resonances, while the number of peaks increased by increasing the radius of spherical nanoalloy where presence of multipolar resonances was proved. Additional peaks may be seen also in metal nanoparticles and their alloys due to interband transitions. Finally, we concluded where plasmon peaks were blue shifted and observed intense peaks by increasing alloy percentages.

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Synthesis of ZnO nanoparticle and investigation of its influence on photodegradation of Rhodamine B pigments in thin polyethylene films

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Keywords: Nanoparticle, Photodegradation, Rhodamine B, Polyethylene

Introduction:

In the past decades, high density polyethylene (HDPE) is one of the most used polymers in many industrial fields such as hoses, packing films, coatings, fire retarded materials, etc for its good properties like low cost, excellent electrical and mechanical properties, good chemical resistance and processability [1].

Pigments are widely used for the coloration of thermoplastics in many commercial applications. Although they are used primarily to impart colour to the polymer, they can also have a marked influence on the thermal and photochemical stability of the polymeric materiales. For example, by absorbing and/or screening light energy they can exhibit a protective effect or may be photoactive and sensitize to the photochemical breakdown of the polymer. With regard to these effects, there are four principal factors which can influence the photostability of a pigment-polymer blend. The first is the intrinsic chemical and physical nature of the polymer itself; other factors are the environment in which the system is used, the chemical and physical nature of the pigment and its concentration and the presence of antioxidants and light stabilizers [2].

Semiconductor nanoparticles have attracted much attention in recent years due to novel optical, electrical and mechanical properties, which results from quantum confinement effects compared with their bulk counterparts. More recently, ZnO nanoparticles have received much attention due to its low cost of production, high photoactivity in several photochemical and photoelectro-chemical processes, and UV light response of band gap 3.2 eV [3].





According to our knowledge, no systematic data on the photodegradation of Rhodamine B dyes in thin polyethylene films and investigation of ZnO nanoparticles influence on photodegradation have been performed so far. The aim of this work is to synthesize and characterize ZnO nanoparticles, and investigation of its influence on photodegradation of Rhodamine B pigments in thin polyethylene films.

Materials and methods:

Zinc oxide nanoparticle was synthesized by wet chemical method by mixing 0.15 M $Zn(NO_3)_2.6H_2O(Merck)$ water solution. After dissolution of zinc nitrate, 0.3 M NaOH(Merck) was added dropwise over a period of 1 hour. After the completion of the reaction, the solution was centrifuged at 1000 rpm. The product is washed with distilled water and then calcined at 450 C⁰ for 30 min in an oven.

The polymer used in this study is high density polyethylene (HDPE) with a melt index of 18 g/10 min, density of 0.952 g/cm³ and melting temperature of 131 C⁰ (Tabriz Pettrochemical. Co) Two kinds of samples have been prepared: HDPE doped with Rhodamine B and HDPE-ZnO nano composite doped with Rhodamine B. Samples were prepared from HDPE pellets blended with the Rhodamine B dye at 0.01, 0.03, 0.05,0.07, 0.1% w/w and HDPE-ZnO nano composite 5% w/w doped with Rhodamine B dye at 0.05% w/w. The films had a thickness of (200 μ m) for photocatalytic degradation experiments.

Apparatus:

The UV-Vis experiments were carried out with an UV-Cecil CE 5501 spectrophotometer (Cambridge, UK). The photochemistry apparatus is ORIEL model 8500 (Stamford, USA).

The average size of the synthesized ZnO was determined by a Philips advance powder X-ray diffractometer (XRD) with Cu K_{α} radiation source (λ =0.1542 nm) and a curved graphite crystal monochromator under 40 kV and 50 mA conditions.

Result and discussion:

Characterization of ZnO nanoparticles:





Figure 1 shows the XRD pattern of nano ZnO powder. The average size (*D*) of the particles can be determined according to the Scherrer equation: $D = k(\lambda/\beta \cos\theta)$. Where *k* is a constant equal to 0.89, λ is the X-raywavelength equal to 0.154 nm, β is the full width at half maximum and θ is the half diffraction angle (18.15°). The calculated value of the nanoparticle diameter was found to be 38 nm.

Photodegradation of the Rhodamine B dyes:

The photodegradation experiments were conducted at various intensities of UV light at different irradiation times. A typical representation regarding the relationship between Rhodamine B concentration and irradiation times was shown in Figure 2. Various kinetic models were used to find the best fitting of the experimental data and to evaluated the rate constants. The results exhibited that the experimental data could be described by a pseudo first-order kinetic model.



Fig. 1 XRD pattern of nano-sized ZnO powder



Conclusion:

ZnO powder was successfully synthesized in nanometer scale as confirmed by SEM and XRD experiments. The role of influencing factors such as UV light intensity, dye concentration, time, and ZnO nanoparticle on photodegradation characters of thin PE-Rhodamine B films were addressed. Our results showed that the presence of ZnO nanoparticle can accelerate the dye degradation in PE matrix.





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Investigation the density of states in presence of a magnetic field parallel to the nanotube axis

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Key words: Carbon nanotube, Density of state, Magnetic field, Van Hove singularity

Introduction:

Using an universal density of states (DOS) function [1], we can calculate an analytic equation for DOS in single walled carbon nanotubes (SWNT's).

In this study the universal model is used to determinate the analytical expression DOS [1] for SWNT's in presence of a magnetic field parallel to the nanotube.

methods:

A SWNT can be constructed by rolling up a single graphene sheet along one of 2D lattice

vectors
$$\vec{R} = n \vec{R}_1 + m \vec{R}_2 \equiv (n,m)$$
.

The contribution of a single, doubly degenerate 1D band $\varepsilon(k)$ to the DOS, can be expressed

as
$$n(E) = \frac{2}{\ell} \sum_{i} \int dk \, \delta(k - k_i) \left| \frac{\partial \varepsilon}{\partial k} \right|^{-1}$$

Then we can write the DOS per carbon atom $\rho(E) = n(E)/2$, that in finally [1]

$$\rho(E) = \frac{1}{\Lambda |V_{pp\pi}|} U\left(\frac{\Lambda E}{|V_{pp\pi}|}\right) , \quad U(E') = \frac{2\sqrt{3}}{\pi^2} \sum_{q=1}^{N} g(E', \varepsilon_q)$$

Where $g(E,\varepsilon_q) = |E|/\sqrt{E^2 - \varepsilon_q^2}$ for $|E| > |\varepsilon_q|$ and zero otherwise. The ε_q denote the energypositions of the VHS's that it's equal $|\varepsilon_q| = \frac{|3q-n+m|}{2} |V_{pp\pi}| \frac{d}{r}$. $\Lambda = 2r/d$ is the dimensionless ratio of the nanotube diameter to the carbon-carbon bond distance d, and r is the nanotube radius. $k_{\perp} \equiv k_q = 2\pi q/L$ is the wave vector perpendicular to the nanotube axis, where giving 2496





the quantized values of the wave vector in the circumference direction (\vec{L}) . The magnetic field induces a shift of k_q by a factor $2\pi\phi/(\phi_{\circ}L)$ [2], which ϕ is the flux threading the tube $(\phi = \pi r^2 H)$, where H is the intensity of the magnetic field) with a period equal to the fundamental flux quantum $\phi_{\circ} = hc / e$. the magnetic field results in a new expression for the quantized values of the wave vector in the \vec{L} direction, which reads $2\pi(q + \phi/\phi_{\circ})/L$. Therefore ε_q can be written

$$\left|\varepsilon_{q}'\right| = \frac{\left|3\left(q + \phi/\phi_{c}\right) - n + m\right|}{2} \left|V_{pp\pi}\right| \frac{d}{r}$$

Using of this equation, we can write the DOS in the presence of a magnetic field

$$U(E') = \frac{2\sqrt{3}}{\pi^2} \sum_{q=1}^{N} g(E', \varepsilon_q')$$

In the presence of a magnetic field, a band gap is opened up for metallic SWNT's, In contrast, the gap in semiconducting SWNT's decreases with the magnetic field. In other words magnetic field leads to ϕ_{\circ} -periodic variation of the energy gap.

Result and discussion:

The result of calculation as it's shown in the below figure. In the low magnetic field the gap of energy that is equal to zero for the metallic (10,10) SWNT, in the absence of magnetic field, begin to increase and it's continued as far as $\frac{\phi}{\phi_0} < \frac{1}{2}$, but for $\frac{\phi}{\phi_0} = \frac{1}{2}$ the procedure is reversed and the reduction in the gap of energy starts. Ultimately in $\frac{\phi}{\phi_0} = 1$ the DOS of zero field is obtained and the figure goes to initial situation (Figure 1).

In semiconductors the gap of energy begin to decrease as the magnetic field increased and it is continued as far as $\frac{\phi}{\phi_0} < \frac{1}{2}$ but the procedure inversely begin to increase before achieving the zero in $\frac{\phi}{\phi_0} = \frac{1}{2}$. Finally in the point of $\frac{\phi}{\phi_0} = 1$ the initial situation of VHS's is obtained in the zero field.



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Medium contains metal nanoparticles as meta-materials

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Key words :Metal, nanoparticles, Mie's theory, meta-materials

Introduction:

In recent years, meta-materials have been studied because of attractive properties such as negative refractive index in especial incident wavelength [1]. Generally, when electric permittivity and magnetic permeability have negative values simultaneously, negative refractive index is achieved [2]. It is well known that electromagnetic waves propagating in isotropic Meta-materials possess several peculiar characteristics, including anomalous refraction, reversal of both the Doppler shift and the Cherenkov radiation, and reversal of radiation pressure to radiation tension. On the other hand, scattering and absorption of light by nanostructures is one of the physicists & chemists motivations. Historically, there are some solutions for light scattering problems in special case, like Rayleigh, Debye, Lorenz approximations and Mie's theory [3]. Mie could propose exact solution for light scattering of spherical nanoparticles by solving of Maxwell's equations in 1908 [4]. Mie's theory was represented for isotropic, homogeneous and spherical particles into isotropic, homogeneous and non-absorbing surrounding mediums [5]. In this work, we suggest that for special wavelength and nanoparticle size, the effective refractive index shows negative value in Mie's theory and hence it could be considered as meta-materials.

Material and methods:

In this work we employed Mie's theory for calculation of scattering, absorption and extinction cross section of nanoparticles in $\epsilon \to 0$ regime, where ∂ is electric permittivity of medium. It must be mentioned that we consider only dipole-terms and ignore other multipole-terms in




Mie's coefficients due to small dimensions of nanoparticles relative to incident wavelength of electromagnetic wave. Moreover, we used Drude – Sommerfeld model for effective electric permittivity(ϵ_{eff}) and effective magnetic permeability (μ_{eff}) [2]. Finally, in this research, it has been chosen Silver as host medium and the real and imaginary part of silver refractive index is achieved from bulk value of silver.[6]

Apparatus:

In this research, we employed the measured refractive indices and electric permittivity of nanosilvers in different wavelengths. [6] Finally, we could calculate them by computational methods and we used "FORTRAN 90" for programming.

Result and discussions:

Refractive index depends on filling factor (f), incident wavelength (λ) and radius of nanoparticle [2]. Negative refractive indices were observed in follow condition:

- a) Radius of nanoparticles = 100 nm, f = 0.1 and incident wavelength $200 < \lambda < 205$ nm.
- b) Radius of nanoparticles = 200 nm, f = 0.1 and incident wavelength $375 < \lambda < 411$ nm.
- c) Radius of nanoparticles = 300 nm, f = 0.1 and incident wavelength $562 < \lambda < 617$ nm.

Conclusion:

In summary, we have studied the influence of fabrication parameters such as radius of nanoparticles on the effective refractive index by using of Mie theory and Drude– Sommerfeld model. An unusual behavior is found at $\partial \rightarrow 0$, which leads, in negative value for effective electric and magnetic permeability, simultaneously and hence effective refractive index which clearly shows that in especial condition medium contains metal nanoparticles should be consider as meta-materials. Generally, meta-materials are applicable in constructing optical instruments such as super lenses due to high resolving power. Therefore, this study could be helpful for experimentalists to design new super-lens by using of metal nanoparticles.





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Synthesis and Application of polyaniline/Multi walled Carbon nanotube nanocomposite for electrochemical determination of folic acid

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Key words: Nanocomposite, Polyaniline, Multi-walled carbon nano tubes, Electrochemical behavior, Folic acid.

Introduction:

Electroactive polymers have been an area of immense interest over the past 30 years since the first discovery of conducting polyacetylene in 1977 by Shirakawa et al. Extensive research on several conjugated polymers including poly (*p*-phenylene), polyaniline (PANi), polypyrrole, polythiophene, polyindole, and their substituted derivatives have led to their applications in rechargeable batteries, microelectronics, sensors, electrochromic displays, light-emitting and photovoltaic devices. Among the various conjugated polymers, PANi has received special recognition owing to its good stability and interesting redox behavior. Carbon nanotubes (CNTs) are an important group of nanomaterials with unique electronic and chemical properties. [1].

Folic acid, N-[p-{[(2-amino-4-hydroxy-6-pteridinyl) methyl] amino} benzoyl]-l-glutamic acid, is chosen at the analyte for this investigation because it is an electroactive component of considerable biological importance [2].

Materials and methods:

Highly purified MWCNTs (95%) with diameter of 60–90 nm were purchased from NanoKarbon Co. Ltd.,Korea. All reagents were of analytical reagent grade and were used as received. Aniline (99%), Ammonium peroxdisulfat (98%), Hydro cloric acid (37%), Ethanol





(99.9%), carbon nano tube, Tetrahydrofuran (THF), Folic acid (96-102%) and phosphate buffer solution (PBS) were merck. Just before synthesis nano composite, aniline was distilled. Aniline was stored in refrigerator. Insert atmosphere was set by passing N_2 over the solution during experiments.

Apparatus:

Electrochemical experiments were performed on a model AUTOLAB/PGSTAT320N Electrochemical Analyzer. A model KQ 3200 ultrasonic cleaner (Kunshan Ultrasonic Industrial Factory) was used. All experiments were done using a three-electrode cell configuration with a modified or unmodified glassy carbon working electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl [KCl(sat)] as the reference electrode. All potentials were measured and reported versus Ag–AgCl–KCl(sat).

Result and discussion:

Cyclic voltammograms were recorded in the potential range of 0.8 to -0.8V vs.Ag/AgCl reference electrode at a scan rate of 0.05Vs⁻¹. FA shows a well-defined cathodic peak at MWCNT-PANI/GCE at -0.19 V. On nano composite with the bare GCE, a 250 mV shift in peak potential and the increase in peak current demonstrate the efficient electrocatalytic behavior of MWCNT-PANI composite film towards the reduction of FA with good background current stability. The cathodic peak at -0.19 V is well developed and could be used for the quantitative and qualitative determination of FA. SEM techniques and TEM were used to investigate the morphology of the PANI/MWNT composites.

Conclusion:

In this present study the preparation of PANi–MWCNTs and their employment for the measurement of FA the have been described .The PANi–MWCNTs were prepared using an in situ chemical polymerization reaction between MWCNTs and PANi monomer. The presence of functionalized MWCNT composites caused an increase in the FA redation current. The morphology of the PANi–MWCNTs was studied by the SEM technique and TEM.





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Excited state of impurity binding energy in symmetrical multiple quantum dots GaN under electric and magnetic fields.

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Key words: Binding energy, Electric field, Magnetic field, Symmetric quantum dots.

Introduction:

Quantum dots (QDs) are typical examples of nanosystems where the electrons are confined in all three dimensional. The three dimensional nanoscale confinements of the charge carriers gives rise to complete quantum nature to these structures. The electron states in GaN QDs are highly affected by the built–in electric field due to the spontaneous polarization. In this article, effects of electric and magnetic fields on impurity energy levels at different impurity position is considered.

Materials and methods:

The system contains three cylindrical symmetric InGaN with radius R and length L_d , surrounded by two large energy gap material $GaN / In_x Ga_{1-x}N / In_y Ga_{1-y}N$. In the effective mass approximation the Hamiltonian of electron in the presence of external field and impurity is written as:

$$H = H_0 - \frac{e^2}{4\pi\varepsilon_0 r\varepsilon} \quad , \qquad H_0 = \frac{-\hbar^2}{2m} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial z^2} \right] + V(\rho, z) + eF|z| \tag{1}$$

$$H = H_0 - \frac{e^2}{4\pi\varepsilon_0 r\varepsilon} \qquad , \qquad H_0 = \left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 / 2m^* + V(\rho, z) \tag{2}$$

The magnetic and electric fields are in \hat{z} -direction. The confinement potential is [1]:





(4)

$$V(\rho, z) = \begin{cases} V(\rho) & z_1 \langle z \langle z_2, z_3 \rangle \langle z \langle z_4, z_5 \rangle \langle z \langle z_6 \rangle \\ V_{II} & otherwise \end{cases} \qquad V(\rho) = \begin{cases} 0 & \rho \leq R \\ V_I & \rho \rangle R \end{cases}$$
(3)

The wave function for H_0 are Whittaker function (in the presence of magnetic field) and Bessel function (in the presence of electric field). The energy levels of H are calculated by variational method with trial wave functions $\phi = \psi(\rho, \varphi, z)e^{-\alpha(\rho-\rho_i)^2 - \beta(z-z_i)^2}$, (ρ_0, z_0) is position of impurity. The impurity binding energy is given as [2,3]:

$$E_{b} = E_{0} - \min_{\alpha,\beta} \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

Result and discussion:

Exited state of binding energy in terms of impurity position z_i is plotted in Fig.1 and Fig.2. In the absence of fields, the binding energy is maximum and symmetric when the impurity is in the center of first and third QDs. The wave function is distributed inside the dot for on-center impurity. In the presence of electic field the wave function is pushed to $-\hat{z}$ direction and the peacks of binding energy are shifted, Fig.1. In the presence of magnetic field, the wave functions localize inside the QDs and binding energy increases Fig.2. (where $\mu = \hbar \omega_c / 2R^*$ is the dimensionless parameter depending on magnetic field).







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Effect of time dependent electric field on quantum dot in the presence of impurity and magnetic field.

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Key words: Dyson series, Impurity, Quantum dot, Time dependent electric field

Introduction:

The interest in the study of the physical properties of the confined quantum systems such as quantum wells, wires and dots has increased with the recent progress in semiconductor nanotechnology. Quantum size effects in these structures, lead to formation of atomic-like discrete energy levels. Recently, investigation of the impurity on the electronic structure and transport properties of QDs has motivated the attention of many researchers [1]. In this paper, the response of system to external sinusoidal electric field is investigated.

Materials and methods:

In the effective mass approximation, the Hamiltonian of electron in the presence of magnetic field is:

$$H_{0} = \frac{\left(P + \frac{e}{c}A\right)^{2}}{2m^{*}} + V(x, y)$$
(1)

Where $V(x, y) = \frac{1}{2}m^*\omega_0^2(x^2 + y^2)$ and A = (By, 0, 0) in Landau gauge. The wave function for

$$H_0$$
 is: $\Psi_0 = \phi_n(\alpha x)\phi_m(\beta y)$ (2)





Where ϕ_s 's are the harmonic oscillator eigen function, $\alpha = \sqrt{\frac{m^* \omega_0}{\hbar}}$ and $\beta = \sqrt{\frac{m^* \Omega}{\hbar}}$. The impurity potential is considered as repulsive (Gaussian) impurity [2]: $V_{imp}(x, y) = V_0 e^{-\gamma [(x-x_0)^2 + (y-y_0)^2]}$ (3) and external electric field is given as: $V(t) = \varepsilon_x \cdot x \cdot \sin(\gamma_x t) + \varepsilon_y \cdot y \cdot \sin(\gamma_y t)$ (4) In this case the Hamiltonian is written as: $H = H_0 + V_{imp}(x, y) + V(t)$ (5) The Hamiltonian, H, is solved by expansion of wave function and diagonolization of

Hamiltonian matrix, for different impurity position. The probability population of states is calculated by Dyson series and the variation of energy levels with time is:

$$E(t) = \sum_{k} E_{k}(0)P_{k}(t)$$
(6)

Where $E_k(0)$ and $P_k(t)$ are the eigen value of H_0 and probability of population of states, respectively.

Result and discussion:

The population versus time for $|2\rangle$ state at different impurity position with (circle symbol) and without magnetic field is shown in Fig. 1. As it is seen, in the presence of magnetic field the peaks are at different time, but without magnetic field the peak are at same times.



Fig.1.







Fig. 2. Shows the variation of energy with time for different impurity position with and without magnetic field. The curves reveal that a shift of impurity center away from the dot center is associated with an increase in the energy fed into the system.

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The role of impurities on the properties of electron transport through the metal /Diamantane /metal system : Green's function approach

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Key Words: Diamantane, Green's function, transmission function, density of state.

Introduction:

Diamondoids (nano diamond) is deemed to be an excellent material for the next generation of electronics. Pure Diamantane(DIM), $C_{14}H_{18}$, one of smallest diamondoid, is a wide-gap electrical insulator (7.24 eV)[1]. In this work, we report our Tight-binding (TB) studies of the quantum transport and electronic properties of DIM molecule either, pure and impure. We present our study on the electronic properties of diamantine and two other artificial molecules (DIM•As•Al) substituting tow carbon atom in diamantane with Arsenic and Aluminum sandwiched between electrodes.

Methodology:

We use a TB Hamiltonian model within the framework of a generalized Green's function (GF) technique as the basis for studying the electron transport of this system. We assume that the system includes the DIM molecule which is bonded one-dimensional metallic electrodes. Hamiltonian system is described with: $\hat{\mathbf{H}} = \sum_{\alpha} (\epsilon_{\alpha} + e\phi_{\alpha}) |\alpha \rangle \langle \alpha| + \sum_{\alpha\beta} t_{\alpha\beta} |\alpha \rangle \langle \beta|$, the first term describes the states with energies ϵ_{α} , ϕ_{α} is the electrical potential, $t_{\alpha\beta}$ at the second term is hopping matrix element between states $|\alpha\rangle$ and $|\beta\rangle$ in TB model. GF of the molecule is coupled to two electrodes in the presence of bias voltage is to: $G(\epsilon) = [(\epsilon + i\eta)I - H_{DIM} - \Sigma_L - \Sigma_R]$ where $\Sigma_{i=L,R}$ is contact self-energy (left and right respectively), H_{DIM} Hamiltonian of





DIM and η is an very small positive number. We used transmission function, $T(E) = Tr(\Gamma_L G^{\dagger}\Gamma_R G)$, that $\Gamma = i(\Sigma - \Sigma^{\dagger})$ and density of state, $Dos(E) = -\frac{1}{\pi}Im[Tr(G(\epsilon))]$, in our calculations[2,3].



Fig.1. (a), (b): metal/DIM/metal,(c), (d): metal/DIM•Al•As/metal

Using the above formalism we first calculated the density of states and transmission for a pure DIM, and DIM \bullet Al \bullet As which is presented in Fig. 1(a),(b),(c) and (d), respectively. According to the figures we see that DOS and T(E) by adding impurities increases.

Conclusion:

Our calculations show that the presence of impurity in Diamantine has significant effect on the energy gap and transmission which provides promising grounds for designing Diamondoid–based molecular devices.

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Kinetic study on photocatalytic degradation of methyl orange using microwave-assisted synthesis of ZnO nanoparticles

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Key words: Methyl Orange, Microwave, Photocatalysts, ZnO nanoparticles.

Introduction:

In recently, many studies have been made to investigate the photocatalytic activity of different semiconductors (e.g. SnO₂, ZrO₂, Fe₂O₃, CdS and ZnO). ZnO nanopowder has received much attention due to high photoactivity and non toxicity. In the present work, ZnO nanoparticles were prepared by microwave assisted combustion synthesis and the kinetics of methyl orange (MO) photocatalytical degradation was studied under UV light irradiation. The effect of catalyst dosage, concentration of dye, pH of dye solution on photocatalytic effect of ZnO nanopowder was investigated. [1, 2].

Materials and methods:

Zinc nitrate (Zn (NO₃)₂.4H2O) and Methyl orange ($C_{14}H_{14}N_3NaO_3S$) were Merck chemicals. Commercial Glucose ($C_6H_{12}O_6$) was used as fuel.

Apparatus:

For UV/ZnO process, irradiation was performed in a batch photoreactor of 500ml in volume with a mercury lamp Philips 15W (UV-C), microwave oven was used for synthesis of ZnO nanoparticles.

Result and discussion:

Photocatalytic degradation rate is related to different parameters such as catalyst dosage, and concentration of dye. Degradation rate of MO was investigated in the range of 100 to 200 ppm





of ZnO in MO solution. It was found that the maximum rate of degradation occurred in 160 ppm of ZnO. Concentration effect was studied in the range of 20-35 ppm of MO solution. Degradation rate decreased by increasing the initial concentration of MO.The effect of pH on the photodegradation efficiency of MO was operated in the range 6-10 in an aqueous ZnO suspension. The results showed that the degradation rate of MO decreases by increasing of pH solution. The plot $Ln(C/C_0)$ versus irradiation time for MO was linear suggesting that the photodegradation reaction follows the first order kinetics. Rate constant was estimated about (K=0.021 min⁻¹) from the slope of the $Ln(C/C_0)$ in the optimized conditions.

Conclusion:

The results obviously showed that ZnO nanopowder synthesized by combustion solution route could be efficiently used to degrade MO. ZnO amount, dye concentration and pH strongly effect photocatalytic degradation rate. The complete degradation achieved in a short time after selection of optimal operational parameters.

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Physicochemical Study on a System Consisting Interpolymer complex and Carbon Nanotube and Its Application in Drug Delivery system

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Keywords: Carbon Nanotubes, drug delivery, interpolymer complex, PEG.

Introduction:

Among the myriad nano material that are used as drug delivery systems carbon Nanotubes (CNTs) have some properties such as high aspect ratios, nanosized stability, and high surface areas that make them promising for preparation of unique drug delivery system. However, functionalized CNTs projected as a promising carrier for many drugs like anticancer agents because of their low citotoxicity and good drug delivery performances. It was proved that mucous adhesive polymer (e.g. PEG and PAA, ...) among the many kind of polymers is successful approach to drug delivery system.

Methotrexate is an anticancer drug belonging to the category of dihydrofolic acid reductase inhibitor used in the treatment of certain neoplastic diseases, severe psoriasis, and adult rheumatoid arthritis. It is used generally in higher doses for cancer treatment than required for other disorders and is often administered intravenously or intramuscularly. The drug's utility is limited due to its high systemic toxicity[1-4].

Hence, in this work, we synthesis a new carrier system consist of PAA/PEG/CNT. Then, Methotrexate was loaded on PAA/PEG/CNT, The result show that the new carrier is suitable and safe for drug delivery respect to CNT, CNT-COOH and CNT/PAA.

Materials and methods:

Multiwalled carbon nanotubes with outside diameter of 10-20 nm and length of 30 μ m was purchased from neutrino, Poly(ethylene glycol) (PEG) with a molar mass of 4000 and poly(acrylic acid) with molar mass of 100000 were gained from Sigma chemical company.





Methotrexate purchased from KOCAK FARMA.

Apparatus:

FT-IR, TGA, Scanning Electron Microscope (SEM), ¹HNMR were used in the analytical part of work. Characterization of functionalized carbon nanotubes and MWNT-PEG-PAA nanocomposite is done by FT-IR and HNMR spectroscopy and TGA method. The morphology of nanocomposite particles has been determined by SEM. Vacuum oven has been used for drying the functionalized carbon nanotubes at each step of the synthesis.

Result and discussion:

Functionalization of MWNTs by COOH group was performed by a technique developed by Esumi et al (1995). MWNT- COOH was reacted with SOCl₂ to form MWNT-COCl. To achieve MWNT -PEG, triethyl amine and PEG was added to MWNT-COCl and the mixture was stirred at 60°C under nitrogen for 3days. Loading of the Methotrexate was done from the stirring of MWNT-PEG and PAA and Methotrexate in phosphate buffer for 24 h.

Conclusion:

Methotrexate loaded in this system were done by functionalization of multiwall carbon nano tubes effectively with drug loading capacity of about 65%.

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Influene of pH on Structural Properties of Mn Ferrite Nanoparticles via Sol - Gel Combustion Method

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Introduction:

Manganese Ferrite belongs to a group of soft ferrite materials recognized by high magnetic permeability. Nanoparticles of Mn Ferrite have widespread applications such as magnetic recording media, drug delivery technology, magnetic resonance imaging (MRI) [1]. Preparation condition affected by several parameters such as pH of precursor, calcination temperature, calcinations time, rate of citrate to nitrate and atmosphere of the process. In this paper, effects of pH of the solution on the formation of manganese ferrite fine particles by sol - gel combustion method, were investigated. The obtained powder was characterized by XRD, TG - DTA, FT - IR and SEM analysis.

Materials and Method:

The chemical materials used were metal nitrates such as $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2.4H_2O$, $C_6H_8O_7.H_2O$ and ammonia to prepare $MnFe_2O_4$ nanoparticles. Molar ratio of nitrates to citric acid was 1:1. During the stirring, ammonia solution is added dropwise to get a transparent solution to adjust the pH. The obtained sol was heated at 80°C in a water bath for about 24 h. The formed gel was ground and then heated at 200°C for 2h in furnace. The auto - combustion of the mixture takes place and it was milled in a mortar. The fine particles were calcined at 300°C for 1 h.

Apparatus:

The heated and combusted specimens were characterized using X-ray diffraction using $Cu_{K\alpha}$ radiation wavelength $\lambda = 1.5406$ Å (XRD; type: SIE: ID 3003), Fourier transform infrared





spectroscopy (FT-IR; Parkin Elmer BXII), scanning electron microscopy (SEM; Philips XL300), thermo gravimetric (TGA) and differential thermal analysis (DTA) at a heating rate of 10°C/min in air. The crystallite sizes of $MnFe_2O_4$ in the obtained specimens were estimated by employing Scherrer's formula in the profiles of (3 1 1) XRD peak of $MnFe_2O_4$.

Result and Discussion:

The TGA curve showed a single major weight loss at 300°C and correspondingly the DTA curve exhibits an exothermic peak about at the same temperature. The XRD analysis identified as MnFe₂O₄ (JCPDS card No.01-074-2403) and demonstrated that the formed crystallites belongs to the space group Fd - 3m and average particle size was 22 nm. This result indicated that, after Combustion, MnFe₂O₄ gel can be directly transformed into single phase nanocrystalline Mn ferrite crystallites. With increasing pH value, \propto -Fe₂O₃ and Mn₂O₃ crystallites were been detected. FT - IR spectra of samples showed that the metal - oxide vibration band 570 cm⁻¹ assigned the band to the tetrahedral group that corroborated the spinel structure [3]. SEM photographs showed that when pH was increased, samples exhibited agglomerated microstructures and for pH = 8 – 9, nanoparticles were uniform sized and sample consists of grains with average size of 40 nm.

Conclusion:

The MnFe₂O₄ nanoparticles have been prepared using sol – gel combustion technique. Nanocrystalline MnFe₂O₄ is unstable and tends to oxidize to form \propto -Fe₂O₃ and Mn₂O₃ in air at changing of pH. The pH value of the mixed precursor solution has a considerable influence on the morphology of the dried gel. With increasing pH value, the combustion rate is increased [2].

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Structural and Magnetic Properties of MnFe₂O₄ nanoparticles Substituted by Co²⁺

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Introduction:

The essential formula for a spinel compound MFe_2O_4 can be written as $(M_{1-i}Fe_i)_A[M_iFe_{(2-i)}]_BO_4$, (M = Mn, Co, Zn, Mg, etc) where M^{2+} is a divalent cation and the amounts in brackets represent the average occupancy of (A) tetrahedral sites and [B] octahedral sites and i is in the inversion parameter. So the special properties of ferrites are strongly related to the distribution of cations between octahedral and tetrahedral sites in the spinel structure [1].

Materials and Method:

 $Co_xMn_{1-x}Fe_2O_4$ compounds with x values ranging from 0.0 to 0.5, have been prepared by solgel combustion method, using high purity metal nitrates and citric acid as starting materials [2]. Ammonia was added to the solution to adjust the pH value. The precursor was calcined at 300°C for 1h.

Apparatus:

The samples were characterized by X - ray diffraction (XRD) using $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å) of a diffractometer (type: SIE: ID 3003). Fourier transform infrared spectroscopic (FT - IR) study was carried out in KBr medium using Parkin Elmer BXII system in the range of 400 – 4000 cm⁻¹. Scanning electron microscope (SEM) (type: Philips XL300) was used to investigate the microstructure. Vibrating sample magnetometer (VSM) has been used to study the hysteresis characteristics at the room temperature under the field up to 6 kOe.

Result and Discussion:





The XRD patterns showed that the formed crystallites were all in the cubic single phase. Lattice parameters were calculated by Bragg's formula. As a result, by increasing Co content up to x = 0.5, lattice parameter increases for 8.363 Å to 8.395 Å. This increase in lattice parameter may be attributed to the replacement of smaller $Mn^{3+}(r = 0.65 \text{ Å})$ ions by the larger $Co^{2+}(r = 0.78 \text{ Å})$ ions and reduction of $Fe^{2+}(r = 0.77 \text{ Å})$ ions to $Fe^{3+}(r = 0.64 \text{ Å})$ ions in the octahedral sites spinel ferrite for charge compensation. According to the data of FT - IR spectra of $Co_x Mn_{1-x}Fe_2O_4$ nanoparticles, it was observed that absorption band at 572 cm⁻¹ can be attributed to tetrahedral sites in spinel. The band associated with water molecule is observed in the region of 3423.09 cm⁻¹ which indicates the presence of water crystallizations in samples [2]. By the SEM micrographs of the CoMn ferrite samples studied, and it can be seen that particles of samples are spherical in shape with the average grain size varies between 30 nm and 40 nm. Also magnetization measurements lead to conclude that the saturation magnetization (M_s) of manganese ferrite goes on increasing with Co^{2+} content up to x = 0.5. These studies demonstrated that by substitution of Co on Mn ferrite, Co^{2+} ions are replaced on Mn^{3+} ions in B sites and Fe^{2+} ions are to be reduced to Fe^{3+} ions and Fe^{3+} ions that occupied on B sites migrated to A sites. Since magnetic moment of $Co^{2+}(3\mu_B)$ is smaller than magnetic moment of $Mn^{3+}(4\mu_B)$, and magnetic moment of $Fe^{3+}(5\mu_B)$ is larger than magnetic moment of $Fe^{2+}(4\mu_B)$, exchange interaction between Fe^{2+}_B - Fe^{3+}_B is stronger than Co^{2+}_B - Mn^{3+}_B and Mn^{3+}_B -Fe²⁺_B, thus exchange interaction between Fe^{2+}_{B} -Fe³⁺_B is dominant interaction, therefore saturation magnetization is enhanced with addition of Co^{2+} concentration in Mn ferrite for x < 0.5.

Conclusion:

 $Co_xMn_{1-x}Fe_2O_4$ nano powders have been successfully synthesized by sol - gel combustion method. The X - ray diffraction study and FT - IR spectra revealed the formation of single phase cubic spinel. The changes in the magnetization at room temperature, on the substitution of Co on Mn ferrite, may be obtained because of the difference in the contributions from the magnetic moments of the substituted ion on the A site and B site of the spinel ferrite.





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Tuning Localized Surface Plasmon Resonance of Nanoshells for Biological Applications

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Keywords: Light scattering, Nanoshell, Plasmon resonance, Biosensor

Introduction:

When a nanoshell consisting of a dielectric core coated by a thin metallic shell is illuminated by a plane wave, localized surface plasmon (LSP) is excited inside the nanoshell. The wavelength at which the resonance occurs depends on the core and shell sizes and refractive index of surrounding medium. Therefore, by proper adjusting these parameters one can tune the localized surface plasmon resonance (LSPR). In particular, since LSPR is very sensitive to background refractive index, it can be utilized as an accurate biosensor. In this work, we compare the sensitivity of gold nanoshell (GNS) with that of gold nanoparticle (GNP) and show that the LSPR of the GNS can be more easily tuned within a wide range of spectrum. Then we illustrate the effect of background refractive index on the LSPR and demonstrate that it can be used as a sensing tool for biological application [1-3].

Method:

The problem geometry is depicted in Fig. 1. A GNS consisting of a silica core and gold shell with radiuses r_1 and r_2 , respectively, is illuminated by a plane wave. To calculate the scattering cross-section (SCS), the electromagnetic fields in each domain are expanded by vector harmonics, and the coefficients are obtained by imposing electromagnetic boundary conditions on interfaces of core-shell and shell-environment.



Fig 1. Schematic of GNS illuminated by a plane wave. 2525





Result and discussion:

Fig. 2 shows the calculated spectra of the scattering efficiency (Q_{sca}) for GNPs with various radiuses. Tunability of the LSPR with size is not enough to be used for biosensing. Fig. 3 shows the same calculations for the GNS. As it can be seen, the LSPR can be tuned over a wide range of spectrum from around 700 to 1200 nm. To investigate the effect of background refractive index, the Q_{sca} is calculated for the GNS in various background media including air (n=1), water (n=1.33), ethanol (n=1.36), ethanol-toluene (n=1.429) and toluene (n=1.495). The result is shown in Fig. 4. It is seen that a minor change in the refractive index can cause a measurable change in the LSPR, so that it can be employed as an accurate biosensor.



Fig 2. a) Scattering efficiency versus wavelength for GNP of various radiuses. b) LSPR versus radius



Fig 3. a) Scattering efficiency versus wavelength for GNS of various thicknesses. b) LSPR versus thickness



Fig 4. a) Scattering efficiency versus wavelength for GNS in various backgrounds. b) LSPR versus background refractive index





Conclusion:

The tunability of LSPR excited in GNS and GNP was compared. It was shown that GNS is a better candidate for biosensing due to its high sensitivity to background refractive index and wide range of spectral shift.

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The Adomian method for nano-sized model including Murrel-Mottram potential and Casimir force

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Keywords: Adomian's method; Murrel-Mottram potential; Casimir force; nano oscillator model

Introduction:

Nonlinear equations attracted a great deal of interested in applied science. The Adomian decomposition method [1] has been applied to solve the nonlinear equation from the onedimensional model including Murrel-Mottram potential [2] and Casimir force [3] with fractional damping. The Casimir force is studied because of its applications in NEMS systems.

The one degree of freedom mass-spring model:

Our model is a one-dimensional oscillator consisting of a sphere with radius R and mass m, which is suspended by means of vertical elastic wire which produces a force originating in particular potential, on a horizontal conducting surface. The Casimir force is present between the sphere and conducting. A perturbing force F, a fractional damping and the weight forces act on the sphere. It is considered that the anharmonic elastic force acting in the case of oscillators of the nano-devices originates from Murrel-Mottram potential. We solved this model with considered three cases including the third, fourth and fifth order coefficients in expansion.

Result and discussion:

The method presented in this work can be applied for other potential of oscillator within our





model and with any potential, but some terms are independent of the nature of the applied potential. One can apply this method to expand the nonlinear terms as higher powers. This work could be evaluated on a three dimensional model. With considered the resulted equations and since all their plots and contour plots for three cases (Fig.1) are perfectly alike, one can result that the series in expansion of exponents and fractional terms converge very rapidly.



Fig. 1. plot and Contour plot of displacements from the equilibrium position for three cases (that are equal).

Conclusion:

A nonlinear equation from the one dimensional oscillator model with fractional damping and nonlinearity due to Casimir force and anharmonic elastic force deriving from Murrel-Mottram potential have been investigated. The solution has been obtained with Adomian's method.

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Effects of External Electric and Magnetic Fields on the Linear and Nonlinear Optical Properties in a Quantum Pseudodot

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Keywords: Quantum Pseudodot, Optical Properties, Electric and Magnetic Fields.

Introduction:

Small solid state devices, such as quantum dots (QDs), can confine a few electrons in all spatial dimensions. The three-dimensional nanoscale confinement of the electrons makes it possible to observe quantum size effects on electronic and optical properties in these structures. Because of their importance in the optical properties, quantum dots have gained significant attention. One of the most interesting properties of the quantum dots is the possible occurrence of the intersubbands optical transitions. The dipole matrix elements of the optical transition between the subbands of the quantum dots have significantly large value. A very large dipole matrix element and small energy separation between subbands dramatically enhance the contribution of nonlinear parts of the dielectric constant and other optical absorption coefficient and index of the refraction of semiconductor nanostructures such as quantum dots [1-4].

Materials and methods:

In the present paper, within the framework of the effective mass approximation, combined effects of external electric and magnetic fields on the linear and the third-order nonlinear optical absorption coefficients and refractive index changes of a three-dimensional spherical quantum pseudodot system, with pseudoharmonic potential are investigated. We considered an





electron confined in a three-dimensional pseudoharmonic QD. Energy eigenvalues and eigenvectors are obtained using the matrix diagonalization method, and the linear and nonlinear optical properties are calculated by the density matrix approach.

Result and discussion:

We have plotted the variations of the linear, the third-order nonlinear and the total optical absorption coefficients and refractive index changes as a function of the photon energy for different values of external electric field strength. We do our calculations for GaAs QD with carrier intensity 3×10^{16} cm⁻³, the effective mass and static dielectric constant are consider to be $0.067m_e$ and 13.18 respectively. As it is seen, the magnitudes of these optical quantities increase and their peaks shift to lower energy regions with the increment of the external electric field. Our results show that the external fields have a great influence on these optical quantities.



Figure 1: The dependence of the linear, the third-order nonlinear and the total optical absorption coefficients and refractive index changes on the photon energy and external electric field strength.

Conclusion:

We have been studied the influence of external electric and magnetic fields on the linear and nonlinear optical properties. We have used the density matrix approach to calculate these properties. According to the results obtained from the present work, we have found that the electric and magnetic fields play an important roles on the linear and nonlinear optical absorption coefficients and refractive index changes of a spherical quantum pseudodot system.





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Corrosion study of nanocomposite epoxy / metal in an alkaline environment

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Introduction:

Nanotechnology, which is currently one of the most active research fields, takes advantage of the fact that nanomaterials have unique mechanical, electrical, and thermal properties. For example, the high surface areas of conducting nanoparticles (NPs) provide continuous conducting pathways and extremely large interfaces when mixed with polymer matrices. Such composites are usually applied as electromagnetic interference (EMI) materials.[1] Controlling the dispersion process remains one of the most serious challenges when preparing polymer nanocomposites because the intrinsic vander Waals attractions [2,3] and high surface energies of NPs result in their tending to aggregate together. As a result, such NPs have very low solubilities in most solvents.

Experimental:

Unless otherwise indicated, all chemicals used were of analytical grade and were used as received. The epoxy resin, Epon 828 (DGEBA), was obtained from Shell Chemicals. All aqueous solutions were prepared to use deionized water.

The DDS, TETA and methanol were purchased from Merck, and cupric sulfate, nickel sulfate and silver nitrate from Alderich. The stock solutions of cupric sulfate, nickel sulfate and silver nitrate $(10^{-1}, 10^{-1}, 2 \times 10^{-1} \text{ mol dm}^{-3})$ were prepared in distilled water.

Sodium Chloride (NaCl, 99%) was purchased from Merck (Darmstadt, Germany).

Result and discussion :

FTIR spectral studies of the homopolymers, mixture of homopolymers and copolymers were carried out, and sample spectra is presented in Figure 1. Figure 1 presents FTIR spectra of the





hybrids prepared by this absorption-transferring process. The intensity of the signal for the epoxide group (860 cm⁻¹) decreased after polyDDS had been added, that is, the amino groups on the surface of polyDDS could have reacted with the epoxide rings. These spectra revealed that polyDDS was also a curing agent of epoxy. The FTIR spectrum of polyDDS (spectrum in Figure 1) exhibited characteristics peaks as reported already and the peak absorption frequencies are given in Table 1. The IR spectrum, Figure 1a (polyDDS-Cu/ DGEBA.TETA), reveals the presence of the different species, which are involved in the fabrication of the composite polymer. The bands at 3470, 3350, and 3215 cm⁻¹ correspond to the N-H stretching vibration, whereas the bands at 3050, 2970, and 2850 cm⁻¹ result from the aromatic C-H stretching vibration. The peak at 1600 cm⁻¹ is due to the stretching deformation of the quinone ring. The 1280 cm⁻¹ band is assigned to C-N stretching in a secondary aromatic amine, whereas the peaks at 1080 and 1150cm⁻¹ represent the aromatic C-H in-plane bending modes. The out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring is located at 835 cm⁻¹.

The bands at 3120 and 3030 and 2980 cm⁻¹ are assigned to aromatic C–H stretching modes. The band at 1270 is assigned to the C–N stretching mode in a secondary aromatic amine. Two bands at 1100 and 830 cm⁻¹ correspond to an aromatic C–H in-plain bending mode.



Figure 1. IR spectrum of the composite material. (a) polymer-Cu.





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Corrosion rate of nanocomposite epoxy / metal in an acid environment

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Introduction:

Conjugated polymers have attracted enormous attention in both science and technology as semiconductors and electro active materials for such applications as batteries, molecular electronic devices and light emitting diodes (LED), etc. [1,2]. Electroluminescence has emerged as a promising application of liquid crystal display (LCD) devices involving semiconducting polymers [3-5]. Inorganic nanoparticles of different sizes and shapes can be combined with conducting polymers to form composite materials. The incorporation of inorganic nanoparticles in conducting polymers can provide an enhanced performance for both the "host" and the "guest" that can lead to interesting physical properties and important potential applications such as electrodes of batteries, display devices, immunodiagnostic assay, etc.[6].

Experimental:

Unless otherwise indicated, all chemicals used were of analytical grade and were used as received. The DDS and methanol were purchased from Merck, and cupric sulfate, nickel sulfate and silver nitrate from Alderich. The stock solutions of cupric sulfate, nickel sulfate and silver nitrate $(10^{-1}, 10^{-1}, 2 \times 10^{-1} \text{ mol dm}^{-3})$ were prepared in distilled water.

Scanning electron microscopy (SEM) images are taken using a VEGA HV (high potential) 1500 V at various magnifications. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) attached to the SEM was used to determine the chemical composition of the samples.





The electrical conductivities of the blends were measured by using a Keithley 6517A electrometer, a multimeter Minipa ET2907 and a homemade four probes device with a medium distance between the probes of 0.171 ± 0.03 cm. The measurements were performed on a disk film with a thickness of 0.5mm.

Result and discussion :

SEM studies, Figure 1, reveal the morphology of the composite material. Image shows a thin layer having a thickness in the range of 70–90 nm.



Figure 1. SEM image of the (a) poly DDS-Cu.

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Hydrogen adsorption of Single-Walled Nano-Cones: a Grand Canonical Monte Carlo Study

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Key words: Single-walled Nano-Cones, Adsorption, Hydrogen Storage, GCMC Simulation.

Introduction:

Hydrogen storage is an important prominent component of many industrial goals, and is of great interest to both scientists and investors for economic and environmental reasons [1]. Extensive studies that were ultimately aimed at efficient hydrogen storage in nanostructures and which utilize either experimental or theoretical approaches have been performed [2, 3]. Since nanotubes discovery by Iijima in 1991 [4], carbon nanotubes (CNTs) have been found to be new suitable materials for hydrogen storage [5]. However, most investigations have indicated that the hydrogen storage capacity of CNTs and CNT arrays at room temperature and moderate pressure cannot reach the U.S. Department of Energy (DOE) targets for vehicular fuel cells. The DOE 2015 targets are reported to be 9 wt% [6]. Ge and Sattler [7] originally discovered carbon nano-cones in 1994, and Krishnan et al. [8] have subsequently synthesized cones with all five opening angles.

In this report, we try to compare the hydrogen storage capability of single-walled nano-cones with single-walled nanotubes numerically using grand canonical Monte-Carlo (GCMC) simulation [9].

GCMC simulation details:

We use GCMC simulations to study hydrogen loading in four single-walled nano-cones (SWNCs): carbon, boron-nitride, silicon-carbide and silicon nano-cones that are abbreviated as SWCNCs, SWBNNCs, SWSiCNCs and SWSiNCs respectively.



Lennard–Jones potential is adopted to model the interactions between two particles with Lorentz–Berthelot combining rules.

During GCMC simulation, SWNCs are taken as a simulation cell and three types of operations with equal probability are performed randomly in the simulation cell: displacement, creation and deletion [9]. The steps are repeated until the number of hydrogen molecules in the cell comes to the equilibrium. Furthermore, periodic boundary conditions (PBC) are set on the SWNCs during displacement [9].

Results and discussion:

By fixing temperature at 298 K and length of SWNCs of 40 Å, and varying pressure of (0–15 MPa) and tube angle of (60, 120, 180, 240 and 300°), we can draw a tuft of hydrogen adsorption in SWNCs. We also simulate hydrogen adsorption of SWNCs at 298 K and varying pressure of (0–15 MPa) and increasing length of SWNCs from 35 to 70 Å (8 length) in fixing tube angles. The results show that hydrogen adsorbability in SWNCs is followed by SWSiNCs>SWSiCNCs>SWBNNCs>SWCNCs respectively.

We also calculate the Langmuir, Freundlich and Langmuir-Freundlich equation parameters for hydrogen adsorption in SWNCs in different nano-cones structural conditions. Although, our study has NOT finished and it is being completed.

Conclusion:

This paper using grand canonical Monte-Carlo simulation tries to explain the existence of the optimal thermodynamics and single-walled nano-cones structural conditions to achieve the best hydrogen storages inside single-walled carbon, boron nitride, silicon-carbide and silicon nano-cones. The energies and the isotherms of hydrogen adsorption in single-walled nano-cones are plotted to we can compare hydrogen adsorptivity property of single-walled nano-cones with adsorptivities of hydrogen inside nanotubes and nanotubes arrays.

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Study of quantum of absorption of toxic gases in the air by the open nanocone coupling with the iron atom

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Keywords: "Nanocone, Toxic gases, Quantum calculation, Optimization"

Introduction:

The annual number of people worldwide, especially in developed countries, effects of inhaling toxic gases and pollutants in the air, lose their lives. Given the critical nature of this problem, various research works has been done by researchers around the world but never as much as it is not desirable to reduce.

Methods:

Among quantum chemical methods, the DFT has some merits, one of which is the inclusion of the relativistic effect as an electron correlation term. So far, a hybrid version of DFT and Hartree–Fock (HF) methods, i.e. B3LYP, has been introduced as one of the most accurate methods for energy calculation [1,2].

Results and discussion:

In this study, the first open Nanocone [3], with apex angle= 38.9° in B3LYP level of theory and the optimal basis set was optimized. Then an Iron atom was placed at the head and with the same basic level optimization was performed. The number of toxic and harmful gases in the air (carbon monoxide, carbon dioxide, chlorine, carbonyl chloride, hydrogen sulfide, sulfur dioxide, cyanogen) each one separately after the initial optimization were absorbed on the structure of open Nanocone coupled with the Iron atom then was obtained their energy and structural information (Fig. 1).



(2)



Figure 1: Optimized structure of the absorbent system of Nanocone coupled with:

a) Fe b) Fe-SO₂ c) Fe-CO2 d) Fe-CO e) Fe-C₂N₂ f) Fe-H₂S g) Fe-COCl₂ h) Fe-Cl₂ with B3LYP In order to achieve energy absorption between toxic gas molecules, Iron atom and Nanocone and also the absorbed energy between the molecules of toxic gas and open Nanocone coupled with the iron atom, the following relationship was used:

$$E^{(1)}_{abs} = E_{NCFe-gas} - E_{NC} - E_{Fe} - E_{gas}$$
(1)

$$E^{(2)}_{abs} = E_{NCFe-gas} - E_{CNFe} - E_{gas}$$

Important point, the difference between $E^{(1)}$ and $E^{(2)}$ in the absorption of a specific gas if these two systems have not very different. This shows that in the hybrid systems, it is important effect of a basic set of a molecule on basic set of other molecule. So can be said that at a closer look may is not correct such an interpretation of absorption because the interaction energy between open Nanocone with Iron atom and toxic gas molecules is not considered. In order to adapt error correction based series and its impact on the energy levels changed during the operation method three organic was used and Energy absorption corrected and not corrected between the molecules of toxic gas and the open Nanocone coupled with the Iron atom were compared with each other. Observations showed that the absorption of chlorine toxic gas by open Nanocone coupled is better than other toxic gases and Carbon monoxide gas is the lowest absorption among other gases.

Conclusions:

In this study to investigate the structure of open Nanocone coupled with the Iron atom and its impact on absorption some of the most toxic and most dangerous gases in the air also were





obtained another very interesting results which represents the greatest role of these structures as absorbing structures to reduce the toxic gases in the air.

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Theoretical study of NO adsorption on the surface of Nanotube doped by Ga

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Keywords: Nanotube ; B3LYP ; sensors ; adsorption

Introduction:

The purpose of this study is Investigation of NO adsorption on carbon nanotube doped by Ga based on the density functional theory (DFT) at various positions of NO gas molecules relative to nanotube (top, and central sites). The optimum structure and vibration frequencies of this system are obtained by using of B3LYP level of theory and 6-311G basis sets with Gaussian 03 program. As the adsorption of NO on Ga doped nanotube is more than non doped nanotube it can use as a gas sensor.Recently researchers have more significant attention on adsorptions of gas by nanotubes due to their important role as components of model-catalysts, sensors and etc[1].

Method:

the calculation studies on this system have been carried out by using the Gaussian 03[2]. The theoretical density functional method with basis sets can be used for determining of the optimum structure and results. Adsorptions energies, the vibration frequencies, thermodynamic properties, HOMO, LUMO energy levels and density of state (DOS) have been extracted from these calculations.

Results and discussions:

This research is a full computational study on the geometry structures of Ga-doped singlewalled carbon nanotubes (SWCNT) fragments capped with H atoms and investigation of NO





atoms adsorption on it. In this order we used the B3LYP methods. The optimum energy of system that was obtained from each method and basis set have been reported in table 1. These data show that the minimum energy and therefore the optimum structure can be obtain from B3LYP/6-311G method and bases set. In the future we decide to calculate other physical and thermodynamic properties for this system by using of B3LYP/6-311G.

Method	Basis set	$E_{calculation(HF)}$	
B3LYP	6-311G	(tube)-2448.7296783	
B3LYP	6-311G	(tube doped by Ga) -4334.8188693	
B3LYP	6-311G	(tube doped by Ga+NO) -4464.6907594	

Table 1: the results of calculation energy by different step

Table 2: The energy level of HOMO and LUMO and hardness.

		\sim		
Method	Basis set	LUMO	НОМО	Hardness
				(eV)
B3LYP	6-311G	-0.13266	-0.23768	0.05251
B3LYP	6-311G	-0.14460	-0.16832	0.01186
B3LYP	6-311G	-0.06635	-0.22428	0.078965

Conclusions:

The adsorption of NO gas on Ga doped nanotube has been studied within density functional theory. The best results have been extracted from B3LYP/6-311G calculation. By exposing an Ga-doped SWCNT to a variety of gas, we envision an application of this proposed material in both sensor technology and nanoelectronics. We believe that such initial investigations should provide experimentalists with a first look into the chemical and physical properties of these new materials and will further encourage continual research in this field in the years to come.





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Synthesis and Characterization of Co/Fe/Sn Nanowire arrays in Alumina Templates

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Key words: alloy nanowire, magnetic properties, anodic aluminum oxide, ac electrodeposition.

Introduction:

Highly ordered nanostructured material arrays with controlled diameter and composition have attracted much attention [1] in recent years due to their unique properties and potential applications in optoelectronics electronics, photonics, and magnetics. Creations of well ordered metallic nanowire arrays have become important aspects to realize their promise in ultrahigh-density perpendicular magnetic recording media. Since the magnetic properties are related to their element component, morphology, and microstructure [2], alloy nanowires are expected to exhibit the perpendicular anisotropy. Among these materials, Co-Fe alloy nanowires, especially chemically ordered Fe₃Co₇ with body-centered cubic (bcc) structure have been the focus of extensive research activities due to their large uniaxial magnetocrystalline anisotropy and good chemical stability [3].

Materials and methods:

An annealed Al (99.99%) sheet was anodized at 25 V in 0.3 M H_2SO_4 for 7 h to get a porous aluminum oxide (AAO) template. The Co-Fe-Sn alloy nanowirees was then deposited into the pores by AC electrolysis in an electrolyte consisting of $[Co_{70}Fe_{30}]_{100-x}Sn_x$ formula of $CoSO_4.7H_2O$, FeSO₄.7H₂O, SnSO₄.7H₂O, sodium gluconate and ascorbic acid (0.25 g/l) at a pH value about 3.0. The electrolysis was conducted at room temperature, 200 Hz and 30 V ac





for 5 min using Pt as the counter-electrode. The magnetic properties were studied at room temperature by alternating gradient field magnetometer (AGFM).

Result and discussion:

Magnetic properties of the Co-Fe-Sn nanowires were investigated at room temperature using an alternating gradient field magnetometer (AGFM) with an applied field of 5 KOe. Fig. 1 shows the magnetic hysteresis loops of $[Co_{70}Fe_{30}]_{100-x}Sn_x$ nanowire arrays as-deposited for 5 min, where the applied field is parallel (//) to the nanowire's axis. Samples measured along the wire are 1097 and 1914 Oe and the squareness ratios are 0.928 and 0.992, respectively. Fig. 2 and Fig. 3 plots the coercivity Hc and squareness (Mr/Ms) as a function of Sn percentage in nanowire.. The coercivity and remanence ration were measured with the magnetic field parallel to the wire axis. For the as-deposited sample the coercivity and remanence ration Mr/Ms are about 1600 Oe and 0.996, respectively. The coercivity decreases with increasing Sn percentage and The remanence ratios Mr/Ms for the samples increases with increasing Sn percentage in nanowire.



Fig. 1. Typical hysteresis loops of the samples measured in a magnetic field parallel to the long axes of



Fig. 2. Composition dependence of coercivity in parallel to the $[Co_{70}Fe_{30}]_{100-x}Sn_x$ nanowir25.49



Fig. 3. Composition dependence of squareness in parallel to the $[Co_{70}Fe_{30}]_{100-x}Sn_x$ nanowires.





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Effect of annealing temperature on magnetic properties of [Co₇₀Fe₃₀]₉₇Sn₃ nanowire arrays

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Key words: Nanowire, Coercivity, Ac electrodeposition, Hysteresis loops, Squareness

Introduction:

Solid metallic nanowire is a one-dimension material. It has been exploited for a wide range of applications that take advantage of their large aspect ratio (length/diameter). Recently, fabricating nanowires by atomic deposition such as, electrodeposition method is emphasized in literature [1]. Nanofabrication allows us to manipulate the size, shape, orientation, and composition of the structure. When the shape anisotropy of magnetic grain was very high, high coercivity and squareness (Mr/Ms) can be obtained, which is very suitable for magnetic recording [2].

Materials and methods:

An annealed Al (99.99%) sheet was anodized at 25 V in 0.3 M H₂SO₄ for 7 h to get a porous aluminum oxide (AAO) template. The Co-Fe-Sn alloy nanowires was then deposited into the pores by AC electrolysis in an electrolyte consisting of $[Co_{70}Fe_{30}]_{97}Sn_3$ ratio of $CoSO_4.7H_2O$, FeSO₄.7H₂O, SnSO₄.7H₂O, sodium gluconate and ascorbic acid (0.25 g/l) at a pH=3.0. The electrodeposition was conducted at room temperature, 200 Hz and 30 V ac for 5 min using Pt as the counter-electrode. To investigate the effect of annealing temperature on the magnetic properties of $[Co_{70}Fe_{30}]_{97}Sn_3$ nanowire arrays, the samples were annealed at different temperature: 200, 300, 400, 500, 550 and 575 °C, in argon atmosphere for 20 min, then slowly cooled down to room temperature. The magnetic properties were studied at room temperature by alternating gradient field magnetometer (AGFM).





Result and discussion:

We found that a significant increasing in the coercivity in all annealing temperature. Magnetic hysteresis loops for the annealed sample showed in Fig. 1. The effects of annealing temperature are showed in Fig. 2 and Fig. 3. This shows clearly that when the applied field is parallel to nanowire arrays, the coercivity increases with temperature and reaches its max value (2050 Oe) at about 500°C then decreases almost linearly to 1888 Oe at 575°C. The squareness of the samples annealed at 500°C temperature was up to 0.99 higher than that of as-deposited samples. The increasing in coercivity and squareness can be explained by a number of factors. Firstly, after annealing, internal stress in the as-deposited samples reduced rapidly and a higher degree of crystallinity was obtained. Furthermore, there is a large mismatch between the thermal expansion coefficients (α) of FeCo alloy and alumina [2]. Additionally, FeCo would react with O₂ existed in AAO template at high temperature(550 and 575) and the present of FeCo oxide would decrease the Ms largely in the sample. All these factors will reduce the anisotropy along the axis of [Co₇₀Fe₃₀]₉₇Sn₃ nanowires arrays.



Fig. 1. Magnetic hysteresis loops for the annealed sampleOut of plane: with external field parallel to the nanowire





Fig. 2. The coercivity as a function of temperature.

Fig. 3. The squareness as a function of temperature.





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Removal of Organic Pollutants from Water by Multiwalled Carbon Nanotube/ Poly(ethylene glycol)/ β-Cyclodextrin Nanocomposite

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Key words: Organic pollutants, Carbon nanotube, β-Cyclodextrin, Nanocomposite

Introduction:

The existence of organic pollutants in soils and water systems is currently a big problem of global concern because of their harmful effects on ecosystem and human health .Such organic compounds which include polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and endocrine disrupting compounds (EDCs) that can be toxic or carcinogenic even at low concentrations and non-reactivity of these species makes it difficult to remove them from water. Several common techniques such as activated carbon, ozonation, zeolites and reverse osmosis are being used for water treatment. However some of these methods are often associated with many problems, such as low efficiency, high cost or generation of some more toxic by-products which make them ineffective. Carbon nanotubes as a new adsorbent, have an excellent absorption capability for removal many organic molecules. However, the insolubility of CNTs in most organic and aqueous solvents limits the application of CNTs in solution phase.

Cyclodextrin based insoluble polymers can remove organic pollutants effectively through the formation of inclusion complexes. CDs cant remove organic molecules directly due to the good solubility in aqueous solutions [1-3].

In this study, Multiwalled carbon nanotube/polyethylene glycol/β-cyclodextrin nanocomposite as an excellent adsorbent for organic species is synthesized and then is used for removal 2-biphenylamine from aqueous solutions.





Materials and methods:

Multiwalled carbon nanotubes with outside diameter of 10-20 nm and length of about 30 μ m was gained from neutrino. Poly(ethylene glycol) (PEG) with a molar mass of 4000 and β -cyclodextrin purchased from Sigma chemical company. The method based on functionalization of carbon nanotubes.

Apparatus:

Vacuum oven has been used for drying the functionalized carbon nanotubes at each step of the synthesis. Characterization of functionalized carbon nanotubes and MWNT/ PEG / β -CD nanocomposite is done by FT-IR spectroscopy and TGA method. The morfology of nanocomposite particles has been determined by Scanning Electron Microscope (SEM).

Result and discussion:

Functionalization of MWNTs by HNO3 was performed by a technique developed by Esumi et al (1995). MWNT- COOH was reacted with SOCl₂ to form MWNT-COC1. Then, we synthesis MWNT-PEG by addition of triethyl amine and PEG to MWNT-COC1 at 60°C under nitrogen for 3days. MWNT/PEG/ β -CD nanocomposite obtained from the stirring of MWNT-PEG and β -CD aqueous solution for 24 h. The adsorption experiments of 2-biphenyl amine on MWCNT/PEG/CD, MWCNT-COOH and MWCNTs were carried out at T = 25°C. The amount of 2-biphenyl amine adsorbed was calculated using the following equation:

$$q = (C_e - C_0) \frac{V}{m}$$

Where q is the amount of organic molecules adsorbed (mg/g), C_0 and C_e are the initial and equilibrium concentration of the adsorbate (mg/ml), respectively; V is the solution volume (ml) and m is the adsorbents dosage (g).

Conclusion:





In this research we synthesized a nanocomposite that can remove organic pollutants from water. Our results demonstrated that MWCNT/PEG/CD is an excellent adsorbent for organic species such as 2-biphenyl amine from aqueous solutions compared to the MWCNT-COOH and native MWCNT.

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Physicochemical study on a new drug nanocarrier made of chitosan and hydroxypropyl-β-cyclodextrin

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Key words: Drug nanocarrier; Chitosan; Cyclodextrins; Physicochemical study

Introduction:

The purpose of this work was to design a new type of nanoparticles made of chitosan (CS) and hydroxypropyl- β -cyclodextrin (HP β CD) and to evaluate their potential for the association and delivery of insulin. The logical behind the design of this new nanosystem was to simultaneously incorporate the Cyclodextrin (CD) drug complexation power and the inherent properties of chitosan nanoparticles, in a unique delivery system. The complexation with the CD allows the solubilization and also the protection for sensitive drugs, whereas the loading in the chitosan is expected to enhance their absorption. Chitosan nanoparticles including HP β CD could be prepared by the ionic gelation of CS with sodium tripolyphosphate in the presence of CD. The resulting nanoparticles were in the size range of 62–514 nm. The association of insulin led to an increase of the size of the nanoparticles. The inclusion complex was investigated in solution by phase solubility diagrams and stability constant was determined at different temperatures (10, 25 and 37 °C) (pH=7.4) to obtain the thermodynamic parameters of inclusion. The release profile indicate that insulin was very fast released (84–97% insulin within 15 min)[1-3].

Materials and methods:





*Materials:*CS in the form of the hydrochloride salt was purchased from Citotec Co. hydroxypropyl-β-cyclodextrin and Tripolyphosphate (TPP) was purchased from Sigma Aldrich. Insulin was purchased from Alborz Company.

*Methods:*Nanoparticles were prepared according to the procedure previously developed by Calvo et al. group [4]. The Phase-solubility and Drug release were also studied.

Result and discussion:

For the loading of insulin to different nanoparticle system, insulin was added in the CS/ HP β CD phase. After 24 h 0.75ml TPP (2mg/ml) solution inserted to CS/HP β CD /insulin and then final solution was stirred for 1h again and then nanoparticles were isolated by centrifugation (13500×g, 30min, room temperature). Supernants were collected for determination of the amount of unbounded insulin.

Physicochemical characterization of nanoparticles:

The size and morphology of colloidal systems were determined by SEM (Hitachi S-4160). Each batch was analysed in triplicate. In general, it was noted that the process yield increased as the HP β CD concentration decreased. The SEM indicates that nanopaticles had a spherical shape. The solubility of insulin as a function of the amount of HP β CD added to their respective dissolution media is investigated. As expected, insulin molecules showed a marked increase in their solubility as the HP β CD concentration increased.

Conclusions:

This paper reports, the possibility to entrap cyclodextrins within CS nanoparticles using a very simple ionic gelation technique. This new approach permits to enhance the entrapment of hydrophobic drugs by forming molecular inclusion complexes with cyclodextrins in aqueous media. Such a device could be of interest for increasing the absorption of poorly soluble and poorly permeable drugs and also for conferring a protection to some specific drug molecules through the complexation followed by entrapment in the polymer matrix. In the final, the





solubility of insulin is investigated. The result shows that the soulibility of insulin can be increased by inclusion complexation whit HPβCD.

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A Study upon the modern Fabrication Method by means of TiO₂/PbO₂ Nanofibers via Electrospinning

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Key words: nanofibers, electrospinning, photocatalysts, fabrication

Introduction:

In this letter, we report a new method to fabricate side-by-side TiO₂ /PbO₂ nanofibers using the DOSE (dual- opposite-spinneret electrospinning). Electrospinning, regarded as a simple, lowcost, and universal technique for fabricating submicrofibers and nanofibers, has been receiving more and more attention over the last 15 years. In addition to general beaded and nonbeaded thin nanofibers, other types of nanofibers with interesting morphology, such as core-shell nanofibers, hollow nanofibers, and side-by-side nanofibers, have been produced by electrospinning[1,2]. A side-by-side structure allows both parts of the nanofibers to be exposed to the surface. Bicomponent side-by-side TiO₂ /PbO₂ nanofiber photocatalysts have been fabricated via side-by-side electro- spinning [2]. Their study demonstrated that the photocatalytic degradation rate of Rhodamine B (RhB) dye on the side-by-side TiO₂ /PbO₂ nanofibers was more than double that on the pure TiO₂ nanofibers. In this research, We know very well that Thin-film heterojunctions and particle heterojunctions have been fabricated via various methods: Kanai et al. deposited PbO2 /TiO2 (TiO2 overcoated with PbO2) thinfilm stacks by reactive DC magnetron sputtering, and Tada et al. produced patterned bilayer of TiO₂ /PbO₂ (PbO₂ overcoated with TiO₂ stripes) using modified sol-gel method. One point to note is that these films were coated on substrates; thus, the photocatalyst lost approximately half of the contact surface between itself and reactants, which decreased the





photocatalytic efficiency. On the other hand, coupled and capped semiconductor particles may expose more surfaces to reactants, but it is difficult to separate powder photocatalysts from the solution after photocatalytic reaction. Therefore, nanofibers would be an appropriate structure for fabricating a type of photocatalyst with a large surface area exposed to reactants while maintain- ing good recoverability. In addition to general beaded and nonbeaded thin nanofibers, other types of nanofibers with interesting morphology, such as core-shell nanofibers, hollow nanofibers, and side-by-side nanofibers, have been produced by electrospinning. A side-by-side structure allows both parts of the nanofibers to be exposed to the surface. Bicomponent side-by-side TiO_2 /PbO₂ nanofiber photocatalysts have been fabricated via side-by-side electro- spinning [1,2]. Their study demonstrated that the photocatalytic degradation rate of Rhodamine B (RhB) dye on the side-by-side TiO_2 /PbO₂ nanofibers.

Experimental:

1. *Electrospinning Apparatus and Parameters.* Electrospinning solution was loaded into the syringe and pumped by the syringe pump. A flat-tipped stainless steel syringe needle was used as the spinneret. Two spinnerets were assembled horizontally in opposite directions, and each was connected to a separate high-voltage power supply. A rotating cylinder covered with aluminum foil was used as a collector.

The distance between the tips of two spinnerets was 12 cm, the applied voltages were +3100 V and -3100 V, the distance between the spinnerets and the collector was about 15 cm, the rotation rate of the cylinder collector (Diameter = 10 cm) was 300 r·min⁻¹. For fabricating PbO₂ /TiO₂ bicomponent nanofibers, the feed rate of solution containing tetrabutyl titanate was 7.2 μ L·min⁻¹ and that of solution containing stannous octoate was 4.2 μ L·min⁻¹.

Results and discussion:

In the DOSE process, two jets ejected from the opposite spinnerets and then merged





into a single one, which was the great difference compared to the single spinneret electrospinning. This difference brought out two advantages. One advantage was that it was easy to get the well-aligned electrospun fibers. When the two oppositely charged jets merged into a single jet, the newly generated jet had an approximately neutral charge over all, which made it minimally affected by electric force. Therefore, it was easy to collect well-aligned and uniform electrospun fibers, as shown in Figure 1(a). The other advantage was that it was easy to make the side-by-side electrospun fibers. Before the two jets stuck together, some solvent had evaporated and jets had partially solidified, which prevented the mixing of the two parts of the newly generated jet. Thus, it was easy to make the side-by-side electrospun fibers, as shown in Figure 1(b) (partial enlarged views of this figure can be found in S₁ Supplementary Material available online at doi: 10.1155/2012/575926). Specifically, it was meaningful when we wanted to make the side-by-side nanofibers from two miscible electrospun solutions. One part contained element titanium (Ti) but no lead (Pb), while the other part contained both Ti and Pb. As Ti was easy to diffuse, the part coming from The calcined side-by-side TiO₂ /PbO₂ nanofiber possesses great potential in photocatalytic applications. Nanofibers with a side-by-side structure expose both TiO₂, mainly consisting of anatase phase and rutile-type PbO₂ to the surface. Because of the different band gaps of anatase TiO₂ and rutile PbO₂, the photogenerated electrons in these fibers would accumulate on one side, and photogenerated holes would accumulate on the other side. Therefore the recombination of photogenerated electrons and holes would greatly decrease, resulting in high photocatalytic activity.



Figure 1: Morphology of electrospun fibers by FE-SEM (a) well-aligned fibers, (b) side-by-side fibers.

Conclusion:





Well-aligned and uniform side-by-side electrospun fibers were fabricated using the DOSE method. DOSE has great advantages for fabricating aligned side-by-side fibers: (a) because the jet instability is almost eliminated after the positive and negative charges neutralize each other, the electrospun bicomponent nanofibers produced via DOSE are well aligned and uniform; (b) because some solvent has evaporated and jets have partially solidified before the final jet is formed, there is much lower immiscibility requirement for making side-by-side structure between the two kinds of solutions used in electrospinning. TiO₂ /PbO₂side-by-side structure between the two kinds of solutions used in electrospinning.

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Studying the electrical conductivity of magnetite nanofluid using SW model

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Key words: Magnetite nanofluid, Fe₃O₄nanofluid, Electrical conductivity, SW model.

Introduction:

Fluids containing suspended nanoparticles called nanofluids, have more usages in agronomy, industry and medicine [1-3]. Recent studies show that some nanofluids may possess significantly greater thermal and electrical conductivities compared to their base fluids. Based on the experimental observations, some different models such as Maxwell's, Hamilton and Crosser's and Prasher's models were proposed to describe the thermal behavior observed in nanofluids [3]. However, the results of the literature survey show that there are a few studies on the electrical conductivity (EC) of nanofluids [1-3]. Recently, in 2012, Shen et al.[3] proposed a new model to describe the EC mechanism of ZnO nanofluids, we called SW model. In the present work, we measured the EC of magnetite nanofluid after preparation and evaluated the experimental results using the SW model.

Experimental and method:

The magnetite nanofluid, Fe_3O_4 in demonized water, was synthesized by chemical coprecipitation method [2] and characterized using XRD and TEM techniques. The EC of the nanofluids was measured using Wagtech Ecmeter, model Con11 and the resultswas evaluated based on the SW model [3]. In this model, the EC of nanofluids can be written as the following:



$$\delta = \delta_0 (1+3\varphi) + \frac{3\varphi \varepsilon U_0}{r^{\frac{3}{2}}} \left(\frac{RT}{L} \frac{e^{\lambda(T-T_0)}}{3\pi\rho v (1+25\varphi+625\varphi^2)} \right)^{\frac{1}{2}} + \frac{2\varphi \varepsilon^2 U_0^2}{\rho v (1+25\varphi+625\varphi^2)r^2} e^{\lambda(T-T_0)}$$
(1)

Where r and φ are the nanoparticles radius and volume fraction, respectively. λ , ε , υ and ρ are the viscosity index, dielectric constant, kinematic viscosity and density of the fluid, respectively. U₀ is the nanoparticle Zeta potential, T is the temperature in Kelvin, and L and R are the Avogadro's constant and the thermodynamic constant, respectively.

Results and discussion:

Figures 1(a) and 1(b) show the XRD pattern and TEM image of magnetite nanoparticles, respectively. XRD pattern confirms the purity of magnetite phase and TEM image shows that the size of nanoparticles is about 15 to 20 nm. Fig. 2 shows the experimental as well as the model results of EC as a function of volume fraction at selected temperatures. It can be seen that the EC of the nanofluid increases with increasing volume fraction at all temperatures. Moreover, there is a good agreement between model and experimental values at high temperatures indicating the validity of SW model. The significant disagreement observed at lower temperatures can be attributed to the agglomeration of Fe₃O₄ nanoparticles which is not considered in SW model [2,3].



Fig. 1.a) XRD pattern and b) TEM image of Fe_3O_4 nanoparticles.



Fig. 2.The model and experimental EC as a function of Fe_3O_4 volume fraction.





Conclusion:

In this study, magnetite nanofluids were synthesized by chemical coprecipatation method and characterized using XRD and TEM techniques. The electrical conductivity of magnetite nanofluid was measured and the experimental data were evaluated using the SW model. Results show the increase of EC with volume fraction at all temperatures and there is a good agreement between the model and experimental values at high temperatures.

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Grand Canonical Monte-Carlo Simulation of Monomeric Alkaloids inside VO(bdc) Metal Organic Framework

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Key words: Adsorption, GCMC, Alkaloids, MOFs.

Introduction:

Metal organic frameworks (MOFs) that are synthesized by coordination bonds between metal clusters and organic linkers, have become considerably during the last few years due to their high specific surface areas [1]. Nowadays, MOFs are known as nanoporous materials which can be at the forefront of attempts to develop many economic and environmental technologies; such as molecular adsorption properties of nanoporous materials that are currently receiving great interest in many areas of science and industries [2].

In this paper, we study considering MOFs for uptaking monomeric alkaloids gas form and their binary separations. Alkaloids are a group of naturally occurring chemical compounds which have low molecular weight nitrogenous compounds. This group also includes some related compounds with neutral and even weakly acidic properties [3].

DFT and GCMC simulation details:

Briefly, grand canonical Monte-Carlo (GCMC) simulations are performed for a model that includes electrostatic and Lennard-Jones (LJ) interactions among the atoms of MOFs and alkaloids molecules. Here, we select pyrrolidine, piperidine and pyridine that are in one class of alkaloids with nitrogen heterocycles (See Fig (1)).



Fig. 1: left hand molecule is: piperidine, Middle is pyridine and right hand is pyrrolidine.





In this research we select $V^{IV}O(bdc)$ [bdc= 1,4-benzenedicarboxylate] [4] as MOF and the LJ parameters for the MOF atoms are taken from the DREIDING force fields. Also, MOF and the individual monomeric molecules of pyrrolidine, piperidine and pyridine are considered to be rigid and partial charges on the MOF atoms are derived from density functional theory (DFT) calculations [5, 6]. At first, the DFT calculations were performed on clusters isolated from the unit cell of each $V^{IV}O(bdc)$, with the atomic coordinates taken from the experimental crystallographic data. The DFT calculation was carried out using the B3LYP level of theory and the 6-31+G* basis set for non-metal atoms and LanL2DZ effective core potential were used to V atom. After this, partial atomic charges were extracted using the ChelpG method. For GCMC simulations, the interaction energy between the atoms was computed through the Coulomb and LJ potentials. LJ parameters between different types of sites were calculated using the Lorentz-Berthelot mixing rules.

Results and discussion:

According to our knowledge, $V^{IV}O(bdc)$ is employed to gas adsorption and adsorptive separation of *p*-Xylene, *o*-xylene, *m*-xylene, ethyl benzene, styrene, ethane, propane, butane and *n*-octane at temperatures range of 298-343 K, that these adsorbates were in liquid or vapor phases [7]. The V^{IV}O(bdc) is 3D framework with 1D diamond shaped channels along *a* axis (window size ~7.0×5.7 Å). So, this MOF can adsorb those aromatic molecules which have one ring. Although, our study has NOT finished and it is being completed, corresponding to some obtained data from simulations; we can predict that pyridine is most adsorbable rather than other selected monomeric alkaloids molecules.

Conclusion:

In this study, we try to suggest, new materials to adsorb some toxin molecules from *ab initio* and grand canonical Monte-Carlo simulations. According to our obtained data as yet, we have concluded weight percentage of adsorption of those molecules that have small rings is almost well but, the intramolecular interaction of small alkaloids is very important in adsorptivity of them.





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Improving Benzene Storage Capacity of Al(OH)(bdc) MOF by Functionalization of 1,4-benzenedicarboxylate with Lithium using GCMC Simulation

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Key words: GCMC simulation, MOF, Lithium, Storage, Benzene.

Introduction:

Metal organic frameworks (MOFs, also known as coordination polymers) have synthesized prior to the mid-1990s and are represented a relatively new family of nanoporous materials that are formed by a network of transition metal ions linked by bridging ligands other than oxygen [1, 2]. In recent years, after discovering MOFs, several studies have concentrated on their use for on-board gas storage, but experimental studies to date have only reported useful uptake at cryogenic temperatures. Although, a few investigations have considered to eliminate organic pollutants; in particular, benzene from toxin medium that are uses extensively in industrials [3, 4]. Then, in order to achieve the safe and efficient benzene storage, we apply a MOF that is called as MIL-53-Al. This MOF has 3D framework with 1D diamond shaped channels along *a* axis (window size $\sim 7.2 \times 5.3$ Å).

The model used and the GCMC simulations performed:

In the present work, we study benzene adsorption properties of MIL-53-AI: [Al^{III}(OH)(bdc)] MOF [bdc=1,4-benzenedicarboxylate], by the means of grand canonical Monte-Carlo (GCMC) simulations. To keep the total system neutral, we have introduced lithium in the form of an alkoxy salt (O-Li group) by substituting some hydrogen atoms of the organic linker by an O-Li group. The Li doped MOF and the individual benzene molecules are considered to be rigid and partial charges on the Li doped MOF atoms are derived from density functional





theory (DFT) calculations [5]. The DFT calculation was done using the B3LYP level of theory and the Li doped MOF and benzene structures are optimized without any symmetry constraints and the minima are verified by performing numerical frequency calculations. Then, the ChelpG method is applied to calculation of the partial atomic charges [6]. For each state of GCMC simulations, a total amount of 2×10^6 runs were accumulated, where the first 10^6 were used for reaching equilibrium and the last 10^6 were used for calculating the ensemble averages. During the simulations, the interaction energy between the atoms was computed through the Coulomb and LJ potentials. LJ parameters between different types of sites were calculated using the Lorentz-Berthelot mixing rules. Also, the temperature is fixed on 300 K in all runs.

Results and discussion:

According to our knowledge, MIL-53-Al is employed to small alkane molecules adsorption and separations at temperatures range of 298-343 K that these adsorbates were in liquid or vapor phases [7]. Up to now, MIL-53-Al and Li doped MIL-53-Al are NOT considered to investigate the aromatic molecules adsorptivity which have one ring such as benzene. Although, our study has NOT finished and it is being completed, corresponding to some obtained data from simulations; we can predict that the Li doped MIL-53-Al can adsorb benzene better than MIL-53-Al in the same thermodynamics conditions.

Conclusion:

Here, we try to improve capability of MOF materials to adsorb aromatic molecules from DFT and grand canonical Monte-Carlo simulations. The main novelty of this work is that Li atoms are chemical part of the MOF and not just dopants. According to our obtained data as yet, we have concluded that Li chemical doping to MOF as alkoxy salt can be improved one ring aromatic molecule adsorption. So, the factories can be employed these advanced materials to delete or surcharge the small aromatic molecules in a certain chemical reactions by Li doped MOFs.




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Gelatin/nano-bioactive glass as macroporous nanocomposite nerve conduit

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Keywords: Nano-bioglass, Gelatine ,Conduit, Porosity

Introduction:

In the 19th century, various options for the surgical management of peripheral nerve injuries were under debate, such as stretching the nerve, mobilizing the nerve by joint flexion or bone shortening or bridging the defect with various organic or synthetic materials [1, 2]. In the early stages, the development of inflammation following nerve crush or transaction is very important for the further nerve regeneration. there is significant scope for improvement with materials. Specifically, the requirement to balance suitable mechanical properties, biocompatibility, and semi-permeability, alongside controlled degradability is preferred in addition to materials which can interact with the body to unlock mechanisms of self-repair and regeneration Biodegradable polymers are widely used in biomedical applications such as tissue engineering and guided tissue regeneration [3]. Bio glasses are a class of inorganic biomaterials used in tissue engineering and regenerative medicine. One of the most popular bioactive glasses has the SiO2–P2O5–CaO (64%SiO2, 5%P2O5, and 31%CaO), and it is known as 45S5 Bioglass. Gelatine is a natural polymer similar to collagen. It is often used to produce drug carriers, wound dressing materials and conduit for tissue engineering [4,5].

Materials and Method:

At first, compound water solution of Gelatin (purchased from Merck) and Bioactive Glass synthesized through Sol/Gel method, was made. Then it was layer cast and freeze dried in order to be emptied of water via sublimation. The resulting product was eluted with 25% glutaraldehyde (purchased from Merck) solution.





In this research study, evaluation of porous size has been studied by SEM analysis and Fourier transform spectroscopy has been applied to study the structure of the Gelatin\nano-bioactive glass particles in the range of 4000–400 cm⁻¹. Each sample was mixed with KBr, ground carefully, and pressed to a disc. Precipitated and dried samples were analyzed by wide angle X-Ray diffraction method using CuKa radiation (k 5 0.15406, 2u 5 20–608).

Resualt and discussion:

1. Chemical characteristics

The FTIR spectrum of the Bioglass/Gelatin conduit shows ordinary functional groups as well and they indicate the presence of bioactive glass phase. SEM micrograph of the composite conduit showed that conduits were macro porous in nature. nBGC particles were seen on the walls of the conduits and were uniformly dispersed in the matrix. Samples were analyzed by wide angle X-Ray diffraction method using CuKa radiation (k 50.15406, 2u 520–608).

2. Citotoxity studies

To observe the cytotoxic effects of the BG conduits on CHO cell lines in vitro, MTT assay was performed. The investigation of the in vitro behavior of CHO cells demonstrated that cells were able to attach to the conduit, migrate through the porous network and colonize the inner sections of the foams.

Conclusions:

Fabrication of bioglass conduits can be a good guidance channel for growing axons. The biological and biochemical characteristics of tissue engineered Nano-bioglass/Gelatine conduits promising us a suitable candidate in peripheral nerve repair instead of autograft.

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Removal of Pb²⁺ by Magnetic Iron Oxide Nanoparticles Modified with Poly Thiophene-3-acetic Acid

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Keywords: Adsorption, Lead, Iron oxide magnetic nanoparticles, Thiophene-3-acetic acid.

Introduction:

Water and wastewaters contaminated by heavy metals have an adverse impact on public health and economy. Exposure to heavy metals even at trace levels is believed to be a risk for human beings. Strict environmental regulations on the discharge of heavy metals and rising demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal from environment [1]. Recently, nanometer-sized hierarchically structured metal oxides have been used for wastewater treatment and have shown remarkable potential because those materials have large surface areas.

Materials and method:

In this work synthesis and application of thiophene-3-acetic acid coated Fe_3O_4 magnetic nanoparticles (Fe_3O_4 /polymer) for the removal of Pb^{2+} is described. The Fe_3O_4 magnetite nanoparticles were prepared by the conventional coprecipitation method . A previously reported method [2] was used to coating magnetite nanoparticles with thiophene-3-acetic acid. Adsorption of lead was carried out by batch technique at room temperature. The isotherm studies were performed by mixing 20 mg adsorbent (dry) with 10 mL of solution containing $Pb(NO_3)_2$ salt at known concentration into 20 mL sample tubes. After reaching adsorption equilibrium, Fe_3O_4 /polymer magnetic nanoparticles were separated from aqueous solution





using a 1.2 T Neodymium Iron Boron magnet. Then metal analysis in solution was executed by atomic absorption spectrophotometry.

Apparatus:

X-Ray diffractometer Bruker, D8ADVANCE Germany with Cu tube anode and Cu K_{α} wavelength (1.5406A^o) was used for collection of powder XRD pattern of magnic nanoparticles. FT-IR spectra of magnic nanoparticles were recorded on Jasco model 6300 FT-IR instrument. CHNS and thermal analysis were done with a Leco model CHNS-932 and METTLER TA 4000 instruments, respectively. The metal analysis in solution was executed by atomic absorption spectrophotometry (AAS) (Shimadzu AA-670, Japan).

Result and disscution:

The synthesized materials were characterized by XRD, FT-IR, CHNS analysis and shown that polymer coated Fe₃O₄ magnetic nanoparticles were synthesized, successfully. Effects of various operating variables namely solution pH, initial Pb²⁺ concentration, contact time, adsorbent dosage, and sample volume on the efficiency of Pb²⁺ removal were studied by batch equilibrium technique. Sorption of the Pb²⁺ to Fe₃O₄/polymer reached equilibrium in less than 10 min. The equilibrium data, analyzed by using Langmuir and Freundlich isotherm models, showed better agreement with the former model. Using the Langmuir isotherm model, maximum capacity of the nonoadsorbent for Pb²⁺ was found to be 66.67 mg/g at room temperature. Kinetic studies were conducted and the resulting data were analyzed using first and second order equations; pseudo-second-order kinetic equation was found to provide the best correlation.

Repeated adsorption-acid regeneration cycles were performed to examine the stability and reusability of the nanoadsorbent. The result of this study proved high stability and reusability of Fe₃O₄/polymer as an adsorbent for Pb^{2+} ions.





Conclusions:

The present study demonstrates that polymer coated Fe_3O_4 nanoparticles are promising adsorbents for efficient removal of Pb^{2+} from aqueous solutions. It was found that the adsorption behavior of Pb^{2+} ions onto the nanoadsorbents is best described by the Langmuir isotherm model. Pb^{2+} showed fast sorption kinetics following pseudo-second order model. The equilibrium for Pb^{2+} adsorption onto the polymer coated Fe_3O_4 nanoparticles reached only after 10 minutes. Furthermore, these magnetic nanoadsorbents may be separated easily from the solution with the help of an external magnetic force and are reusable after removing the adsorbed Pb^{2+} ions.

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Photo-physical Characteristics of ME-Capped CdSe Nanoprticles Synthesized by Wet-Chemical Route

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Introduction:

Over the last decade, semiconductor nanoparticles have attracted tremendous interest due to their unique size dependent optical and electronic properties [1,2]. The chemical growth of high-quality CdSe, ZnSe, CdTe, *etc.* nanoparticles is now becoming a routine procedure due to the attractive features present in these materials [3]. Here, we report a simple, safe and economical procedure for synthesis of capped CdSe NPs at room temperature ($RT\sim 25$ °C) via a direct reaction between CdCl₂ and Na₂Se in the presence of Mercaptoethanol (ME) as a capping agent.

Results and Discussion :

The most dramatic property of semiconductor nanoparticles is the size evolution of the spectroscopy analysis. The UV-vis absorption spectrum of as-prepared CdSe NPs reveals the broad and less symmetric excitonic peaks at 405 nm (Fig. 1). The blue shifting of absorption wavelength, compared to the bulk value (716 nm, 1.73 eV), reflecting size quantization effect [4]. Using the well known Brus equation [1], the nanoparticles diameter was estimated to be around 5 ± 1 nm. Absorbance wavelength shift and band gap versus ME concentration are shown in Fig. 1 (right graph). The band gap increases from 3.02 eV (410 nm) to 3.23 eV (383 nm) as the concentration of ME capping agent increasing from 0.01 M to 0.1 M. Therefore, the capping agent dependence on the band gap appears clear but small (~ 0.24 eV).





Fig. 1. (Left): UV-visible spectra of CdSe NPs; (right): Profiles of E_g - λ_{abs} versus ME conc.

Fig. 2 presents the PL spectrum of the ME-capped CdSe NPs at 1:1:1 and 5:1:1 (ME:Cd:Se) mole ratio. It revealed a strong emission peak at 517 nm, which could be attributed to recombination from the defect states, such as an interstitials, selenium vacancies and surface traps [4]. The emission peak observed at 517 nm confirms a blue shift (~ 199 nm), when compared with the reported PL peak centered on 716 nm for the bulk CdSe [5]. On the other hand, the enhancement at luminescence intensity was observed with increasing concentration of ME capping agent. Sondi *et al.* [6] observed a similar behavior for CdSe nanoparticles synthesized in aqueous solution of Na₂Se and CdCl₂ in the presence of aminodextran as stabilizing and capping agent.



Fig. 2. (left): PL spectra, (right): STM image of ME capped CdSe NPs.

The morphologies of CdSe NPs obtained were also examined using the surface topographic data with atomic resolution. Fig. 2 (right image) shows typical real space morphology of CdSe 2580





NPs captured by contact mode scanning tunneling microscope (STM). Observation of figure shows that CdSe particles are nearly spherical shape in nature. The size of particles was estimated by line shape analysis. The average diameter of NPs thus estimated is \sim 5-15 nm.

Conclusions :

In brief, spherical CdSe nanoparticles have been synthesized by wet chemical route in the presence of Mercaptoethanol as a capping agent. The absorption spectra of capped CdSe nanoparticles exhibit a blue shift (~ 30 nm) with enhancement of ME, whereas the emission spectrum shows a high intensity luminescence. Structural results demonstrated to be nearly spherical shape, well dispersion and diameter of the NPs was confined within 5-15 nm.

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Enhancement of ferromagnetic and dielectric properties in barium and lanthanum doped nano powedrs BiFeO₃ by sol-gel synthesis

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Keywords: BiFeO₃, Nano Powedrs, ferromagnetic, dielectric, sol-gel, Barium doped, Lanthanum doped.

Introduction:

Multiferroic $Bi_{1-x}.Ba_x.Fe_{1-y}.La_y.O_3$ (x = 0.0, 0.05, 0.08, 0.12 and 0.15) microparticles were successfully synthesized by a Solgel technique at the temperature as low as 600 °C.

The obtained sol was transparent and homogenous when the mixture ionic concentration was properly controlled with the help of ethylene glycol alcohol. The preparation process of crystalline BiFeO₃could be divided into three stages: (i) the evaporation of organics and decomposition of nitrogencontaining organics below 200 °C ; (ii) the collapse of BiFe gel network in the temperature range of 200-300 °C and (iii) the formation of BiFeO₃ nanopowders by the solidstate reaction between Fe₂O₃ and Bi₂CO₃O₂.Multiferroic materials, which exhibit both ferroelectric and magnetic ordering, have attracted broad interests due to their potential applications for novel magnetoelectric devices and for exploring fundamental science in the coupling mechanism between electronic and magnetic order pa-rameters. Solgel process is widely used for preparing purephase powders and thin films. In the sol-gel synthesis of BFO, the sol is usually prepared based on citric acid route. In order to compensate the evaporation loss of bismuth during postannealing process, the excess bismuth source is usually added to the solution. In the present paper, a simple solgel method based on ethylene alcohol is used to prep are BFO nanopowders. The process from the sol to the final inorganic materials is investigated in detail. A micromechanism for crystallization of BFO gels is proposed.





Materials and methods:

Using solgel methods: 50 ml distilled water in 60 °C, 1.74 citric acid, 2.06 gr Bismuth nitrat, 0.196 gr barium nitrat, 2.02 gr iron nitrat, and 0.34 gr Ethylene Glycol. after mixing, PH adjusted with ammonia in 2.8, and placed 12 hours in water bath at 90 °C, and placed it 24 hours in oil bath at 120 °C.

after that put in the oven at 200 °C for 2 hours, In the last 3 hours leave in the furnace at a temperature 600 °C.

Apparatus:

Structural characterization of the nanocrystalline powders was carried out using xray powder diffraction (XRD) with monochromatic Cu K α radiation ($\lambda = 1.5406$ Å) in the 2 θ range of 1090° in a continuous scan mode with a step width of 0.05°. Sample morphology was studied using transmission electron microscopy (TEM) (LEO 912 AB, Carl Zeiss SMT, Germany, 120 kV). In the case, specimens were prepared from deposition of suspensions of powders in ethanol on copper grids coated with a carbon film.

Result and discussion:

Xray diffraction patterns of BFO gel powder annealed at different temperatures. When thermal treatedat and below 200 °C, the powders were still in the amorphous state. The amorphous precursor gelwas fired at 300 °C to make organics burn and decompose. It was observed that crystalline phases, including bismutite ($Bi_2O_2CO_3$) and bismuth oxide (Bi_2O_3), appeared. The phase has transforma-tion of the BFO precursor to perovskite was started at a temperature as low as 550 °C.

BFO was completely crystallized into perovskite phase at 580 °C. Ethylene glycol as solvent can keep the different electronegativities of bismuth and iron during hydrolysis and its linearly structured molecule makes it easy to obtain a stable precursor. Acetic acid as a catalyst in the sol system can control the hydrolysis speed and adjust the solution concentration.

 $Bi_2CO_3O_2 + Fe_2O_3 \rightarrow 2BiFeO_3 + CO_2$.





Conclusion:

A simple sol-gel method based on ethylene glycol alcohol to synthesize multiferroic BFO is proposed. The ethylene glycol alcohol plays an important role in the formation process of the transparent and homogenous BFO sol. The phase-pure BFO powders are obtained at the temperature as low as 600 C. The magnetization measurements suggest an antiferromagnetic ordering in the BiFeO₃ system. The anomalous temperature dependence of magnetization suggests that paramagnetic spins or uncompensated antiferromagnetic spins exist in the antiferromagnetic domains. We are currently investigating the ferroelectric properties of these nanoparticles, and will report them in near future.

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Synthesis of multiferroic BiFeO₃ nanopowder by sol-gel process

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Keywords: BiFeO₃, Nanopowder, Chemical synthesis, Multiferroic materials.

Introduction:

BiFeO₃ with a perovskite-type structure has been extensively studied as a multiferroic material during recent years. It is well established that BiFeO₃ is antiferromagnetic with the Neel temperature $T_N \approx 370$ °C and ferroelectric with the Curie temperature $T_C \approx 830$ °C [1-3]. Because of this magnetoelectric coupling, BiFeO₃ may be used to develop novel applications such as spintronics and sensors. Purity phase of the BiFeO₃ is important for high quality of magnetoelectric devices. The first, BiFeO₃ powders have been synthesized by solid-state reaction of Bi₂O₃ and Fe₂O₃ at temperature greater than 800 °C in micro size with unavoidable impurities such as Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ [4]. It is well known that BiFeO₃ nanostructures exhibit unique electrical, magnetic, and optical properties due to their low dimension [5]. Therefore, various wet chemical methods have been developed to prepare BiFeO₃ nanopowders [5]. The aim of these methods is decreasing of impurities and purity phase with high quality. In this work, we synthesized BiFeO₃ nanopowders by a sol-gel method. The effect of annealing temperature, values of pH and ratio of citric acid and ethylene glycol is investigated.

Materials and methods:

Analytical grade $Bi(NO_3)_3.5H_2O$, $Fe(NO_3)_3.9H_2O$, citric acid ($C_6H_8O_7$. H_2O) and ethylene glycol (EG) were used as starting materials. In the term of the atomic ratio Bi:Fe=1:1, was dissolved into deionized water under continuous stirring to form a mixed solution. Citric acid





(CA) in the molar ratio 1.5:1 respect to the cations was added as complexation, and then ethylene glycol was added as polymerization with various molar ratio respects to citric acid (ethylene glycol:citric acid= 3:2, 1:1, 2:3, 1:3). The pH values were kept between 3 and 5. The mixed solution was heated in a water bath at 80-90 °C until a highly viscous gel formed. Finally, the annealing temperature (T_A) was varied from 500 to 700 °C for 2 h in air.

Apparatus:

Structural characterization of the nanocrystalline powders was carried out using x-ray powder diffraction (XRD) with monochromatic Cu K α radiation ($\lambda = 1.5406$ Å) in the 2 θ range of 10-90° in a continuous scan mode with a step width of 0.05°. Sample morphology was studied using transmission electron microscopy (TEM) (LEO 912 AB, Carl Zeiss SMT, Germany, 120 kV). In the case, specimens were prepared from deposition of suspensions of powders in ethanol on copper grids coated with a carbon film.

Result and discussion:

The first, effect of pH on BiFeO₃ phase is investigated for EG:CA= 1:1 and $T_A = 500$ °C. Results of the XRD patterns for pH = 3.0, nanopowders have lower impurity phase. Secondly, influence of EG:CA mole ratio is studied for $T_A = 500$ °C and pH = 3.0. Results show that BiFeO₃ phase is pure for EG:CA= 1:3. Finally, annealing temperature is varied from 500 to 700 °C for pH = 3.0 and EG:CA= 1:3. From the XRD patterns is observed that with increasing of T_A up to 600 °C peak of XRD enhance and with more increasing T_A intensity of peaks do not change. Also, the TEM photographs of BiFeO₃ for $T_A = 600$ and 700 °C show that the size of nanoparticle is enhanced with increasing T_A .

Conclusion:

BiFeO₃ perovskite has been successfully papered by the sol-gel method with nanometer size and the effect of pH, the ratio EG:CA and T_A was studied on the structural of BiFeO₃. X-ray diffraction results showed a pure phase for pH = 3.0 and EG:CA = 1:3 and $T_A = 600$ °C. The TEM measurements confirm that the particle size is nanometer.





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Deposition Of Nanocrystalline ZnS:Cu Thin Films by Chemical Solution Method

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Keywords: Nanostructures, ZnS:Cu thin films, Chemical deposition, Deposition time.

Introduction:

Zinc sulfide (ZnS) is a wide band gap and direct transition semiconductor. Consequently, it is a potentially important material to be used as an antireflection coating for heterojunction solar cells [1]. In particular, ZnS is believed to be one of the most promising materials for blue light emitting laser diodes and thin films electroluminescent displays [2]. Among various chemical methods for deposition of thin films, the chemical solution has been proved to be the most suitable method to produce ZnS:Cu thin films for photovoltaic applications because of its efficient, cost effective and large scale capability [3]. In this work, we producing of nanocrystalline ZnS:Cu thin films prepared by a chemical solution deposition route [4-5].

Materials and methods:

Commercial microscope slide glass substrates were mainly used as the substrate. The deposition solution was prepared by mixing 6 mL of a 1 M zinc acetate solution, 15 mL deionized water, 20 mL of a 1 M ammonium acetate solution and optimum of a 0.05 M copper nitrate solution (for 0.2 mL to 3 mL with increase value 0.2 mL in various steps) in a glass beaker and the pH was about 6. In the next step, 30 mL of a 0.4 M thioasetamide (TAA) solution was added and the pH was adjusted about 6 again. This solution was poured into a glass tank being used as a reaction vessel for the film deposition. Glass substrates were





immersed vertically in the reaction vessel, and the glass tank was placed in a thermostat bath set at 75 °C for 8 hours.

Apparatus:

The Nanocrystalline ZnS:Cu thin films were characterized by XRD [Model: X'pert- PW1800], SEM [Model: Cam Scan MV2300] and UV-Vis spectrophotometry [Model: Cary 300 Bio].

Result and discussion:

Fig. 1a shows the variation of the ZnS:Cu films thickness with deposition time at 75 °C. There is a continuous increase of the film thickness with deposition time, while the rate of the film growth gradually decreases. This can be understood by considering two processes which are taking place in the bath solution; the film formation and homogeneous precipitation [6]. The XRD pattern (Fig. 1b) of ZnS:Cu thin film shows three broad peaks at around 28.56°, 47.43° and 56.25° reveal a cubic lattice structure of ZnS. These peaks can be assigned to the planes (111), (220) and (311), respectively, of the cubic zinc blend structure [5]. From the Debeye-Scherrer equation, the average nanocrystallite size in the ZnS:Cu film was estimated to be 9.14 nm. SEM image (Fig. 1c) of the ZnS:Cu film prepared at 75 °C shows the surface of film is homogenous with grain size of about 200-350 nm.



Fig.1: (a) Relationship between the thickness of the films and the deposition time, (b) XRD pattern, and (c) SEM image of the ZnS:Cu film prepared at 75 °C.

Conclusions:

Nanocrystalline ZnS:Cu thin films with different thickness were deposited by a chemical deposition technique. The film thickness was controlled by the deposition time. The XRD





pattern showed that the films consisted of small ZnS:Cu nanocrystallites, 9 nm in size, showing quantum size effects. The band gap energy of ZnS:Mn films is blue-shifted by about 0.17 eV with respect to the bulk value (3.67 eV), probably due to the quantum size effect as expected from the nanocrystalline nature of the ZnS:Cn thin films.

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The effect of Mn substitution on structural and magnetic properties of strontium hexaferrite nanoparticles

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Key words: Strontium hexaferrite, Nanoparticles, Sol-gel method, Magnetic properties.

Introduction:

Strontium hexaferrite (SrFe₁₂O₁₉) has been extensively used as a permanent magnet due to its low cost, relatively high coercivity, corrosion resistance and chemical stability [1]. The conventional method for production of this material is the solid-state reaction at temperatures higher than 1100 °C. This method has inherent disadvantages such as chemical homogeneity, coarse grain size and entrance impurities during the milling process. In order to get pure crystalline single domain particles of strontium hexaferrite, different chemical methods are reported. In this work, the doping effect of manganese (Mn) on the crystal structure and magnetic properties of nano crystalline strontium hexaferrite was investigated that prepared by sol-gel combustion method.

Experimental Details:

The initial chemical materials used for the synthesis of $SrMn_xFe_{12-x}O_{19}$ (x=0-1) nanoparticles are Fe(NO₃)₃.9H₂O, Sr(NO₃)₂, Mn(CH₃COO)₂.4H₂O, NH₃ and citric acid. The sol prepared by a proper ratio of metal nitrates, citric acid and ammoniac (pH=7) and was heated on a hotplate stirrer. Then the resulted viscous residue was dried at 250 °C for 1h and finally was calcined at 1000 °C for 5h with a heating rate of 5°C/min.





Results and discussion:

The XRD patterns and hysteresis loops of $SrMn_xFe_{12-x}O_{19}$ (x=0-1) nanoparticles are shown in Fig. 1 and 2, respectively and also, the various structural and magnetic parameters are listed in Table 1. All of the XRD peaks matched with the standard pattern (ICSD-00-051-1879) confirming the formation of a single hexagonal phase ($SrFe_{12}O_{19}$). The a lattice constants remains almost constant while c decreases with the increasing in Mn content (Table. 1). The decreases in lattice constant c and lattice cell volume (V) probably indicated the existence of oxygen vacancies in the M-type structures [2]. The crystallite size of samples found by Scherrer formula was found in the range 25-29 nm that due to larger ionic radii of Mn^{2+} (0.72 Å) than ionic radii of Fe³⁺ (0.64 Å). The coercivity (H_c) of the nanoparticles decrease continuously with the substitution of Mn contents while saturation magnetization (M_s) reveals an decrease at first and then increases because of decrease in the values of magnetocrystalline anisotropy constant. The larger ionic radius Mn^{2+} as compared to that of Fe³⁺ caused decrease in superexchange interaction and decrease in the magnetocrystalline anisotropy constant [3].





Fig.2. Hysteresis loops of SrMn_xFe_{12-x}O₁₉ (x=0-1)

x	a (Å)	c (Å)	$V (Å)^3$	D (Å)	$H_{c}(G)$	M _s (emu/g)
0	5.8583	22.939	682.238	250.393	5531	63.091
0.25	5.8571	22.925	681.080	264.276	5257	57.933
0.5	5.8570	22.916	681.593	285.377	3334	53.344
0.75	5.8494	22.903	679.531	286.444	2570	55.392

Table1. Structural and magnetic parameters of SrMn_xFe_{12-x}O₁₉ (x=0-1) nanoparticles.





1	5.8412	22.898	677.490	296.594	1995	55.681
 		•			•	•

Conclusion:

In this work, the doping effect of Mn on the crystal structure and magnetic properties of nanoparticles ($SrMn_xFe_{12-x}O_{19}$ (x=0-1)) was investigated. The XRD patterns of nanoparticles confirm the $SrFe_{12}O_{19}$ single phase and their crystallite size are found in the range 25-29 nm. Coercivity (H_c) of samples decrease with the increase in Mn content that due to decrease of magnetocrystalline anisotropy and superexchange interaction.

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Determination of diffusion coefficient of chloride in reinforced concrete containing nano SiO₂

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Key words: Chloride Diffusion, Nano SiO₂, Warburg coefficient, Nyquist plot, Randel plot

Introduction:

Reinforced concrete structure and chloride diffusion in concrete are experimently studied by different researchers. According to different researches chloride diffusion is main cause of corrosion and degradation of steel in concrete. Chlorides can come from several sources. They can be cast into the concrete or they can diffuse in from the outside. In this study Electrochemical Impedance Spectroscopy (EIS) was used to determine chloride diffusion in concrete. Nanoparticle has been found to improve concrete properties. Much of the work to date on concrete with nanoparticles has been with nano-silica (nano-SiO2). The aim of this study is to investigate the nano SiO₂ addition effect on the concrete sample's chloride diffusion. Diffusion coefficient of chloride (D) determined using Warburg coefficient (σ_w) from the Nyquist plot obtained by EIS measurement. On a Nyquist plot, at high frequencies the Warburg impedance is small . At low frequencies (linear range) chloride ions have to diffuse further, increasing the Warburg impedance.

Materials and methods:

Cubic concrete samples ($150 \times 150 \times 150$ mm) were used at each test age. Two types of concrete sample with water to cement ratio of W/C=0/4 (first type; without nano, second type; with nano) were prepared. Nano SiO₂ synthesized by ultrasonic method. The samples





were moulded 24h after casting and placed in water bath. After 28 days of curing, they were removed from the water bath and exposured 2 months in 3.5% NaCl solution at a room temperature. Consequently samples were ready for testing by EIS.

Result and discussion:

Nyquist plots for two concrete samples after 2 months of exposuring at 3.5% NaCl solution obtained by EIS measurement. Then Randel plot obtained from drawing $\omega^{-1/2}$ (angular frequency) versus Z. Slope of Randel plot introduced Warburg impedance (σ_w) in Ω . ($m^2.s^{-1/2}$). Chloride diffusion coefficient in ($m^2.s^{-1}$) is proportional to the (σ_w)⁻¹. According to Table 1, the Chloride diffusion coefficient of sample with 2% nano SiO₂ is lower than that of sample without nano SiO₂. This result is expected in this work, because nano SiO₂ can act as nuclei for cement phases, further promoting cement hydration due to their high reactivity, densifying the microstructure and the interfacial transition zone, thereby, leading to a reduced porosity and chloride diffusion. Finally nano SiO₂ has been found to improve concrete properties.

Table 1. Warburg impedance and Diffusion coefficient of chloride values

	%NaCl	%Nano SiO ₂	$\sigma_{\rm w}$	D
1	3.5	0	0.2014	1.45×10 ⁻¹¹
2	3.5	2	0.3601	0.454×10 ⁻¹¹

Conclusion:

Nano SiO_2 replacement showed a decrease in the value of diffusion coefficient of chloride in concrete sample after 2 months of exposure at 3.5% NaCl solution.

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The influence of nano SiO₂ on the rate of corrosion of steel embedded in reinforced concrete

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Keywords: Tafel plot, Impedance spectroscopy, Estern-Geary, Calcium hydroxide

Intrudution:

Corrosion of reinforcing steel in concrete has become a major problem world-wide, especially for such structures as bridges, parking decks, tunnels, offshore structures and other buildings exposed to aggressive environments due to seawater. Corrosion rate is an important parameter for quantitatively predicting the service life of reinforced concrete structures which is limited by the corrosion deterioration. Thus the performance of different types of additives as example inhibitors, super plasticizer, nanoparticle.... against corrosion in chloride contaminated concrete made with different types of cement can be evaluated by measuring the corrosion rate, so that the best possible combinations can be recommended for use in aggressive chloride environments. The various non-destructive techniques used for the determination of corrosion rate are linear polarization resistance (LPR) method, AC impedance spectroscopy and Tafel plot technique. This paper aims to study the effect of nano SiO₂ on the corrosion of steel reinforcement by using the Tafel plot (TP) technique.

Material and methods :

A total of two concrete samples with W/C ratio of 0.4 (first sample; without nano SiO2, second sample; with 1% nano SiO₂) were prepared. The samples were demolded 24 h after





preparation; and curing was done in water for 28 days. Consequently they were removed from the water bath and exposured 2 months in 3.5% NaCl solution at a room temperature.

Results and discssion :

The Tafel plots (Fig 1) of potentiodynamic polarization method were determined. The corrosion rate (CR) of concrete samples obtained from Estern-Geary eqution. According to Table 1, sample with 1% nano reached corrosion rate lower than that of sample without nano SiO₂. This result is expected in this work, because nano SiO₂ improved the concrete polarization resistance due to follow chemical effect: Chemical effect is mainly due to the pozzolanic reactions between nano SiO₂ and calcium hydroxide (CH) produced by the hydration of cement to form secondary calcium silicate hydrates (C-S-H) ,Thus the size and amount of calcium hydroxide crystals are significantly decreased, and the resistivity against corrosion of the concrete increased. The physical effect, which can also be considered as filler effect, is that nano SiO₂ particles increase the packing of the solid materials by filling the spaces between the cement grains and aggregates. Finally chloride diffusion and corrosion rate decreased.



 Table 1.Corrosion parameters for samples

X	7	NaCl	Nano	E _{Corr}	Rp	I _{Corr}	CR
		%	SiO ₂	(V)	$(\Omega.cm^2)$	$(A.cm^{-2})$	(mm/y)
	1	3.5	0	-0.6	18634.7	6×10 ⁻⁵	0.697
	2	3.5	1	-0.548	259729	4×10 ⁻⁶	0.048





Conclusion:

Specimen with 1%nano SiO₂ show lower corrosion rate, compared with specimen without nano. The lower chloride diffusion and formation the calcium silicate hydrate could result in a lower corrosion rate.

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Non -Pt nanoparticles as cathode for passive direct methanol fuel cells

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Key words: Alloy electrocatalyst, Methanol crossover, Passive DMFC

Introduction:

Direct methanol fuel cells (DMFCs) offer a lot of promise as the next-generation power source for portable devices [1]. In particular, a passive air-breathing DMFC system consisting of an anode that absorbs methanol from the built-in reservoir and a cathode that "breathes" from the ambient atmosphere works without any auxiliary devices such as heat exchangers, humidifiers, fuel pumps, gas blowers/compressors, etc. [2]. Methanol is an attractive fuel because, Firstly, methanol is a liquid, and therefore it can be easily transported and stored, and can be dispensed within the current fuel network. Secondly, methanol is cheap and plentiful [3]. However, further development of the DMFC is still facing some technical issues, among which are the most significant obstacle for DMFC development is methanol crossover.

However, the permeation of methanol through the membrane produces a loss of efficiency and a decrease of the fuel cell voltage due to parasitic methanol oxidation at the cathode, which remain as one of the major problems for the performance of the DMFC [16-19]. In DMFCs when Pt is used as the cathode catalyst the problems are exacerbated by the methanol crossover from the anode that results in mixed potential at the cathode [20,21]. Therefore, a non-Pt catalyst with high activity and selectivity towards ORR is urgently required.

Passive direct methanol fuel cell tests :

The home-made, oxygen-breathing DMFC with stainless steel (SS316) current collectors, used to evaluate the electrochemical performance of the optimum synthesized carbon supported Pd





and Pd₃Co electrocatalysts in comparison with Pt/C(E-TEK). A pretreated Nafion 115 membrane with a thickness of 125µm was employed in this work. The pretreatment procedures included boiling the membrane in 5 vol% H₂O₂, washing in DI water, boiling in 0.5M H₂SO₄ and washing in DI water for 1.5 h at 80°C. The pretreated membranes were kept in the DI water prior to the fabrication of MEAs. Carbon paper was used as the backing support of anode and cathode electrodes. 10 wt.% Pt/C(E-TEK) used as anode and 20 wt.% Pd₃Co on Vulcan XC-72 used as cathode for MEA-1, 10 wt.% Pt/C(E-TEK) used as anode and 20 wt.% Pd on Vulcan XC-72 used as cathode for MEA-2 and 10 wt.% Pt/C(E-TEK) used as anode and 20 wt.% Pt/C(E-TEK) used as cathode for MEA-3 and MEA catalyst loadings for both the anode and cathode were 3 mg_{metal}/cm². The Active area of MEAs was 4.75cm² and the methanol reservoir volume was 12.5mL.

Result and discussion:

Fig. 1 shows the polarization and power density curves of the Pd₃Co/C, Pd/C and commercial Pt/C (E-TEK) electrocatalysts as cathode in passive DMFC under the identical testing conditions filled with 1M methanol solution. The Pd₃Co/C and Pt/C (E-TEK) electrocatalysts exhibited relatively similar performance at low current densities but Pd₃Co/C exhibited relatively higher performance in high current densities. Moreover, both the electrocatalysts show an open circuit voltage of 0.53 V.



Fig.1: Passive DMFC polarization curves obtained for MEAs 1,2 and 3.





Conclusion:

 Pd_3Co/C electroocatalyst have a very good ORR selectivity in the presence of methanol. Carbon supported Pd_3Co electrocatalyst also showed high catalytic activity for oxygen reduction in a 4.75 cm² direct methanol fuel cell.

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Synthesis and characterization of LiFePO₄ nanoparticles via hydrothermal method

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Key words: LiFePO₄, Hydrothermal method, Lithium ion batteries, Cathod matherials, Nano particles

Introduction:

Phosphates LiMPO₄ (M = Mn, Fe, Co, or Ni) have been investigated intensively as promising cathode materials for lithium batteries.[1]

Among several materials under development for use as cathodes in lithium-ion batteries, LiFePO₄ appears to be a promising candidate because of its high theoretical capacity (170 mAh g⁻¹), low cost, excellent cycling stability, low toxicity, and environmentally benign nature.[2] LiFePO₄ has a highly stable three-dimensional framework due to strong P_O covalent bonds in $(PO_4)^{3^-}$ polyanion, which prohibits the liberation of oxygen. These characteristics provide an excellent safety under abuse conditions of the batteries. LiFePO₄ can be synthesized using conventional solid-state reactions. However, it is difficult to attain its full capacity, because its electronic conductivity is very low, and diffusion of Li⁺ ion in the olivine structure is slow. Several alternative synthetic methods have been applied to the preparation of LiFePO₄. In addition, highly dispersed conductive substances such as carbonaceous materials and some metals in the cathode composite electrode were reported as being efficient additives.

The hydrothermal synthesis is a useful method for preparing fine particles. It also has other advantages such as a simple process and energy efficient.

In this study LiFePO₄ was hydrothermally synthesized at slightly basic and neutral conditions by adding a little amount of sucrose as a redusing agent.





Materials and methods:

LiFePO₄ was prepared by hydrothermal process from Li₂CO₃ 99.5% (Merk) , NH₄H₂PO₄ 99.5% (Merk) ,FeSO₄.7H₂O (ACROS ORGANICS) in the molar ratio of 1.0: 1.0: 3:0. At frist FeSO₄.7H₂O was dissolved in deionized water after some minutes NH₄H₂PO₄ was added to the solution under vigorous stirring then o.15 gr of sucrose was added to the solution under vigorous stirring After 5 minutes Li₂CO₃ was added to the mixture. PH was controlled to be around 7-8 by adding HNO₃ %65 (Merk). When the mixture was strirred well, a light green suspansion was obtained. The suspanson was transferred to an autoclave. And heated at 160 °C for 15 h. After the hydrothermal reaction, the autoclave was cooled to room temperature. The precipitated pawder was washed with deionized water. Then the obtained powder was dried at 110°C for 1 h in the oven.

Apparatus:

The crystalline phases were identified with X- ray diffraction (model: D8Advance Bruker axs).



Fig. 1 shows the general view of LiFePO₄ structure along the [0 1 1] direction. In this structure, LiFePO₄ has a hexagonally close-packed oxygen array, in which the octahedra share both edges and faces. In this structure, a general view is obtained, where tunnels via which lithium ions can be removed are clearly identified in the [001] direction [3].





The x-ray diffraction (XRD) Pattern of the sample obtained by hydrothermal reaction are shown in fig.2. The result shows that the single phase LiFePO₄ with olivine type structure are synthesized.

Conclusion:

LiFePO₄ was hydrothermally synthesized from Li_2CO_3 , FeSO_{4.}7H2O, NH₄H₂PO₄ by adding a little sucrose as a redusing agent at 160 °C. The control of pH was important to obtain LiFePO₄ as a main Product by hydrothermal process.

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Synthesis and Characterization of LiFePO₄ Nanoparticles via Hydrothermal Method

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Key words: LiFe PO4, Hydrothermal method, Lithium ion batteries, Cathod Materials, Nanoparticles

Introduction:

Phosphates LiMPO₄ (M = Mn, Fe, Co, or Ni) have been investigated intensively as promising cathode materials for lithium batteries. [1]

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The hydrothermal synthesis is a useful method for preparing fine particles. It also has other advantages such as a simple process and energy efficient.

In this study LiFePO₄ was hydrothermally synthesized at slightly basic and neutral conditions by adding a little amount of sucrose as a reducing agent.





Materials and methods:

LiFePO₄ was prepared by hydrothermal process from Li_2CO_3 99.5% (Merk), NH₄H₂PO₄ 99.5% (Merk), FeSO₄.7H₂O 99.5% (ACROS ORGANICS) in the molar ratio of 1.0: 1.0: 3:0. Initially FeSO₄.7H₂O was dissolved in deionized water, and then NH₄H₂PO₄ was added to the solution under vigorous stirring afterwards o.15 gr of sucrose was added to the solution under the same conditions. After 5 minutes Li_2CO_3 was added to the mixture. PH was controlled to be around 7-8 via the addition of HNO₃ %65 (Merk). When the mixture was stirred well, a light green suspension was obtained. The suspension was transferred to an autoclave, and heated at 160 °C for 15 h. After the hydrothermal reaction, the autoclave was cooled to room temperature. The precipitated powder was washed with deionized water. Then the obtained powder was dried at 110°C for 1 hour in the oven.

Apparatus:

The crystalline phases were identified with X- ray diffraction (model: D8 Advance Bruker).





Fig. 1

Fig. 1 shows the general view of the LiFePO₄ structure along the $[0\ 1\ 1]$ direction. In this structure, LiFePO₄ has a hexagonally close-packed oxygen array, in which the octahedra share both edges and faces. In this manner, a general view is obtained, where tunnels via which lithium ions can be removed are clearly identified in the [001] direction [3].




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Conclusion:

LiFePO₄ was hydrothermally synthesized from Li_2CO_3 , FeSO_{4.7H2}O, NH₄H₂PO₄ by adding a little sucrose as a reducing agent at 160 °C. The control of pH was important to obtain LiFePO₄ as a main Product by hydrothermal process.

Reference:

[1] Kaoru Dokko, Shohei Koizumi, Keisuke Sharaishi, Kiyoshi Kanamura, Electrochemical properties of LiFePO₄ prepared via hydrothermal route, Journal of Power Sources, 2007

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Theoretical Studies of the Free Energies of Electron Transfer in Nanostructure Complexes of *Cis*-Unsaturated Thiocrown Ethers and A18-Membered Open-Cage Fullerene [X-UT-Y][18-MOC-C₆₀]

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KeyWords: Open-Cage Fullerene; Electron transfer process; *Plank's* equation; *Marcus* theory; Unsaturated thiocrown ethers; Molecular modeling.

Introduction:

Several methods have been reported for the synthesis of open-cage fullerene derivatives.Unsaturated thiocrown ethers with *cis*-geometry are a group of crown ethers that, in light of the size of their cavities and their conformational restriction compared to a corresponding saturated system (1-9), demonstrate interesting properties for physicochemical studies. One of 18-Membered Open-Cage Fullerene [18-MOC-C60] (10) has been shown to possess a host-guest interaction for electron transfer processes. The relationship between an index (μcs) and oxidation potential ($^{ox}E_1$) of 1-9, as well as the free energies of electron transfer (ΔG_{et} , by the Electron-Transfer (ET) equation) between 1-9 and 10 as [X-UT-Y][18-MOC-C₆₀] (11) were investigated.

Materials and Methods:

All graphing operations were performed using the Microsoft Office Excel 2003 program. The ratio of summation of the number of carbon atoms (*nc*) and the number of sulfur atoms(*ns*)to the product of these two numbers(μcs) seems to be a useful numerical and structural value for the unsaturated thiocrown ethers **1_9**(See Equation(1)).that were utilized here.

$$\mu cs = (ns + nc)/(ns \cdot nc) \quad (1)$$
2609





Result and discussion:

The relationship between μcs and oxidation potential (${}^{ox}E_1$) of **1-9**, as well as the free energies of electron transfer (ΔG_{et} , by the Electron-Transfer (ET) equation) between **1-9** and **10** as [X-UT-Y][18-MOC-C₆₀] (**11**) were investigated. In this study, the first to fourth free energies, activation free energies of electron transfer and maximum wave length of the electron transfers, $\Delta G_{et(n)}$, $\Delta G^{\#}_{et(n)}$ and λ_{et} (n=1-4), respectively, which is given by the previous studies for [X-UT-Y][18-MOC-C₆₀] (**11**) complex, were calculated in accordance with the *Plank*'s equation and *Marcus* theory. the relationship between the values of μcs and the free energies of electron transfer (*Get*) between **1_9** and the first reduction potential (*redE1*) of (**11**) shows the *Nieperian* logarithmic behavior.



Conclusion:

The *cis*-unsaturated thiocrown ethers 1_9 have important physicochemical properties. Using μcs the equations of the model can derive sound structural relationships between the aforementioned physicochemical data. By utilizing the equations of this model, one can calculate the values for the unsaturated thiocrown ethers [X-UT-Y] (1_9) with (10). The compounds (11) supramolecular complexes were previously neither synthesized Nor reported.

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Interaction of Functional Amino Acids with Gold NanoParticles; Theoretical and Experimental Investigation

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Introduction:

The study of the interactions between biologically relevant molecules and nanoparticles has attracted increasing interest because of potential applications in sensors, biosensors, and biomedical diagnostics. Gold nanoparticles have attracted much attention in chemistry and material science because of their good biocompatibility, facile synthesis, and conjugation to a variety of bimolecular ligands, antibodies, and other targeting moieties. There have been several demonstrations of bioaffinity sensors based on the plasmon absorption and scattering of nanoparticle, and most experimental and theoretical investigations are focused on the interaction of gold with amino acids and DNA. In this paper we investigated theoretically and experimentally the interactions different functional groups of amino acids with gold nanoparticle.

Experimental and Calculation Section:

Hydrogen tetra-chloroaurate (HAuCl₄, 99%) and sodium citrate (99%) were used to prepare citrate-capped Au nanoparticles following the method pioneered by J. Turkevich. The amino acids includes L-Lysine (99%), DL-Methionine (99%), L-Cysteine monohydrate (99%), L-Histidinemonohydrochloride (99%),DL-Isoleucine, DL-Serine,DL-Threonine which will be refered as Lys, Met ,Cys, His, IIe, Ser and Thr ,respectively have been used to conjugate with Au nanoparticles. Geometries of the functional amino acids complexes with gold cluster were fully optimized using the density functional theory (DFT) with B3LYP functional. The 6-





31+G** basis set was used for the atoms in functional amino acids, while for gold atom the Los Alamos effective-core potential (ECP) Lanl2DZ basis set was applied.

Result and discussion:

Figure 1 shows the absorption curves of the gold nanoparticles after addition of various amino acids. The obtained results show that the amino acids with thiol groups have an absorption peak at 600~750 nm in addition to the Au nanoparticles peak (about 520nm).



Fig1.Visible peak for Au colloidal particles with aminoacids

The amino acids with amine groups do not display any interacting peak at the normal conditions. Amine groups have been interacted with gold nanoparticles in acidic solution. Table 1 shows the binding energy of different functional groups of amino acids with gold trimer.

E _b	O, S-group	~	E _b	C-group)	E _b	N-grou	ıp
-61.49	но сн3	Glu		CH4	Gly	-27.76	H ₂ N H H ₂ N H H	Arg
-61.27	HO CH ₃	Asp	-4.87	$H_3C_CH_3$	Ala	-31.21	N HN	His
-16.14	он снз снз	Thr	-5.39	сн₃ н₃с∕сн₃	Val	-15.16	CCH3	Trp
-11.93	HO CH3	Tyr	-5.53	H ₃ C CH ₃	Leu	-15.67	H ₂ N CH ₃	Asn
-15.64	но СН3	Ser	-5.45	CH3 H ₃ C CH ₃	IIe	-16.43	H ₂ N CH ₃	Gln
-28.70	CH3 CH3	Met	-7.17	CCH3	Phe	-13.75	ОН ОН	Pro

Table 1. Binding energy of functional amino acids with gold trimer.





-46.5 HS CH3 Cys

-90.12 H₂N Lys

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113, 4338-4347





Interaction of Amine Compounds with Gold Nanoparticles; Theoretical and Experimental Investigation

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Introduction:

With their excellent compatibility with biomolecules and distance-dependent optical absorbance, colloidal Au nanoparticles have drawn intense scientific and technological interest. Au colloids bearing surface negative charge are seen to readily bind amine group. In this paper we investigated theoretically and experimentally the interactions of amine compounds with gold nanoparticle.

Experimental and Calculation Section:

Hydrogen tetra-chloroaurate (HAuCl4, 99%) and sodium citrate (99%) were used to prepare citrate-capped Au nanoparticles following the method pioneered by J. Turkevich.Amines compound includes Propan-1-amine ,Dodecylamine, 1,2-dimethylcyclohexane, 4,7,10-trioxa-1,13 tridecanediamine and L-Lysine which will be refered as Pro , ddc , Cyc , oxa and Lys, respectively have been used to conjugate with Au nanoparticles. Geometries of the functional amino acids complexes with aniongold cluster were fully optimized using the density functional theory (DFT) with CAM-B3LYP functional. The 6-31+G** basis set was used for the atoms amine compounds, while for gold atom def2-TZVP basis set was applied.

Result and discussion:

Figure 1 shows the absorption curves of the gold nanoparticleswith (A) addition of various amines and one of amino acid with amine group (Lysine) and (B) addition of Lysine, Histidine, and Arginine.The obtained results show that the amine compounds and amino acid with amine group have an absorption peak at 600~750 nm in addition to the Au nanoparticles





peak (about 520nm). The experimental data has been explained by means of theoretical calculations.Table 1 shows the binding energies of different amine compoundscomplex with gold trimer anion.



Fig1.Visible peak for Au colloidal particles with (A) amine compounds and (B) aminoacids.

Amine	Structure	E _b	Structure	Amine	E _b
Piperidine	H ₂ ⁺	-89.88	NH3 ⁺	Propan-1-amine	-92.95
1-methylpiperidine	CH3 NH+	-86.34	NH2*	N-methylpropan-1- amine	-90.87
1,2-dimethylcyclohexane	NH3 ⁺	-186.26	NH+	N,N- dimethylpropane-1- amine	-87.63
Butane-1,4-diamine	NH5*	-170.78		Dodecylamine	-91.65

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Effect of doping and defects on the electronic structure of graphane:A first principle study

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Although graphene is considered as a prime candidate for many applications, the absence of a band gap is a worrisome feature for the application to solid state electronic devices. In the past, several studies have been proposed to open a band gap [1, 2]. The most interesting one is the recent discovery of a completely hydrogenated graphene sheet named as graphane. Graphane was first predicted by Sofo et al [3] through the first principle total energy calculation and recently, Elias et al [4] through exposing graphene under hydrogen plasma surroundings have sensitized the graphane sheet.

The density functional theory (DFT) calculations were performed using QUANTUM ESPRESSO [5] with an ultrasoft pseudopotential [6]. For the exchange correlation term, we used the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [7]. Kohn Sham wave functions are truncated at energy cutoff of 600 eV. Geometry structure, were relaxed until the force on each atom was less than 0.01 eV/Ű and the convergence criteria for energy was 10^{-7} eV. The break up for the graphane layers in the supercell was set at 15 Ű, to avoid spurious interlayer fundamental interactions.

Upon hydrogen passivation, the electronic band structure of graphane produces remarkable changes as compared to the pristine graphene. Our calculations showed that the direct band gap at the Γ points approximately is 3.4 eV, which is close to previous works [3].

However, we analyze the effects of doping on graphane with nitrogen and boron. In the case study of doping, we replaced one nitrogen or boron atom with a carbon atom. Our calculations showed that bond and angle length in doped graphane close to pristine graphane. Since



nitrogen has one more valence electron than carbon, it acts as an electron donor and its presence makes the sheet more reactive. It also makes the material an n-type conductor and raises the Fermi energy. Boron, in contrast to nitrogen, serves as an electron acceptor, induced the emptying of electronic state below the Fermi energy for pristine graphane, and creates p-type graphane. After doping graphane with nitrogen, boron is the first atom that comes to mind as a dopant, because it is located in the same row of the periodic table as nitrogen and carbon, and boron is readily available in nature.

The Stone-Wales (SW) defect is a typical topological defect in the carbon nanostructures and is comprised of two pairs of five-mebered and seven-membered rings. From band structure and DOS calculations, we found that graphane with SW defect has a direct band gap of 2.5 eV in Γ point and as compared with pristine graphane, this defect causes that Fermi level shift to conduction bond.

The structural and electronic properties of pristine graphane, B-doped, N-doped and defective graphane were calculated using density functional theory. We realized that boron (nitrogen) has a p-type(n-type) effect. Furthermore, effect of SW and vacancy defect on the electronic structure are same as n-type. These changes have significant effect on the electronic structure as compared with pristine graphane. The maximum change on energy gap is occure in single vacancy defect and only this defect has an indirect band gap. Our calculations showed that doped unlike defect has a small effect on geometery.

Keywords: Graphane, Electronic Structure, Boron-Doped, Nitrogen-Doped, Defect.

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Investigation of Adsorption of pure Acetaminophen on carbon nanotube

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Key words: Adsorption, Carbon nanotube, Pure Acetaminophen

Introduction:

After discovering carbon nanotube by Lijima in 1991, these compounds developed so much physically and chemically [1]. The synthesis methods of these compounds developed fast [2]. Carbon nanotube can absorb so many atoms and molecules namely lithium [3], Rubidium [4] and some metal elements.

Materials and methods:

In order to provide Acetaminophen solution, twice distilled water was used .multi walled carbon nanotube was used as an adsorbent. first 100ppm of acetaminophen was provided using this sample, some solutions with different concentrations of 5 to 11 mg/lit of pure Acetaminophen were prepared specific amount of carbon nanotube (0.01gr) was added to flasks containing pure acetaminophen ,as an adsorbent .it was stirred , using a stirrer for 10 minutes. Then liquid and solid phase were separated by means of a filter paper. The concentration of pure acetaminophen was measured using a atomic absorption machine before and after the absorption .all test have been performed at the lab with the temperature.

Apparatus:

With the help of spectra photometry (uv/vis) the absorption diagram was obtained based on wave length for pure Acetaminophen so that the absorption diagram could be obtained based on concentration.





Result and discussion:

Table (1) shows the amount of pure Acetaminophen absorption without carbon nanotube on distilled water solvent. F diagram shows the amount of adsorption of pure Acetaminophen without carbon nanotube in different concentration. E diagram shows the amount of adsorption in the presence of carbon nanotube. Using the diagrams (F & E) and data in table (1). The absorption of pure Acetaminophen on 0.01 carbon nanotube could be determined. The results are shown in table (2).

Pure Acetaminophen	Maximum Absorption
concentration (mg. l^{-1})	(nm)
5ppm	0.33
7ppm	0.46
9ppm	0.59
11ppm	0.73

Table (1): Adsorption of pure Acetaminophen without carbon nanotube

Table (2): adsorption of pure acetaminophen on 0.01 carbon nanotube

Pure Acetaminophen concentration (mg)	Grams of material absorbed on 0.01 carbon nanotube (mg. g^{-1})		
5ppm	2.96		
7ppm	4.96		
9ppm	5.52		
11ppm	6.51		







Figure: Effect of concentration on adsorption

Conclusion:

In this research, the possibility of adsorption of pure Acetaminophen on carbon nanotube was studied. If showed that pure Acetaminophen had an acceptable absorption on carbon nanotube. Pure Acetaminophen with higher concentrations had better efficiency for the adsorption on carbon nanotube. The absorption of pure Acetaminophen on carbon nanotube was more than the absorption without carbon nanotube because some the solution was absorbed into the carbon nanotube

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Investigation of Adsorption of pure Naproxen on carbon nanotube

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Key words: Adsorption, Carbon nanotube, Pure Naproxen

Introduction:

After discovering carbon nanotube by Lijima in 1991, these compounds developed so much physically and chemically [1]. The synthesis methods of these compounds developed fast [2]. Carbon nanotube can absorb so many atoms and molecules namely lithium [3], Rubidium [4] and some metal elements.

Materials and methods:

In order to provide Naproxen solution, twice distilled water was used .multi walled carbon nanotube was used as an adsorbent. first 100ppm of Naproxen was provided using this sample, some solutions with different concentrations of 5 to 11 mg/lit of pure Naproxen were prepared specific amount of carbon nanotube (0.01gr) was added to flasks containing pure Naproxen ,as an adsorbent .it was stirred , using a stirrer for 10 minutes. Then liquid and solid phase were separated by means of a filter paper. the concentration of pure Naproxen was measured using a atomic absorption machine before and after the absorption .all test have been performed at the lab with the temperature.

Apparatus:

With the help of spectra photometry (uv/vis) the absorption diagram was obtained based on wave length for pure Naproxen so that the absorption diagram could be obtained based on concentration.





Result and discussion:

Column (1) in table shows pure Naproxen concentration in terms of PPM. Column (2) in table shows the amount of pure Naproxen absorption without carbon nanotube on distilled water solvent. (a) diagram is drawn based on data. Column (3) shows adsorption of pure Naproxen on 0.01 carbon nanotube .(b) diagram is drawn based 0n data. Using the diagrams (a &b) and data in table the absorption of pure Naproxen on 0.01 carbon nanotube could be determined. The results are shown column (4) in table.

Pure Naproxen	Maximum	adsorption of pure	Grams of material absorbed	
concentration	Absorption (nm)	Naproxen on 0.01 carbon	on 0.01 carbon nanotube	
(mg.l ⁻¹)		nanotube	$(mg. g^{-1})$	
5ppm	0.123	0.09	1.16	
7ppm	0.169	0.11	2.33	
9ppm	0.215	0.14	2.95	
11ppm	0.271	0.18	3.29	



Conclusion:

In this research, the possibility of adsorption of pure Naproxen on carbon nanotube was studied. If showed that pure Naproxen had an acceptable absorption on carbon nanotube. Pure Naproxen with higher concentrations had better efficiency for the adsorption on carbon nanotube. The absorption of pure Naproxen on carbon nanotube was more than the absorption without carbon nanotube because some the solution was absorbed into the carbon nanotube.





Reference:

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Biogas Adsorption-Based Separation by Metal Organic Frameworks: a Grand Canonical Monte Carlo Study

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Key words: Separation, GCMC, Biogas, MOF, Sulfur.

Introduction:

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Typical composition of biogas is methane (50–75 %) carbon dioxide (25– 50 %) nitrogen (0-10 %) hydrogen (0-1 %) hydrogen sulfide (0-3 %) [1], however, in some cases, biogas contains siloxanes. The composition of biogas varies depending upon the origin of the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. Advanced waste treatment technologies can produce biogas with 55-75% methane, which for reactors with free liquids can be increased to 80-90% methane using in-situ gas purification techniques. As-produced, biogas also contains water vapor. The fractional volume of water vapor is a function of biogas temperature; correction of measured gas volume for both water vapor content and thermal expansion is easily done via a simple mathematic algorithmwhich yields the standardized volume of dry biogas [2, 3]. The existence considerable amount sulfur compounds in biogas is caused to this type of gas would be the most harmful components. So, the separation of sulfur compounds in particular; sulfur dioxide, hydrogen sulfidethrough the physical adsorption has been considered by many scientific researchers and they try to find new materials to remove gas emissions from human living environments. This research intends to study the biogas adsorption-based separation by using a MOF and powerful molecular simulation tools.





Models and Methods of GCMC simulation details:

Grand canonical Monte Carlo (GCMC) simulations at fixed temperature, chemical potential, and pore volume were carried out to investigate the adsorption and separation of biogas inside MIL-53-Al and MIL-47 [4]. During the simulation, the periodic boundary conditions were used in three dimensions. It should be noted, before the use of GCMC, MOFs must investigate by density functional theory (DFT) using the B3LYPlevel of theory to achieve partial atomic charges. In our GCMC simulation, each run consisted of 4×10^6 GCMC moves. The first 2×10^6 moves were considered to correspond to an equilibration period, and were thus discarded; only the final 2×10^6 moves were used to calculate ensemble averages of thermodynamic parameters. The multipurpose simulation code of a molecular simulation package was used for all simulations [5].

Results and discussion:

In 2009, Hamon et al. have been carried out experimentally, hydrogen sulfide gravimetric isotherm adsorption measurements on MIL-53-Al, and MIL-47 MOFs. In their work, a twostep adsorption mechanism related to a breathing effect was observed for MIL-53-Al terephthalate-based MOFs. In 2011, Wang et al. also have been investigated pure and binary mixture of sulfur dioxide, hydrogen sulfide with methane, nitrogen and carbon dioxide considering single-walled carbon nanotube arrays by using GCMC simulations. Both previous works have not considered to the actual composition of biogas, whereas this work try to pay attention to this. According to our obtained data, the adsorption of pure sulfur dioxide, hydrogen sulfide, methane, nitrogen and carbon dioxide is more considerable in MOFs while these adsorptions is lower in carbon nanotube arrays. Although, our study has NOT finished and it is being completed.

Conclusion:

Some metal organics frameworks are considered to biogas adsorption-based separation using grand canonical Monte-Carlo Simulation. The actual composition of biogas is selected while





temperature is fixed at 300 K and moderated pressure is applied. The results show that MOFs are more adsorbable than other nano-structures such as nanotubes. Also, the observations emphasize that the elimination of sulfur compounds from gas mixtures which are included of them, is easier when MOFs are employed at ambient thermodynamics conditions.

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Hydrogen Physisorption of Cu–BTC and Zn–BTC metal-organic frameworks: a Molecular Simulation Approach

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Key words: Physisorption, MOFs, Hydrogen, GCMC.

Introduction:

Hydrogen is one of the leading candidates to adsorbinnanoporous metalorganic frameworks (MOFs). Hydrogen isas an energy carrier of the future because of its high energy content and clean burning, potentially renewable nature. Hydrogen adsorptionestablishesMOFas new class of materials to one of the most promising hydrogen storage materials for on-board applications and fuel cell vehicles. This capability of hydrogen is revealed by the continuously increasing number of new nonoporous MOFs reported in recent papers [1]. As we know, theoretical studies have proposed many promising MOFs whose simulated hydrogen uptakesreach the target of U. S. Department of Energy [2-3]. Up to now, many MOFs are considered to this filed. One of the famous MOF that has been selected to adsorption based mainly on the molecular sieving effect with large surface area and high thermal stability is copper benzene tricarboxylate (Cu-BTC). Cu-BTC was first reported in 1999 and named HKUST-1 [4]. This work tries to estimate hydrogen adsorptivity in Cu-BTC and Zn-BTC using molecular simulation methods.

Molecular simulation details:

We used Grand Canonical Monte Carlo (GCMC) simulations to compute hydrogen adsorptionat 298 K in Cu-BTC and Zn-BTC. Figure 1 shows the framework geometry of the Cu-BTC that employ in this work.







Fig. 1. Framework geometries of the Cu-BTC MOF materials that studied here.

At first, density functional theory (DFT) is applied to MOFs and hydrogen molecules to obtain the force field parameters for the interaction between hydrogen molecules and MOF atoms by fitting the calculated interaction energies and optimized interaction distances to potential functions(e.g., the Lennard-Jones (LJ)potentials) [5]. In molecular simulations, the LJ potential is generally used to describe the adsorbate–adsorbate interactions. Hydrogen generally represented by the two-site LJ potential model insimulations [6]. Using the derived force field parameters discussed briefly above as input, GCMC simulations can thus be performed to obtain hydrogen adsorption isotherms in MOFs. In GCMC simulations, the temperature, volume, and chemical potential are specified in advance. Each Monte Carlo simulation consists of two millions of random insertions, deletions, translations and rotations, which are accepted or rejected according to the criteria of a Boltzmann-type weighting. Also, periodic boundary conditionsare generally applied to eliminate boundary effects [7].

Results and discussion:

The hydrogen adsorption isotherms are investigated in terms of excess weight percent hydrogen (gravimetric uptake) forCu-BTC and Zn-BTCat 77 to 300 K and pressures under 10 atm. The Langmuir and Freundlich isotherm models were used to correlate the adsorption isotherms. Although, our study has NOT finished and it is being completed, nevertheless, the brief results are obtained, show thatCu-BTC has high hydrogen adsorption capacity than Zn-BTC, because of stable electronic structure of copper than zinc.





Conclusion:

In this paper, first, with the assistance of DFT and then perform the GCMC simulation, we haveproduced quantitatively the isotherm at vapor pressures below 0.01 atm, up to a near-complete filling of the pores (around 10 atm) in Cu-BTC and Zn-BTC. The indications emphasize that applying Cu-BTC to hydrogen adsorption is suitable than Zn-BTC.

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Effect of calcination temperature on structural and morphological properties of cobalt ferrite nanocrystals prepared by co-precipitation method

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Keywords: Co-precipitation, Calcination temperature, CoFe₂O₄, Nanoparticle.

Introduction:

In recent decades, the synthesis of nanosized ferrites with magnetic properties that differ substantially from those of macroparticles of the same composition has attracted considerable interest [1-4].

Ferrites are materials of significant importance because of the large number of technological applications they find, as well as because they can be used as model materials and thus provide an opportunity for better understanding of the magnetic interactions in nanoscale [5]. Many attempts have been made to design and synthesize various MFe₂O₄ nanostructures in order to explore their properties and potential applications[6]. Cobalt ferrite nanoparticles have been synthesized by a number of methods, including sol-gel [7], sol–gel auto-combustion [8], hydrothermal [9], co-precipitation [10], and microwave synthesis [11].

In this work Cobalt ferrite (CoFe₂O₄) nanoparticles have been synthesized successfully by coprecipitation method. Synthesized nanoparticles have been annealed at 500, 600 and 700°C for 2 hours. The effect of calcinations temperature in Structure and morphological properties investigate.

Material and methods:





All the reagents used in the experiments were analytically pure and used without further purification and treatment. Cobalt nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$, ferric nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, and Sodium hydroxide, NaOH, were all supplied by Merck Company.

 $CoFe_2O_4$ nanoparticles have been obtained by Co:Fe mole ratio of 1:2. The pH value of the metal nitrate solution was adjusted at 11 by adding stiochiometry amount of NaOH as precipitator. The deep brown colloidal solution continuously stirred by mechanical stirrer at 80°C for 9 hours. The resulting precipitate drying in Oven at 80 °C, the dried powder washed with distilled water and absolute ethanol. Final powder was calcinated at 500°C, 600°C, and 700°C for 2 hours.

Result and discussion:

The average particle size was estimated from the width of the diffraction line, which corresponds to a particular (h k l) reflection using the Scherrer equation. X-ray diffraction (XRD) studies showed that the crystallite size increased with increasing of calcination temperature. The average crystalline size of $CoFe_2O_4$ nanoparticles which were prepared at 500, 600 and 700 °C were 20, 32 and 47 nm, respectively. SEM images revealed that the nanoparticles were shaped in spherical form with size of 40 nm which was adapted with XRD calculations.

Concolution:

In this work, $CoFe_2O_4$ nanoparticles synthesized with coprecipitaion method at different calcinations temperatures. Structural and morphological properties investigate with XRD and SEM analysis.

Results indicates that the cobalt ferrite nanoparticles obtained by this method are uniform in both crystallite size and morphology, but having agglomeration to some extent, due to the relative higher annealing temperature and interaction between particles. Crystallite size and crystallinity percent shows increase with increase calcinations temperature.





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A comparative study on the structural, morphological and magnetic properties of cobalt ferrite nanoparticles synthesized by sol-gel autocombustion and microwave methods

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Keywords: Microwave, Sol-gel Autocombustion, Cobalt Ferrite, Nanoparticle.

Introduction:

Exploiting the unique magnetic properties of CoFe₂O₄ nanoparticles (e.g., tunable coercivity, large anisotropy, moderate saturation magnetization, site specific and strong binding to the serum albumin proteins etc.) many interesting biomedical applications are developed e.g. drug delivery, DNA separation, Magnetic Resonance Image (MRI) contrast and hyperthermia. Further, due to the strong spin orbital angular momentum (L-S) coupling, CoFe₂O₄ nanoparticles are highly stable up to 1000 °C and have good wear resistance and electrical insulation Property [1-3].

Many attempts have been made to design and synthesize various MFe_2O_4 nanostructures in order to explore their properties and potential applications[1]. Cobalt ferrite nanoparticles have been synthesized by a number of methods, including sol-gel [4], sol–gel auto-combustion [5], hydrothermal [6-9], co-precipitation [10-11], and microwave synthesis [12].

In this work cobalt ferrite Nanoparticles synthesized via Sol-gel Autocombustion and Sol-gel microwave method and next Structure, morphology and magnetic properties investigate.

Material and methods:



All the reagents used in the experiments were analytically pure and used without further purification and treatment. Cobalt nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$, ferric nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, Urea, and ammonia were all supplied by Merck Company.

 $CoFe_2O_4$ nanoparticles have been obtained by Co:Fe mole ratio of 1:2. The pH value of the metal nitrate solution was adjusted at 7 with ammonia. The obtained solution was stirred continuously at 60 °C for 6 hours. The resulting gel being ignited in air at 350 °C, the dried gel burnt in a self-propagating combustion way to form a loose powder.

A little amount of gel of previous section as a precursor was transferred in to a container suitable for microwave and then placed in a microwave oven for 10 minutes. The obtained powder was collected and washed with ethanol and deionized water. In both case, the final powder was calcined at 600 °C for 2 hours.

Result and discussion:

The crystallographic phase of the samples has been examined from the X-ray diffraction (XRD) spectrum. Peaks of both synthesized sample match well with the ferrite standard card. Average crystallite sizes can be estimated using Scherrer's formula. A Philips XL-30 scanning electron microscope was used to characterization the morphologies and microstructure of the samples.

Well-defined sharp peak indicate the good crystalline quality and confirm the formation of spinel magnetic ferrite and several peaks were attributed to α -Fe2O3 sub-phas in both case. The impurity phase was probably due to the occurrence of local combustion. XRD and SEM results shows that both technique produce same particle size (20 and 23 nm for sol-gel microwave and microwave respectively) but applying of microwave irradiation increased crystallinity percent of CoFe₂O₄. Hysteresis loops shows decrease in H_r about 1491.59 O_e to 1045.8 O_e in sol-gel autocombustion and microwave method respectively. The results revealed that the formation of cobalt ferrite spinel structures is influenced by changing methods.

Concolution:





In this work, $CoFe_2O_4$ nanoparticles synthesized with sol-gel Autocombustion and sol-gel microwave method. Structural and morphological properties investigate with XRD and SEM analysis. Both techniques were effective and lead to the production of spinel phase and crystalline nanopowders. In the same average particle size with different crystallinity the values of saturation magnetization and coercive fore of nanoparticles were prepared with sol-gel autocombustion method was less than those were obtained by microwave synthesis.

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Nano-Hydroxyapatite Supported MoO₂(acac) : Structure Characterization and Catalysis for Cyclooctene Epoxidation

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Keywords : nano-hydroxyapatite(HAP), catalyst, molybdenum, epoxidation

Introduction:

Catalytic olefin epoxidation in the liquid phase is an important topic for the synthesis of fine chemicals, because of their versatility as intermediates, epoxies are of great value in both synthetic organic chemistry and chemical technology [1]. Many soluble metal salts or complexes have been found to be active catalysts in this reaction during the last few decades. Recently, soluble compounds of early transition metals such as rhenium , titanium , vanadium, manganese and molybdenum have been used for alkene epoxidation [2-3]. In the case of molybdenum-containing complexes, oxomolybdenum species have been particularly investigated because of their good catalytic activity for selective oxidation. Different approaches have been used for immobilization of molybdenum complexes on various supports to obtain heterogeneous catalysts. Sherrington and coworkers have reported efficient epoxidation of alkenes with tert-butyl hydroperoxide catalyzed by reusable Mo(VI) supported on imidazole containing polymers. Hydroxyapatite $[Ca_{10}(PO_4)_3(OH)_2]$, (HAP) materials have been of great interest because of their mineral components being similar to human hard tissues [4].

Materials and methods:

Hydroxyapatite (HA) nano powders (30–40 nm) were synthesized using a sol–gel route with calcium nitrate and phosphoric acid as calcium and phosphorus precursors, respectively.





Double distilled water was used as a diluting media for HA sol preparation and ammonia was used to adjust the PH. After aging, the HA gel was dried at 65°C and calcined to different temperatures ranging from 200–800°C. Bis (acetyl-acetonato)dioxo-molybdenum (VI) [MoO₂(acac)₂] was immobilized on hydroxyapatite (HA) surface.

Apparatus:

Characterization of this catalyst was carried out with FT-IR, atomic absorption spectroscopy, SEM & TEM, powder X-ray diffraction (XRD) and BET nitrogen adsorption–desorption methods. The XRD and BET analyses revealed that textural properties of support were preserved during the grafting experiments.

Result and discussion:

The ability of this new heterogeneous catalytic system to selective epoxidation of alkenes reaction, using CCl_4 as solvent and TBHP as oxidizing agent has been investigated. the effect of reaction time, different solvent and oxidizing agent, amount of catalyst and oxidizing agent was investigated in epoxidation of cyclo-octene. The reusability of this catalyst is high and can be reused five times without significant decrease in its initial activity.



Scheme 1.cyclooctene epoxidation with tert-BuOOH catalyzed by HAP-MoO₂(acac).

Conclusion:

We have successfully inserted molybdenum(VI) complexes on HAP surface and investigated their performance as catalysts in the epoxidation reaction of cyclo-octene (scheme1). This heterogeneous $[MoO_2(acac)_2]$ immobilized on hydroxyapatite showed high stability and reusability in the epoxidation reactions without loss of its catalytic activity.

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Statistical properties of Plasma Enhanced Chemical Vapor Deposition nanoparticles

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Key words: Chemical Vapor Deposition, Statistical properties, Fractal dimension, nanoparticles

Introduction:

Chemical Vapor Deposition (CVD) process is an important method to fabricate uniform layer with low-porosity, high-purity, high-performance and local deposition. The process is often used to produce nanothin films and nanoparticles. It will be very useful and practical if we could produce nanoparticles with the desired size. A number of forms of CVD's are in wide use and are frequently referenced in the literatures. These processes differ in the means by which chemical reactions are initiated (e.g., activation process) and process conditions. In semiconductor technology three methods are used for the deposition of layers on semiconductor wafers[1,2]:1-APCVD. Atmospheric Pressure Chemical Vapor Deposition requires rather high temperatures.2-LPCVD.low Pressure Chemical Vapor Deposition. 3-PECVD. Plasma Enhanced Chemical Vapor Deposition. The necessary energy for the chemical reaction is not introduced by heating the whole reaction chamber but just by heated gas or plasma. The properties of the coated layers can be better influenced with PECVD than in simple thermal deposition technique, because more process parameters can be varied.

Fractal dimension (FD) is a useful feature for texture segmentation, shape classification, and graphic analysis in many fields. The box-counting approach is one of the frequently used techniques to estimate the FD of an image. Fractal geometry provides a mathematical model for many complex objects found in nature [3–5], such as coastlines, mountains, and clouds.





Different methods have been proposed to estimate the FD. The box-counting dimension is the most frequently used for measurements in various application fields[5].

Materials and methods:

In this study we have developed the box-counting method to analyze PECVD nanoparticles which Ag nanoparticles embedded in TiO_2 matrix. Formation of Ag/TiO₂ was carried out under hydrogen plasma bombardment system. Ag/TiO₂ nanostructure was successfully grown on glass substrates. An atmospheric pressure PECVD method was used to fabricate crystalline TiO_2 nanostructure. It has been compared with TiO_2 CVD nanothin film on glass substrate.

Result and discussion

Figure 1 shows AFM image of TiO_2 nanothin film(CVD) and Ag/TiO_2 nanoparticles (PECVD). It is clear that nanoparticles appear after applying plasma. It can be confirm by distribution function (Fig. 2).Contour pattern of TiO_2 and Ag/TiO_2 (Fig.3) demonstrates the nanostructure of CVD and PECVD. Left contour shows bigger islands than the right one, it means Ag nanoparticles with size about 50-100 nm have been created. It is verified by FD in figure 4 which illustrates that FD for TiO_2 is 1.8 for box size 10 < r < 80 while for Ag/TiO₂ is













Fig 4: Fractal dimension of TiO₂(Left) and Ag/TiO₂ (Right).

Conclusion:

We fabricated TiO_2 and Ag/TiO_2 nanothin films and showed that PECVD created nanoparticles which for Ag was smaller than TiO_2 and distribution function including Ag has been expanded. Fractal dimension indicates that the Ag nanoparticles are fractal in the greater range of box sizes.

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Poly terthiophene Mn(II) is a new nano biosensor of bilirubin: A quantum mechanical approach

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Key words: Poly terthiophene Mn(II), Nano bio sensor, Bilirubin, QM calculations.

Introduction:

Bilirubin is a tetrapyrrole compound that is formed from breakdown of heme in red blood cells, Figure 1A. The determination of bilirubin, in blood serum samples is considered as a true test of liver function. The high concentration of bilirubin is associated with liver diseases, such as cirrhosis or hepatitis, jaundice, brain damage or even death especially in new borns. Thus, the accurate determination of bilirubin is clinically important. Various methods have been developed for the detection of bilirubin in clinical samples, but most of them suffer from interference from other heme proteins [1]. The results of recent amperometric study show poly terthiophene Mn(II) (PTTCA Mn^{2+}) can be used as a nano biosensor of bilirubin [2], Figure 1B.



Figure 1. Presentation of natural δ -bilirubin (A) and poly terthiophene Mn(II) (B).




In the present study we have studied the complexation between PTTCA Mn^{2+} and different forms of natural bilirubin by using quantum mechanical calculations.

Computational Methods:

Ab initio calculations were carried out with the Gaussian program series 2003. The geometries of different complexes between PTTCA Mn^{2+} and δ -, β - and γ -bilirubin were fully optimized employing B3LYP/6-31G* basis set. Full optimizations were performed without any symmetry constrains.

Results and discussion:

Optimization of different forms of bilirubin indicate that γ -bilirubin with shorter conjugation length compared to the δ – and β -isomers, has been found less stable. The results of complexation between δ – and β -bilirubin with PTTCA Mn²⁺ biosensor in the present of water molecule indicate that one bilirubin molecule interacts with Mn(II) atom through three nitrogen atoms and one oxygen atom, Figure 2. Also the result of calculations show the interaction of bilirubin with PTTCA Mn²⁺ is energetically exothermic.



Figure 2. Presentation of optimized structure of PTTCA Mn^{2+}/δ -bilirubin complex.

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Characterization of Cysteine Coated Magnetite Nanoparticles as MRI Contrast Agent

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Key words: Magnetite; nanoparticles; Co-precipitation; Cysteine; MR imaging.

Introduction:

Ferrofluids containing magnetic nanoparticles, have potential applications in drug delivery, cancer therapy, magnetic resonance imaging (MRI) contrast enhancement agent, etc [1-4]. One of the fundamental preconditions for mentioned medical applications is high stability of synthesized ferrofluid with time and environmental variations. Among various parameters affect this stability, surfactant layer density plays an important role.

Formation of a high density coating will prevent agglomeration or sedimentation of solid phase. Besides, the nature and composition of surfactant is an important factor. Cysteine with three functional groups have a certain binding affinity to metal atoms specially Fe atoms.

In this work, a kind of stabilized ferrofluid based on magnetite nanoparticles (mean core and its coating size about 25.2 and 1.1 nm, respectively) was synthesized via coprecipitation method. Cysteine was used as surfactant due to its proper conjunction to the surface of magnetite nanoparticles. Coating density was measured using TEM and TGA results based on an indirect approach. Synthesized ferrofluid was characterized using Transmission Electron Microscope (TEM), Thermogravimetry Analysis (TGA), Dynamic Light Scattering (DLS) and Fourier transform infrared spectroscopy (FT-IR) techniques. MRI studies show that the synthesized ferrofluid can used as a potential contrast enhancement agent especially for imaging lymphatic system.





Materials and methods:

All chemical reagents in this study were of analytical grade and used as received without further purification. Briefly speaking, co-precipitation procedure performed using FeCl₃.6H₂O and FeCl₂.4H₂O as Fe resources, NaOH as reducing agent and Cysteine as surfactant. N₂ blowing was employed through three-naked balloon. Optimizing experimental conditions such as temperature, pH, molar ratio of reactants, ultrasonicating frequency and power, magnetite Cysteine capped nanoparticles were synthesized. Black precipitates were removed from liquid phase, washed, centrifuged, rewashed with distilled water and Hexane and finally dried and prepared for characterization experiments. Some suspension samples were prepared for DLS tests, whereas TGA and

FT-IR samples were dried powders. TEM samples were prepared via conventional method in which a suspension drop is trickled on the Carbon coated grid surface and studied after droplet drying.

Apparatus:

ZEISS EM-10C and high resolution Philips CM200 TEMs were used to determine the average particle and coating size, and morphology of the powders at accelerating voltage of 80 and 200 KV, respectively. FT-IR was performed using a Nicolet Magna 500 instrument. Malvern 4.2 DLS instrument was employed for hydrodynamic diameter measurement. TGA was performed using TGA Q50 instrument in order to investigate specimen weight changes. MR imaging performed with a 1.5 T (GE medical system) by using a knee coil for transmission and reception of the signal.

Result and discussion:

Synthesized ferrofluid (containing cysteine coated 25 nm magnetite nanoparticles characterized with TGA, FT-IR and TEM) was administered to rat intravenously via lateral tail vein. MR imaging performed with a 1.5 T (GE medical system) using a knee coil for transmission and reception of the signal. Rat was anaesthetized by pentobarbital sodium at the dose of 40 mg/kg body weight. MRI scan was performed 24 h after contrast agent





administration at a dose of 2.5 mg (Fe)/kg body weight. As is explained by theory [1], larger and aggregated particles are mainly accumulated in tissues such as liver and spleen, however, smaller ones (20-40 nm) are phogositosed by macrophages of lymphatic system. Enhancement of these tissues through substantial shortening of T2 relaxation times leads to hypo signal intensity of related tissues on MR images. Fig. 6 demonstrates signal enhancement in the area of lymph nodes 24 hours after injection of synthesized ferrofluid.

Conclusion:

A stable ferrofluid with mean magnetic core size and coating thickness about 25.2 and 1.1 nm, respectively, was synthesized using ultrasonic-assisted co-precipitation method. Synthesized ferrofluid had mean hydrodynamic diameter of 36.4 nm. Coating density equals to about 1.54 gr.cm⁻³ was measured using TEM and TGA results which show a high density coating is formed on the surface of nanoparticles. In animal study, good MR contrast enhancement was seen for lymph nodes after IV injection of synthesized ferrofluid.

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Preparation of ZnO nanostructure thin film on the glass and study of its ability for adsorption of Cu²⁺ from aqueous solution

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Key words: adsorption, ZnO, Thin film, Copper ion.

Introduction:

Microwave-assisted chemical bath deposition (MACBD) is an emerging technique for quick preparation of nanoscale and nanostructure particles. In this study a simple and rapid process for synthesis of ZnO nanostructure thin film on the glass was presented. The effect of pH and time of irradiation on morphology and composition of deposited films, were investigated too.

Experimental details:

ZnO thin films on the glass were prepared from precursor solution (PS) of $(CH_3COO)_2$ Zn.2H₂O and NH₄OH with certain concentration. pH adjustment has been done with certain concentration of NaOH and CH₃COOH solution. The substrate was put in the prepared solution and irradiated with microwave for a certain time.

Result and discussion:

The SEM micrographs of ZnO nanostructure thin films at different irradiation time were taken and the progress of flower like ZnO particle formation was presented.

The prepared ZnO thin films are able to remove Cu^{2+} from aqueous solution. Kinetic studies has been investigated in three different concentrations of $CuSO_4$ solution (100, 200, 300 ppm).



The results of kinetic studies are presented in Figure 1. The kinetic data were modeled with different kinetic models [1,2]. The equilibrium studies for adsorption of Cu^{2+} were carried out at 25 °C and the results were fitted with different isotherm equations [3].



Fig1. Adsorption of Cu²⁺ as a function of time.

Conclusion:

A simple and rapid process for synthesis of ZnO flowers by microwave-assisted chemical bath deposition (MACBD) from aqueous solution of tetra ammonium zinc hydroxide has been developed. Formation of flower like ZnO particles can be achieved at pH=9.7. The prepared ZnO films can remove Cu^{2+} from aqueous solution with a proper rate and high adsorption capacity.

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Copper iodide nanoparticles immobilized onpoly(4-vinyl pyridine): a new and green catalyst for click synthesis of 1,4-disubstituted-1,2,3-triazoles in water

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Key words: Click chemistry, Poly(4-vinyl pyridine) supported, Nanoparticles, copper(I) iodide

Introduction

The main method for the synthesis of 1,2,3-triazoles is the Huisgen 1,3-dipolar cycloaddition reaction of azides with alkynes [1]. This reaction has become the model for click reactions. Since the nanoparticles possess a high surface-to-volume ratio, which enhances their activity and selectivity, while at the same time maintaining the intrinsic features of a heterogeneous catalyst [2]. Herein we wish to report the applicability of a new, green and reusable catalytic system based on Cu(I) nano particles supported by poly(4-vinylpyridine)(P_4 VPy-CuI) for one-pot multicomponent click synthesis of 1,4-disubstituted-1H-1,2,3-triazoles from benzyl halides, sodium azide and terminal alkynes in water (Scheme1).

Materials and methods:

Preparation of the polymer supported catalyst:CuI (381mg) was put in 30 mL ethanol, and magnetically stirred at reflux temperature for 4 h under nitrogen atmosphere in the presence of dry poly(4-vinylpyridine) (1.0 g, mesh 50-60). The solvent was filtered, the resin washed with CH₃CN (2x20 mL) and dried under vacuum at 60°C overnight. The weight increase was 0.31 g (1.63 mmolCuI), which gave a polymer loading of 1.24 mmol CuI·g⁻¹. The loading of supported catalyst was calculated to be 1.32 mmol CuI·g⁻¹ of resin. Scanning electron 2651





microscopy (SEM), X-ray diffraction (XRD) analysis, atomic absorption and IR experimental techniques were used to characterize the catalyst.General procedure for synthesis of 1,4-disubstituted triazoles:Benzyl halide(1 mmol),alkyne(1 mmol) and sodium azide(1.1 mmol) were placed together in a round-bottom flask containing 10 mL of water. Poly(4-vinylpyridine)-CuI (0.1 g), was added to the mixture. The suspension was magnetically stirred under reflux conditions for appropriate time. After completion of the reaction as followed by TLC, the resin was filtered and washed with hot ethanol (2×5 mL). The recovered catalyst was washed with acetone, dried and stored for another consecutive reaction run. The filtrates were evaporated to dryness, and then the solid residue was recrystallized in ethanol/water(1:3 v/v) to give pure product crystals.

Result and discussion:

The copper(I) iodide catalyst immobilized on poly(4-vinylpyridine) was readily prepared in a one-step procedure. Poly(4-vinylpyridine) was refluxed with CuI under N_2 atmosphere in EtOH to afford the Poly(4-vinylpyridine)-CuI nanoparticles. This method was developed for the effective synthesis of copper nanoparticles incorporated heterogeneously as catalyst in some organic reactions [3].



At the first, to optimize the reaction conditions, the reaction between benzyl bromide, phenyl acetylene and sodium azide was chosen as a model. The best result was achieved by caring out the reaction of benzyl bromide, phenylacetylene and sodium azide (with 1: 1: 1.1 mol ratio) in the presence of 0.1 g of P₄VPy-CuI under reflux condition in water. This procedure was extended to various benzyl halides and terminal alkynes with electron donating or electron releasinggroups. In the all cases, the reactions were completed during short times.





Conclusion:

We have developed a mild, simple and green procedure for the one-pot regiospecific1,4disubstituted-1H-1,2,3-triazoles via Huisgen 1,3-dipolar cycloaddition reaction. The introduced catalyst can promote the yields and reaction times over 8 runs with very low leaching amounts of supported catalyst into the reaction mixture.

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Synthesis and Characterization of magnenic nanohollow spheres

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Keywords: sol-gel process, silica nanohollow sphere, magnetic nanoparticle, magnetic properties.

Introduction:

Magnetic nanoparticles have been received extensively research interest due to their wide applications [1-3]. Controlled synthesis of nanostructured materials including magnetic nanomaterials is the basis for in-depth research of nanoscience and technology because the shape, size and structure of the materials play the key roles determining their optical, catalytic, magnetic, or mechanical properties. As one of important members of magnetic composite hollow spheres, magnetic/silica composite hollow spheres have been extensively studied owing to the advantages of silica (nontoxic, biocompatible, stability against decomposition and hydrophilic character). It is known that SiO₂ can be modified via a sol–gel reaction using a silane coupling agent to disperse it in a polymer matrix, as silane coupling agents belong to a class of organosilane compounds in which at least two different types of reactive group are bonded to the silicon atom in a molecule.

In the present work, we report a facile method for the fabrication of monodispersed sizecontrollable silica nanohollow sphere (SNHS) by sol-gel method, then coated with magnetic ferrite by coprecipitation of $FeCl_2$ over the surface of SNHS. The crystal structure, morphology and magnetic property of the MF-SNHS spheres were studied in detail.

Materials and methods:

The synthesis of hollow mesoporous silica spheres was achieved by the ammonia-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in mixed ethanol-water





solvents by using cetyltrimethylammonium bromide (CTAB) as surfactant. The surface of silica was coated with mercaptopropyltriethoxysilane (MPTMS) by a silanization reaction. In a typical procedure, silica hollow sphere was dispersed in toluene to produce a homogeneous suspension, followed by adding MPTMS. The reaction mixture was kept at room temperature and stirred for 24 h. The resulting thiol functionalized hollow silica spheres (TFHSS) was washed several times with toluene to remove unreacted MPTMS. To synthesis sulfonic acid functionalized hollow silica spheres (SAFHSS), TFHSS was dispersed in hydrogen peroxide and kept the oxidation reaction under N₂ protection for 12 h. The obtained SAFHSS dispersion was separated again by centrifugation, following by washing with deionized water several times. To synthesis of hollow magnetic/silica composite spheres, firstly, SAFHSS were dispersed in deionized water and ethylene glycol mixture solution. Secondly, hexamethylene tetramine and potassium nitrate were added into the system. Finally, aqueous iron ion solution was injected into the system then the system was heated and reacted for 3 h under nitrogen protection. The resultant particles were separated with a magnet and washed with deionized water.

Result and discussion:

The SEM image of hollow silica spheres shows that the particles are monodispers with the size about 200 nm in diameter (Figure 1). Figure 2(a) shows the FT-IR spectrum of thiol functionalized hollow silica spheres. There occur to a distinctively weak characteristic absorption peak at 2553 cm⁻¹, which is assigned to S–H stretching vibration. After oxidization of hydrogen peroxide, the characteristic peaks of –SH groups disappeared, as shown in Figure 1(b). The characteristic peak of –SO₃H groups in the bands of 1150–1250 cm⁻¹ is hidden by the bands of 1000–1200 cm⁻¹. The magnetic properties of as prepared particles were studied at room temperature by alternating gradient field magnetometer (AGFM) (not shown).







Fig. 2. FT-IR spectra of TFHSS (a) and (b) SAFHSS.

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Degradation of an organic dye at acidic, neutral and basic buffer solutions by photocatalytic process in the presence of titanium dioxide nanoparticles

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Keywords: Nano-Titanium dioxide, Azo, dye, Photocatalytic.

Introduction:

A common way to perform the decolorization of pollutants is the use of photocatalytic removal processes that are known by the generation of OH radicals under mild experimental conditions [1-4]. 3, 7-Diaminophenazathionium chloride (DAPTC) is harmful if swallowed and may be harmful by inhalation or through skin contact. In this work we wish to report photocatalytic decolorization of DAPTC on nano-structure titanium dioxide at acidic, neutral and basic buffer aqueous solution. The kinetic study of decolorization of DAPTC in each buffer pH is described.

Materials and methods:

All chemical reagents were prepared from Merck and Fluka chemical companies. 3, 7-Diaminophenazathionium chloride was purchased from Aldrich. Nano-structure titanium dioxide with average size of 70 nm was used as photocatalyst. The photodecolorization experiments were done by illumination of 20 mL continuous aerated, stirred buffer solutions of DAPTC containing 10-20 mg of nano-titanium dioxide in a photoreactor cell under 400W high pressure mercury lamp at constant temperature.

Results and Discussion:

The photodegradation of DAPTC obeys the pseudo-first order kinetics:(-dC/dt=kC) Where c is





the concentration of DAPTC and k is the observed first-order rate constant (k_{obs}). From the integration of this equation, the concentration-time equation of $\ln(C_0/C_t) = k_{obs}t$ will be derived. The first-order rate constant, k_{obs} of photodegradation can be obtained from the plot of $\ln(C_0/C_t)$ versus time(figure 1).



Figure 1- The Plots of $\ln(C_0/C_t)$ vs. time for photocatalytic decolorization of DAPTC

Kinetic parameters of photodegradation of DAPTC were derived using Langmuir-Hinshelwood model from the diagram of 1/R vs. 1/C₀ at various buffer pHs(R= reaction rate and C₀ = initiated concentration)(figure 1). From the slope and intercept of this diagram, the adsorption constants K_A, and photocatalytic degradation rate constants, k_r are resulted. The amounts of K_A are, 527.48×10², 23.736×10² and 3.824×10² (M⁻¹). The values of k_r are 3.033×10, 5.41 ×10 and 1.80×10^2 (M.min⁻¹) and finally the observed rate constants of decolorization are 2.41, 4.92×10 and 2.11×10² (S⁻¹) for pHs of 2, 7 and 9.

Conclusion:

In this research we reported kinetic investigation of thionine (DAPTC) photocatalytic degradation. The nanostructure titanium dioxide was used as photocatalyst. Rate constants are evaluated at different buffer pHs. Also the Langmuir-Hinshelwood (L-H) rate constant, (k_r) and adsorption constant, (K_A) at various buffer pHs were estimated.

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Biological Effects of Surfactants (SDS CTAB (Triton X-100) Used in the Preparation of Nano Fluids

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Keywords: Biosensor, Vibrio Fischeri, Bioluminescence, Toxicity, surfactant

Introduction:

The term surfactant is a blend of surface active agents. A surfactant is briefly defined as a material that can greatly reduce the surface tension of water when used in very low concentrations.

Companies and Nanomanufacturing Center use various surfactants in preparation of suspensions of nanoparticles that all of them are not safe in term of toxicity.

In recent years much research has been conducted in the field of biological sensors for detecting various types of pollution.

Vibrio Fischeri is a biosensor and has bioluminescent properties which is highly sensitive to the presence and effects of pollutants and detects the presence of contamination with low light. We provide an experiment to evaluate the possible toxic effects of surfactants (SDS, CTAB, Triton X-100) by this biosensor [1-4].

(1) Sodium lauryl sulfate SLS its chemical formula is NaC12H25SO4 or Sodium dodecyl sulfate, SDS are anionic surfactant.

(2) Cetyl trimethyl ammonium bromide (CTAB) its chemical formula is C19H42BrN is anionic surfactant.

(3) Polyoxyethylene octyl phenyl ether (Triton X-100) its chemical formula is C14H22O(C2H4O)n (n = 9-10) and is a nonionic surfactant.





Materials and methods:

After preparing the medium and the bacterial inoculum, we used the incubator at 20 °C for 48 hours for bacterial growth. After optimizing bacterial culture, appropriate growth temperature and time to reach equilibrium, we examine the changes in the biological effects of surfactants of nanomaterial by luminescence of vibrio fischeri.

For the beginning, use serial dilution to prepare various concentrations of surfactants. Then load 200 μ l of bacterial suspension in each cuvette and place them in the luminometer and record the value. Afterwards, add 100 μ l of concentrations of surfactants to the cuvettes. After 30 minutes and the clash of bakeries with nanomaterial, record the value again [3,4].

Result and discussion:

Test criterion is reduction of emitting light. In this step, the rate of the inhibition of bacterial luminescence (INH%) is obtained. Then, the diagram of the rate of the inhibition of bacterial luminescence (INH%) toward the concentrations of surfactants is drawn and line equation is obtained [3,4].

Subsequently, important indicator in toxicity assessment, called EC_{50} which is the criteria for evaluation of toxic effect and pollution of different materials on the bacteria Vibrio Fischeri, can be determined from graphs: SDS: 143.98 mg/l

Conclusion:

Among the tested surfactants, SDS has rather severe toxic effects on the bacteria and categorized as harmful. However, surfactant Triton X-100 doesn't have toxic effects on the bacteria and doesn't reduce its light. This surfactant is suitable for homogeneous suspension of metal oxide nanoparticles preparation and its gel-like state contributed to its stability and suspension of particles during the experiment.

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Study of the Biocidal Effects of Nanotube Single Wall, Nanotube Multi Wall, Fe and Al₂O₃ Nanoparticles by Biosensor

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Keywords: Biosensor, Vibrio Fischeri, Bioluminescence, Toxicity, Nano Materials

Introduction:

There are many risks associated with Nanoscale particles. Because of small size of Nanomaterials and a high surface to volume ratio, they tend to be more reactive. The high reactivity leads to an increase in production of active oxygen species (ROS) such as free radicals. These free radicals attack other molecules, particularly lipids, proteins, and nucleic acids causing an increase in cell membrane fatty acid peroxidation, eventually causing damage, inflammation, and cell death.

Our Biosensor is composed of two parts: a biological section made of a luminescence bacteria called vibrio fischeri and an electrical device called luminometer which help to examine bacterial exposure in a variety of conditions [1,2].

Materials and methods:

After preparing the medium and the bacterial inoculum, we used the incubator at 20 °C for 48 hours for bacterial growth. For preparation of suspensions of Nano-powders, powders should be mixed with deionized water. For better stability and prevention of sedimentation we used proper surfactant and ultrasonic device. Using the ultrasonic device for nanomaterial for 30 minutes makes the concrete and mass particles be separated.





After optimizing bacterial culture, appropriate growth temperature and time to reach equilibrium, we examine the changes in the biocide effects of nanomaterial by luminescence of vibrio fischeri. For the beginning, use serial dilution to prepare various concentrations of nanomaterial. Then load 200 μ l of bacterial suspension in each cuvette and place them in the luminometer and record the value. Afterwards, add 100 μ l of nanomaterial to the cuvettes. After 30 minutes and the clash of bakeries with nanomaterial, record the value again [1,2].

Result and discussion:

Test criterion is reduction of emitting light. In this step, the rate of the inhibition of bacterial luminescence (INH%) is obtained. Then, the diagram of the rate of the inhibition of bacterial luminescence (INH%) toward the concentrations of nanomaterial is drawn and line equation is obtained [1-4].

Subsequently, two important indicators in toxicity assessment, called EC_{50} and EC_{20} which are the criteria for evaluation of toxic effect and pollution of different materials on the bacteria Vibrio Fischeri, can be determined from graphs (Table1):

	Nano Materials	Particles Sizes (nm)	Surface Area (m ² /g)	EC50 (mg/L)	EC20 (mg/L)
	Nanotube single wall	Diameter= 2-3 Length=10	700	25.85	2.63
	Nanotube multi wall	Diameter= 10-20 Length=10	250	28.54	3.04
	Fe	8-18	60-80	51.12	3.5 <mark>6</mark>
1	Al ₂ O ₃	Dimension= 43-47 Length=1.8	350	41307.02	21. 1 7

Conclusion:

Based on this study, it can be concluded that the chemical composition of nanomaterial play an important role in causing toxicity. Therefore, as the particle size becomes smaller nanomaterial may exhibit higher toxicity.

Based on the results, nanotube single wall, nanotube multi wall and Nano Fe have higher toxicity and categorized as toxic and Nano Al₂O₃ has a low toxicity and categorized as not classified.





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An Investigation of growth time effect on morphological and structural properties of SiO₂ nanowires deposited by thermal evaporation method

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Keywords: Silicon Oxide, Nanowire, Thermal Evaporation

Introduction:

Silicon oxide (SiO_2) has been attracted due to its various potential applications in optical sensors, with high sensitivity, solar cells and field effect transistors [1, 2]. In this work, we are interested to investigate the effect of growth time (2.5 and 3.0 hours; sample **a** and **b**, respectively) on morphological and structural properties of SiO₂ nanostructure samples.

Experiments:

In this study 0.3 grams silicon monoxide powder (purity 99.8%, Aldrich) was used as the source material in an alumina boat placed at the middle of the horizontal quartz tube. The growth temperature and vacuum pressure were $1150 \,^{\circ}$ C and 10^{-6} torr, respectively. Argon was used as the carrier gas at a flow rate of 100 sccm to grow the thin layers on p-Si (100) wafers, 10 cm apart from the boat. Through this study we have characterized the grown samples by SEM, XRD and EDS methods.

Results and Discussion:

Fig. 1 shows the SEM images of our samples. As it is obvious although both samples are grown with a relative uniformly spread nanowires (\sim 100 nm in diameters and few microns in length) and nodes, sample **a** is more packed than the other one.







Fig. 1. The SEM images of SiO₂ nanowire samples, **a** and **b**, together with their higher resolutions.

In order to find out the material compositions the EDS images were prepared for sample **a** (Fig. 2). Figs. 2(a) and 2(b) show the correspding spectra at the nodes and wires, respectively. According to these results although the nanowires compositions are silicon and oxygen atoms, at the node sites it consists of silicon, oxygen and iron (due to carrier gas impurity) atoms.



Fig 2. The EDS spectra for sample a at the nodes (a), and nanowires (b).

To find out the material structure we have prepared the XRD spectrum of this sample as well, Fig. 3. According to this data nanowires are grown in single phase polycrystalline structure with (210) as the preferential orientation.



Fig 3. The XRD image of sample a.





Conclusion:

The SiO₂ nanostructures have been synthesized on p-Si (100) by thermal evaporation at two different growth times of 2.5 and 3.0 hours, sample **a** and **b**, respectively. The SEM images show sample **a** is more compact with nanowires (diameters of ~100 nm) than the other one. The XRD data confirms it is in single phase polycrystalline structure.

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Synthesis, Determination of physicochemical properties and cytotoxicity study of Mitoxantrone loaded magnetic nanoparticles

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Key words: Mitoxantrone, Drug Delivery, Fe₃O₄ magnetic nanoparticles, MCF-7, Folic acid

Introduction:

Drug delivery and gene targeting using magnetic nanoparticles (MNPs) is a promising way for cancer chemotherapy and cancer gene therapy because their remarkable accumulation behaviour at the tumour site [1, 2]. MNPs have high tendency to agglomerate, So macrophages can quickly clear agglomerated nanoparticles. Accordingly, the surface of nanoparticles can be modified with hydrophilic polymers such as polyethyleneglycol (PEG). This surface engineering of magnetic nanoparticles improve stability of MNPs in physiological media [3, 4]. On the other hand, Magnetic nanoparticles can conjugate with chemical or biological endocytosed reagents such as folic acid [5]. Conjugation of folic acid to the surface of magnetic nanoparticles may increase targeting of magnetic nanoparticles to the tumours because endocytosis phenomena [5, 6]. Magnetic nanoparticles drug delivery systems may be useful for delivery of cancer treatment drugs into the tumour cells[6, 7]. In the present work, we discuss the synthesis of bi-functional drug delivery system consists of Fe₃O₄-DPA-PEG-NH₂. These magnetic nanoparticles covalently bounded to the folic acid via amide bond and then chemically grafted to the mitoxantrone.

Materials and methods:

We first synthesized Fe_3O_4 magnetic nanoparticles (average size of ~10nm) by thermal decomposition reaction of $Fe(acac)_3$. A bromoacetyl-terminal polyethylene glycol dopamine





(DPA-PEG-BrAc) was synthesized by treating polyethylene glycol (PEG) first by excess bromoacetyl chloride (BrAc) to form bis-bromoacetyl polyethylene glycol (BBrAc-PEG) and second, reaction of BBrAC-PEG with one equivalent of dopamine afforded DPA-PEG-BrAc. The DPA-PEG-BrAc was treated with ethylene diamine to form bifunctional PEG moiety containing dopamine at one end and amino group at the other end (DPA-PEG-NH₂). The DPA-PEG-NH₂ can easily self-assemble on iron oxide nanoparticles. The Fe₃O₄-DPA-PEG-NH₂ nanoparticles have the flexibility to conjugate with cell targeting agents via amine terminal groups. In this paper activated folic acid chemically coupled to the Fe₃O₄-DPA-PEG-NH₂ via amide bond to form Fe₃O₄-DPA-PEG-FA. Mitoxantrone was then reacted with activated carboxylic acid of folic acid to form the final product Fe₃O₄-DPA-PEG-FA-MTN.

Result and discussion:

The sizes of the composite nanoparticles were nearly 37 nm, determined by SEM and particle size analyzer methods. The XRD pattern of the composite nanoparticles shows a cubic structure. Magnetometery was done by vibrating sample magnetometer (VSM) that showed superparamagnetic behavior for the synthesized composite nanoparticles. Among composite nanoparticles only Fe_3O_4 -DPA-PEG-FA-MTN showed same efficacy with free mitoxantrone on MCF-7 breast cancer cell lines. The IC₅₀ of free mitoxantrone and Fe₃O₄-DPA-PEG-FA-MTN were 0.9 and 1.5, respectively.

Conclusion:

In this work, for the first time, we have implemented a method for chemically grafting of mitoxantrone to the surface MNPs armed with folic acid as homing device. The MTN conjugated MNPs (Fe_3O_4 -DPA-PEG-FA-MTN) exhibited sustained release profile for liberation of dug molecules and significantly inhibited the growth of MCF-7 cells even after 72 h post-treatment.

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Immobilization of cobalt over functionalized magnetic nonoparticles for liquid phase oxidation of cyclohexene

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Key words: Catalytic oxidation, Magnetic nanoparticle, Cyclohexene

Introduction:

Olefin catalytic oxidation is an important process, as they arevaluable intermediates in both living and industrial systems [1].Deactivation in the reaction matrix and non-recovery are twoserious flaws of these homogenous systems. One way toovercome these problems is immobilization on a solid support [2].Magnetic particles such as Fe_3O_4 have attracted moreattention as they could be easily separated from the solution a magnetic field [3]. In this work, we have reported preparation of novel functionalized Fe_3O_4 nanoparticles and applied the for cyclohexene oxidation.

Method:

Functionalized Fe₃O₄ nanoparticles were synthesized according to [4] and their formation wasestablished by X-ray powder diffraction. For oxidation experiments, in a 10 mL round-bottom flask, the prepared catalyst(0.1 g, 0.005 mmol), cyclohexene (0.05 mmol) and oxidant (0.1 mmol) were added inorder. All experiments were repeated in the various solvents such as methanol, dichloromethane, acetone, and acetonitryl. The effect of temperature, type of oxidant, and amount of the catalyst were also investigated. The products were analyzed by GC/MS.

Results and discussion:





The results showed that the amount of the catalyst had a key role on the amount of the catalytic activity and selectivity. In the low amount of it (0.01 gr), the main product was cyclohexenone andby increase of the catalyst (0.1 gr) the main product was glycerol. It was found that among the various oxidants, urea hydrogen peroxide and H_2O_2 had the high and low activity, respectively.

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DOS Spectra and NBO Analysis of the NO₂Surface Interactions on the Cyclic (WO₃)_n (n=2-6) Nano-Clusters

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Keywords: Density of States (DOS); WO₃, Adsorption, NO₂, ;Quantum computations

Introduction:

The research on atomistic understanding of gas-surface interactions of MxO_Ysemiconductor gas sensors hasattracted more and more attention. Tungsten oxide (WO₃) is one of them and has a wide band gap semiconductingmetal oxide [1]. For WO₃-based gas sensors, WO₃ plays a role as asensitive layer for detecting small quantities of NOx, NH₃, O₃,H₂, SO₂ and so on. In case of the NOx adsorption onWO₃, to the best of our knowledge,no theoretical study has been reported. In this paper the electronic structure changes due to adsorption of NO₂ molecules on WO₃ were studied by using B3LYP and X3LYP DFT (density functional theory) calculations.In our previous studies we found that NO adsorption can modify theband structure and order of the electronic energy level. This mechanismmay have primary importance in determining the properties of oxide as a gas sensor.



Figure 1. Optimized strutures of cyclic clusters of (WO3)n

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First principles calculations at the DFT level were used for the study of the structures of $(WO_3)_n(n=2-6)$ clusters. The geometries were optimized at the B3LYP and X3LYP methods. LANL2DZ and 6-311++G(d,p) basis sets were used for clusters and NO₂, respectively, using the GAUSSIAN 09 package [2]. The interaction energy of the NO₂ molecule with seven different substrates has been computed in the following manner according to equation 1:

$\Delta E = E(NO_2@(WO_3)_n - E((WO_3)_n) - E(NO_2)1$

Cyclic clusters of WO3 were chosen as the starting point ofour calculations, as presented in Figure 1.



Figure 2. Different stable NO2 adsorption sites on W2O6 edge as an example

Results and discussion:

Figure 2 shows four different adsorption structures (1-4) for NO₂ adsorption on the $(WO_3)_n$ edge. Figure 4 is the most stable mode of adsorption for n=2 and represents no dissociative condition with an energy of adsorption of 2.0 ev. Mode 3 possesses the energies of 0.32, 0.32, 0.29 and 0.30 ev for the structures with n=3-6, respectively. Calculated bandstructures and density of states (DOS) were calculated for all structures with two dominant modes of adsorption. NO₂adsorption not only affects the surface structure ofWO3, but also changes the electronic structure substantially.DOS comparisons of the WO3 beforeand after NO₂ adsorption shows that the most obvious change is that all bands shift towards low energiesafter adsorption, leading to the partial filling of the conduction band maximum(CBM). DOS analysis suggests that the new occupied electronicstates involve mainly 5*d* states of W with slight 2*p* states ofO. which is contributed tofurtherhybridization





between 2p states of O and 5d states of W. Fermilevel is shifted by 4.0eV towards high-energy direction(from -10.0 to -6.0eV), which corresponds to the partial fillingof CBM and the increase of the conductivity resulting from the NO₂ adsorption. NBO analysis show that a positive character for N atom and negative characters for O and W atoms, which in turns confirmed the electron localization between W of WO₃ and O of NO₂ molecules. HOMO-LUMO energy differences for all systems were calculated and correspond to DOS and NBO data.

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Removal of benzoic acid, *p*-nitro phenol and resorcinol from aqueous solutions by modified maghemite nanoparticles

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Key words: Maghemite nanoparticles, CTAB, Waste water samples, Benzoic acid (BA), *p*-Nitrophenol (PNP), Resorcinol.

Introduction:

Because of benzoic acid (BA) and some of phenolic compounds harmful effects, adsorptive removal of BA, p-nitro phenol (PNP) and resorcinol from aqueous solutions was investigated in this study [1-4]. Here cetyltrimethylammonium bromide modified maghemite nanoparticles (CTAB- γ -Fe₂O₃), as an efficient adsorbent, was used for removal of BA, PNP and resorcinol from water samples. Pollutants were entrapped on the surface of surfactant coated nanoparticle sorbents as in the SPE method. Maghemite nanoparticles (γ -Fe₂O₃) were prepared by co-precipitation method and characterized by SEM, XRD and BET measurements [5]. Then the surfaces of the prepared maghemite nanoparticles, were modified by CTAB cationic surfactant [6].

Materials and methods:

All the chemicals and reagents used in this work were of analytical grade and purchased from Merck (Merck, Darmstadt, Germany). A stock solution 1000 mg L^{-1} of BA, PNP and resorcinol were prepared in double distilled water (DDW), and experimental solutions of their desired concentrations were obtained by successive dilutions of the stock solution with DDW.

Apparatus:





A Metrohm model 713 pH-meter was used for pH measurements. A single beam UV-mini-Agilent 8453 UV-Vis spectrophotometer was used for determination of BA concentration in the solutions. Scanning electron microscope (SEM, Philips, XL30, Netherd land) was used for preparation of SEM images. The size and properties of the produced maghemite nanoparticles was determined by an X-ray diffractometer (XRD) (38066 RIVA, d/G.Via M. Misone, 11/D (TN) Italy) at ambient temperature. A 40 \pm 5% kHz (power: 100 W) ultrasonic water bath (DSA100-SK₂, Korea) was used in this work.

Result and discussion:

The influences including initial pH, amount of adsorbent, dosage of surfactant, amount and kind of elution, and contact time for adsorption and desorption processes have been investigated in order to find the optimum adsorption/desorption conditions. Results showed that synthesized maghemite nanoparticles are such a good candidate for removal of BA, PNP and resorcinol in a wastewater treatment process. The adsorption isotherm data were derived at room temperature and treated according to different equilibrium models. The extra adsorption capacity of nanoparticles was evaluated for BA, PNP and resorcinol as 989.1, 302.8 and 1110.0 mg g⁻¹ respectively. Also kinetic parameters were calculated from different kinetic models.

Conclusion:

In summary, the presented SPE method combines the advantages of mixed hemimicelles and magnetic nanoparticles, which are expected to provide distinctive benefits such as high extraction yields, significant high adsorption capacity and easy separation. They avoid the time consuming of other previous troublesome process and/or sorbents. At last other than the prominence of strong magnetic properties of the CTAB- γ -Fe₂O₃ nanoparticles, the satisfactory results can be achieved by using fewer amounts of nanoparticles than routine applied sorbents due to its higher surface areas.

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Nano Filtration for Water Treatment

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Key Words : Nano filtration, Water treatment, Nano materials, Membrane

Summary:

Due to limited access to water resources requires appropriate methodology for reducing water consumption, reduce water pollution and recycling, which provides water treatment plant feasibility of nanotechnology. [1] This study introduces a variety of water treatment methods, the introduction of suitable materials for water treatment, process water treatment, membrane types and methods of making them and their structure is discussed. Review and compare specifications and the introduction of nano-filtration membrane processes is also desired. With the intention to review the cases mentioned in the diagnosis and select the best method of membrane filtration for water treatment according to its application are better. That some membrane with respect to the application of pressure and capable of passing Flax have different performance for each specific material removal process work better.

Introduction:

Reverse osmosis and ultrafiltration nanofiltration process between the molecules in the size of 1 nm at low pressure disposal which requires no chemicals and has little operation and maintenance costs. [2] Membranes used in water purification and sewage treatment with the selective permeability properties and the need for the propulsion force that the difference in concentration, pressure, temperature and electric potential are. Performance by two parameter flow through the membrane and the membrane selectivity of the is determined. [3]

Nano-filtration membranes with low energy consumption and taking into account the need to build a system to measure various Vashkal. Higher separation efficiency and the process 2680





temperature is typical of the advantages of this method. They can be heat-sensitive solutions, especially in the food industry, pharmaceutical, biotechnology can be used. [4]

Retention rate of charged particles in the nano-filtration, ion which is a function of time. Molecular mass retention by the membrane is placed between 200 -2000 g mol. This membrane is composite, dual and Bardarnd. Their physical and chemical properties of organic or inorganic nature, enjoy a special relationship. The asymmetric membrane fabrication methods, including phase separation, polymerization surface coating is solvent correction methods. Twenty polymerization was the best method is first used by Kadvt. Membranes for the need for basic information, including chemical resistance, thermal, mechanical, membrane module and claims retention is for refining electrolyte solution.

Applications:

Nano-filtration of surface water, groundwater and seawater is used. Including removing hard water applications, the separation of heavy metals in order to reuse the water, brackish water, salt reduction, removal of pesticides from ground water, recycling of effluent home sewage and nitrate is removed. The membranes of the two mechanisms act to remove the physical and electrostatic discharge.

Conclusions:

Research has been done in China in the nano-filter with water arising from the long-term incidence of heart disease - cancer, vascular, respectively 40% and 20% have declined. Cost far less energy than reverse osmosis process and power Gary selected ion removal is high.

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Structural, magnetic, and ferroelectric properties of BiFeO₃ and BiFe_{0.96}Co_{0.04}O₃multiferroics

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Key words: Multiferroic, Ferromagnetic, Ferroelectric, Ball-mill

Introduction:

Multiferroic materials, exhibiting simultaneously the magnetic and ferroelectric ordering, have been widely studied in recent years, due to their abundant physics and potential applications in the sensors, data storage, and spintronics[1]. Among the rare multiferroic materials, BiFeO₃ is one of the well knownmultiferroic with G-type antiferromagnetic behavior below $T_N \sim 643 K$ and ferroelectric behavior below $T_C \sim 1103 K$ [2]. Much efforthave been paid to improve the magnetization in BiFeO₃. Fe ion substitution whit other magnetic ions is veryattractive, and enhanced ferromagnetism was reported[3]. In this work we have studied structural, magnetic, and ferroelectric properties BiFeO₃ and cobalt doped BiFe_{0.96}Co_{0.04}O₃nano-powders and ceramics.

Methods:

The samples were synthesized using the high purity precursor oxides, Bi_2O_3 , Fe_2O_3 , and Co_3O_4 , in stoichiometric amounts. They mixed and subsequently milled up to 5h in ahigh energy SPEX 8000 ball-mill using aball to powder ratio of 10:1. The powder was taken out of vial and annealed at 700 °C in air for 1h. The structure of samples was studied by X-Ray diffraction (XRD) method with Cu K α radiation and the XRD patterns were refined by MAUD program (ver 2.33). The magnetic properties were measured by a vibrating sample





magnetometer (VSM) at room temperature. Then the powders pressed into 1.5mm thick disks of 13mm diameter and were sintered at 800 °C for 20 min, for ferroelectric measurements.

Result and discussion:

From XRD patterns shown in figure.1 both BiFeO₃ and BiFeO₂₀CO_{0.04}O₃exhibit the similar trigonal structure with space group R3c:H. Small impurity peaks corresponding to Bi₁₂(Bi_{0.5}Fe_{0.5})O_{19.5}and Bi₂Fe₄O₉ were observed that marked with star. The lattice constants are a = 5.583Å, c = 13.883Å for BiFeO₃ and a = 5.583Å, c = 13.879Åfor BiFeO₂₀₀₄O₃. The *c* parameter is reduced in cobalt doped compound, which is due to the smaller ion diameter of Co^{+3} from that of Fe^{+3} . The M-H hysteresis loop of each nano-powder sample is shown in figure.2. In BiFeO₃, the magnetization varies nearly linearly with the applied magnetic field, confirming that sample is antiferromagnetic (with a G-type magnetic structure[4]). The M-H loop of BiFe_{0.96}CO_{0.04}O₃ exhibits a clear hysteresis loop of each ceramic samplewas measured at room temperature (not shown). The loops are not really saturated but show the ferroelectric behavior. A decrease in remnant polarization was observed with cobalt doping that can be due to reducing in c/a. However, the cobalt doped sample is yet ferroelectric.



Figure.2 M-H loop ofBiFeO₃ (left) and BiFe_{0.96}Co_{0.04}O₃ (right)

Conclusion:





BiFeO3and Cobalt substituted nano-powdersand ceramics were synthesized. The magnetic and ferroelectric measurements were performed. The cobalt doped sample exhibit both ferromagnetic and ferroelectric properties and hence possess a higher potential application as amultiferroic material.

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Preparation of Co₃O₄ Nanoparticles by Thrmolysis of Novel Complex Containing Bithiazole Rings

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Keywords: Nanoparticles, Co₃O₄, Thermolysis, Complex; Bithiazole

Introduction:

Spinel cobalt oxide (Co_3O_4) is considered to be an important functional material and has been widely used in electrochemistry, magnetism, catalysis and energy storage. Cobalt oxide, with excellent cycle reversibility and high specific capacity, has received a considerable amount of attention over the last few years as one of the promising potential electrode materials for lithium-ion batteries. Owing to the origin of the poor durability and their rapid degradation on cycling, many methods have been attempted to prepare nanoscale cobalt oxide, including solid state reaction, hydrothermal reaction, sodium nitrate-mediated synthesis, and microwave irradiation. The shape and size of these nanomaterials are critical for improving their performance. Moreover, Co_3O_4 nanostructures with various morphologies have been synthesized, such as nanowires, nanorods, nanowalls, nanoplatelets and nanotubes [1, 2].

Materials and methods:

To prepare complex nanoparticles a proper amount of the solution of cobalt(II) cloride (0.1 M) in EtOH was placed in an ultrasonic bath, then into this solution, a proper volume of DADMBTZ solutions (0.1 M) was added in drops [3]. The complex was calcinated at 450°C in oleic acid as surfactant at moderately elevated temperature under air atmosphere for 1h in an electric furnace alumina boat. The whole organic components were combusted and Co_3O_4 nanoparticles were produced.





Apparatus:

Infrared spectra were recorded on a Shimadzu model IR-60 spectrometer. An ultrasonic bath was used for the ultrasonic irradiation. The measurements were performed using PL- STA 1500 Thermal/Sciences in static air atmosphere. The samples were characterized with a field emission scanning electron microscope (FESEM). X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company.

Result and discussion:

The thermal stability of complex nanoparticles was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The XRD pattern match the standard of spinel Co_3O_4 with lattice parameters (Sys: Cubic S.G.: Fd3m a=z= 8.083 A°) which are the same as the reported values (JCPDS: 42-1467). The average diameter of Co_3O_4 nanoparticles indicated in the SEM image. The FTIR spectra of calcinated sample shows two distinctive bands around 592 cm⁻¹ and 674 cm⁻¹ are associated with Co^{3+} –O and Co^{2+} –O vibration in octahedral and tetrahedral sites of Co_3O_4 lattice, respectively.

Conclusion:

New complex of cobalt(II), were produced by sonochemical method using cobalt(II) chloride and DADMBTZ in an efficient and quick way. The sonochemical method is rarely used for syntheses of complex nanoparticles, but can be easily controlled and is expected to be applicable to fabrication of other nano-sized particles of other metal ion complex. Synthesis of bithiazole complex nanoparticles, making use of this method, is a novel approach in the literature.

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Synthesis and characterization of Cobalt Sulfide Nanostructures via Direct Thermal Decomposition

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Keywords: Nanostructure; Cobalt Sulfide; Thermal; Decomposition; Bithiazole.

Introduction:

In the past decade, much effort has been devoted to the synthesis and application of transition metal sulfide nanostructures due to their excellent electronic, optical and mechanical properties and wide applications including solid lubricants, catalysts, lithium battery cathodes, scanning probes, photoconductors and shockwave resistance materials. Among these materials, cobalt sulfide compounds are especially important because their chemical bonds Co–S have several forces and binding mechanisms that can form ionic bonds, covalent bonds and metallic bonds which are bound in a molecule. CoS have been used to serve as a low-cost replacement for the state-of-the-art EC material RuO₂ in electrochemical capacitors (EC) and as a negative electrode material for rechargeable lithium batteries. So far, various synthesis methods including hydrothermal/solvothermal routes, electrochemical syntheses, wet-chemical methods, colloidal syntheses and catalytic chemical vapor deposition have been successfully applied in syntheses of cobalt sulfide nanostructures [1-2].

It was found that aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five member rings. This study demonstrates that bithiazole complexes may be suitable precursors for the preparation of nanoscale materials [3].

Materials and methods:

To prepare complex nanoparticles a proper amount of the solution of cobalt(II) cloride (0.1 M) in EtOH was placed in an ultrasonic bath, then into this solution, a proper volume of





DADMBTZ solutions (0.1 M) was added in drops. Cobalt sulfide nanostructure was obtained by direct thermolyses of compound at 500°C under argon atmosphere.

Apparatus:

Infrared spectra were recorded on a Shimadzu model IR-60 spectrometer. An ultrasonic bath was used for the ultrasonic irradiation. The samples were characterized with a field emission scanning electron microscope (FESEM). X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company.

Result and discussion:

This article focuses on the simple synthetic preparation of a new Co(II) bithiazole complex and its conversion into cobalt sulfide nanostructure by calcination at moderately elevated temperature under argon atmosphere. The XRD pattern matches the standard of hexagonal Cobalt Sulfide with lattice parameters which are the same as the reported values (JCPDS No 750605). The average diameter of cobalt sulfide nanoparticles indicated in the SEM image.

Conclusion:

Cobalt sulfide nanostructure was obtained by direct thermolyses of compound at 500°C under argon atmosphere. The cobalt sulfide nanostructure was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. This study demonstrates that bithiazole complexes may be suitable precursors for the preparation of nanoscale materials.

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Spectroscopic Studies of Silver (Ag) Nanocrystalls Using Biological Process

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Introduction:

In recent years, several reports in the literature have discussed the cell-associated biosynthesis of Ag-NPs using several microorganisms, such as bacteria and fungi. However, the interaction between inorganic nanoparticles and biological structures are one of the most exciting areas of research [1]. However, to the best of our knowledge, there is no published reported on the biosynthesis of Ag-NPs using P. *aeuroginosa*. Our attention became focused on developing a relatively simple, safe and eco-friendly procedure to achieving of Ag-NPs. Among the noble metal, silver nanoparticles (Ag-NPs) have potential application; for example, it is widely used as catalyst in chemical reaction, solar energy absorption, as bio-labeling *etc.* [2]. Biological preparation of Ag-NPs synthesized by the procedure reported in our previously work [3].

Results and Discussion:

The optical properties of silver nanoparticles are related to the excitation of plasma resonance or inter-band transition, particularly on the size effect. According to 'MIE' theory silver nanoparticles less than diameter 52nm result in a broadening of the plasma absorbance bands, meanwhile the height of the absorbance peak also decreases [4]. Fig. 1 (left graph) shows the UV-vis spectrum obtained from biologically synthesized Ag-NPs at AgNO₃ different concentrations. As illustrated in Fig. 1, a strong surface Plasmon resonance was centered at \sim 426 nm. Observation of broad surface Plasmon peak has been well documented for various metal nanoparticles, with sizes ranging widely from 2 to 100 nm [5].







Fig. 1. (Left): UV-visible spectra, (right): X-ray diffraction of Ag-NPs.

Fig. 1 (right graph) shows the X-ray diffraction profiles of Ag-NPs synthesized using *P. aeuroginosa.* As shown in Fig. 1, a number of Bragg reflections with 20 values of 38.03° , 44.05° , 63.93° and 77.18° correspond to the (111), (200), (220) and (311) sets of lattice planes, which may be indexed to FCC cubic crystal structure. Using the well known Scherer equation [6], the nanoparticles diameter was estimated to be around 7 ± 1 nm. The morphologies of Ag-NPs obtained were also examined direct measurement such as TEM or STM. Fig. 2 (right image) shows a typical TEM micrograph and STM image of Ag-NPs. Observation of Fig. shows that Ag-NPs are nearly spherical shape. The average diameter of NPs thus estimated is $\sim 5-25$ nm.



Fig. 2. (left): TEM micrograph, (right): STM image of Ag-NPs.





Conclusions

In brief, silver nanoparticles were synthesized by a biological process using *P. aeuroginosa*. The UV-vis spectroscopy of Ag-NPs showed characteristic absorption peak at 426 nm. The FCC crystalline structure of Ag-NPs was confirmed by 2θ values of XRD pattern. The size of Ag-NPs is about 5-25 nm which are mostly spherical shapes, stable and remain intact under light proof conditions for nearly two months. Hence, the biological approach appears to be cost efficient alternative to conventional techniques of Ag-NPs synthesis and would be suitable for developing a biological process for large-scale production.

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Enhancement solubility of poorly water soluble oxcarbazepine drug by nanoporous alumina as a nano carrier

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Key words: Mesoporous alumina, Oxcarbazepine, Solubility, Drug delivery systems.

Introduction:

Recently mesoporous materials are widely used for drug delivery systems. In this field inorganic nano porous materials are emerging as a new category of host/guest systems. Those materials are a field of intensive activity due to their high potential in a very broad range of applications. The large pours and well-defined structure make mesoporous materials to be used as medical devices, for some interesting features such as their biological stability and drug release property. Oxcarbazepine is an anti seizure drug with low solubility and high permeability classified in class II of BDC [1-2]. The aim of the recent work was to propose mesopurous alumina synthesis, an inorganic nano structure material, as a carrier to improve the dissolution rate of poorly water-soluble oxcarbazepine drug, to enhance the bioavailability of poorly adsorbed drugs, entailing a lowering of therapeutic dose. Mesoporous alumina is a good model for some interesting properties, such as biocompatibility, amphoteric properties, very highly pore volume and wide pore diameter.

Materials and methods:

Mesoporouse alumina synthesized by aluminum tert-butoxide with sol-gel method and then calcined [3]. Then mesoporous sample were loaded with oxcarbazepine by soaking them for 48h under stirring conditions at ambient temperature. A DMF solution of oxcarbazepine with 40 mg/ml concentration with 2.5:1 (W/W) ratio of solid sample to drug was used.





Subsequently, the amount of the drug loaded was investigated by UV/Vis spectroscopy, FT-IR and TGA. The release experiment was performed at 310 K by putting the sample into a simulated body fluid with the amount of 0.03 mg sample in 300 ml of fluid. The drug delivery rate was monitored by UV spectrometry.

Apparatus:

FT-IR (Bruker), UV/Vis spectroscopy (Agilent), TGA (Netzch F209), DSC (Netch 204 F1)

Result and discussion:

Amount of drug loading into the mesoporous channels demonstrated by UV-Vis spectroscopy, TGA, DSC, and N_2 sorption. TGA showed that 15% of drug was loaded on the alumina surface (Fig 1). The drug-adsorbed were characterized by FT-IR, verifying presence of functional groups after the drug adsorption. Results of XRD significantly indicate that the drug incorporated into the pores of alumina without aggregation between drug molecules because it has a strong interaction with hydroxyl rich nanoporous surface. So the drug can disperse inside the pores and prevent to recrystallization.



Fig. 1: TGA spectra before (a) and after (b) drug loading.

The kinetic study of oxcarbazepine release in SBF exhibited that it completely transferred into the solution after 35min. This important result proves the solubility increase of the drug from the nanoporous alumina compare to the pure solubility of the drug which is only 83 mg per L of water.

Conclusion:

The inclusion was submitted to in vitro dissolution tests and remarkable dissolution rate improvement was observed in comparison to the crystalline drug in all tested condition.





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Catalytic Epoxidation of Cyclooctenewith Vanadium-oxo-Sulphate Supported on Amin Functionalized Nano-Boehmite

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Keywords: Sol-gel method, Nano-Boehmite, Heterogeneous catalyst, Epoxidation of alkenes

Introduction:

Supported metal complexes as heterogeneous catalyst have been used extensively for a wide variety of application. In these systems, the most important phenomenon is the catalyst elucidation from the support which will be overcome by use of covalent bonding of metal complexes to the functionalized support.

Methods:

Hydrothermal assisted sol-gel derived nano-boehmite with high surface area $(326m^2/g)$ and high degree of surface hydroxyl groups [1, 2], was used in this research. 1g nano-boehmite was refluxed with 0.35mmol 3-(tri-methoxysilyl)propyl amine in toluene for 24hr(AFNB). Then 1.05mmol Vanadium-oxo-sulphate was supported on AFNB by refluxing in ethanol for 7 hours. This supported catalyst was used in epoxidation of 0.7mmol cis-cyclooctene and yields of products were investigated by GC. The catalytic procedure was optimized for different parameters such as amount of catalyst (5-30mg), solvent (1-3ml), oxidant (0.28-1.68mmol), temperature (25-80°C) and time (30-180min).

Results and Discussion:

CHN analysis showed that the amount of imine group supported on nano-boehmite was 0.33 mmole/g. ICP analysis showed that V loading on AFNB was 0.23 mmol/g. XRD pattern





confirmed the retention of the nano-boehmite structure after functionalizing and metal supporting procedures. Results showed that the optimum conditions with over 95% yield for epoxidation of cis-cyclooctene with V-AFNB was 20 mg of catalyst, 1ml CCl₄ as solvent, and 1.4mmol t-butyl-hydro-peroxide as oxidant at 85°C after 180 min.

Conclusion:

These results showed that our catalyst produced cis-cyclooctene epoxide as efficient as Mo carbonyl supported on functionalized PVC with 0.43mmol/g of Mo loading [3]. Retention of the efficiency with lowering the Mo loading could be referred to the high surface area of nanoboehmite catalytic bed which must be confirmed by further experiments.

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Catalytic Application of Molybdenum Hexa-Carbonyl Supported on Functionalized Nano-Boehmite

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Keywords: Sol-gel method, Heterogeneous catalyst, alkene epoxidation, Molybdenum hexacarbonyl, nano-Boehmite .

Introduction:

Supported metal complexes as heterogeneous catalyst have been used extensively for a wide variety of applications. In these systems, the most important phenomenon is the catalyst elucidation from the support which will be overcome by use of covalent bonding of metal complexes to the functionalized support.

Methods:

Hydrothermal assisted sol-gel derived nano-boehmite with high surface area (326m²/g) and high degree of surface hydroxyl groups [1, 2], was used in this research. 1g nano-boehmite was refluxed with 0.35mmol 3-(tri-methoxysilyl)propyl amine in toluene for 24hr. Then the terminal amine group changed to imine by refluxing the above product with 0.35mmol salicylaldehydein ethanol for 16 hours (IFNB). Then 1.05mmol Molybdenum hexa-carbonyl was supported on IFNB by refluxing in THF for 6 hours. This supported catalyst was used in epoxidation of 0.7mmol cis-cyclooctene and yields of products were investigated by GC. The catalytic procedure was optimized for different parameters such as amount of catalyst (5-30mg), solvent (1-3ml), oxidant (0.28-1.68mmol), temperature (25-80°C) and time (30-180min).





Results and Discussion:

CHN analysis showed that the amount of imine group supported on nano-boehmite was 0.32mmole/g. ICP analysis showed that Mo loading on IFNB was 0.29mmol/g. XRD pattern confirmed the retention of the nano-boehmite structure after functionalizing and metal supporting procedures. Results showed that the optimum conditions with over 95% yield for epoxidation of cis-cyclooctene with Mo-IFNB was 15mg of catalyst, 1ml CCl₄ as solvent, and 1.4mmol t-butyl-hydro-peroxide as oxidant at 85°C after 90 min.

Conclusion:

These results showed that our catalyst produced cis-cyclooctene epoxide as efficient as Mo carbonyl supported on functionalized PVC with 0.43mmol/g of Mo loading [3]. Retention of the efficiency with lowering the Mo loading could be referred to the high surface area of nanoboehmite catalytic bed which must be confirmed by further experiments.

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Synthesis and study magnetic properties of NiFe_{2-x}Ga_xO₄ (0≤x≤0.3) ferrite nanoparticles

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Keywords: Ferrite Nanoparticles, XRD, Magnetization.

Introduction:

In the recent years, magnetic nanoparticles have been a subject of great interest from both technological and fundamental points of view [1]. Spinel ferrite is one of the most important classes of magnetic materials owing to their interesting applications. Particularly, mixed spinel ferrite nanoparticles have generated a large research effort because their magnetic properties differ markedly from single ferrite. Spinel ferrites crystallize into a cubic close packed structure of oxygen ions. In the spinel structure, the magnetic ions are distributed among two different lattice sites, tetrahedral (A) and octahedral (B) sites. The magnetic properties of these ferrites such as transition temperature and saturation magnetic moment are strongly depend on the relative distribution of cations at the different sites, type of doping atom and as well as the preparation condition [1]. Therefore, the magnetic properties of these materials can be tailored by using the doping of the different transition metal cations. In the present work, we have study the effect of Ga doping on structural and magnetical properties of NiFe2xGaxO4 ($0 \le x \le 0.3$) ferrite nanoparticles. Structural and magnetic properties of NiFe₂- $_{x}Ga_{x}O4$ ($0 \le x \le 0.3$) ferrites nanoparticles have been studied by X-Ray diffraction (XRD) and Vibrating sample magnetometer (VSM). Nanoparticles of NiFe_{2-x}Ga_xO₄ ferrite were synthesized using sol-gel method.

Experimental:

Sol-gel technique has been used to fabricate the nanoparticles of NiFe2-xGaxO4





(0≤x≤0.3) [2].

The prepared nanoparticles were characterized using XRD and magnetization measurements were performed using VSM.

Result and Discussions:

Fig. 1 represents the XRD patterns of the NiFe_{2-x}Ga_xO4 ($0 \le x \le 0.3$). The reflection peaks observed from the samples can be well indexed with the standard pattern of the cubic spinel ferrites. The particle size of NiFe_{2-x}Ga_xO4 ($0 \le x \le 0.3$) nanoparticle was calculated from the most intense peak of XRD data using Debye Scherrer formula [1] and estimated about 24, 23 and 23 nm for x=0, 0.1 and 0.3 respectively.

One may notice that, the particle size is slightly decreased with increasing x. It is due to the fact that the radius of the Ga³⁺ ion (0.62Å) is smaller than that of Fe³⁺ ion (0.645 Å).

The dependence of magnetization on the Ga concentration (x) is measured by VSM and magnetic properties such as saturation magnetization (Ms) and Hc values for samples are given in table 1. One may notice that the Ms and Hc increase with increasing Ga concentration. It can interpretation as fellows: In the spinel structure, the magnetic ions are distributed among two different lattice sites, tetrahedral (A) and octahedral (B) sites. The magnetization of these ferrites depend on the relative distribution of cations at the different sites [3]. The magnetization of either site can be reduced or increase relative to the other one by substitution of non magnetic ions in the corresponding site, in case of Ga³⁺ substituted ferrites, Maxwell et al [4] studied the system of NiGa_xFe_{2-x}O₄ (Using Mössbauer spectra) and found that the magnetization increased with increasing Ga concentration up to x = 0.63. They concluded that Ga ions prefer to occupy the A-sites for $x \le 0.63$.

samples	M _s (emu/g)	H _C (Oe)
NiFe ₂ O ₄	49.221	75.164
$NiFe_{1.9}Ga_{0.1}O_4$	50.102	76.524
NiFe _{1.7} Ga _{0.3} O ₄	53.639	77.127

Table1. The saturation magnetization (M_S) and the coercive field (H_C) of the as-prepared NiFe_{2-x}Ga_xO₄







Fig. 1.XRD patterns of NiFe_{2-x}Ga_xO₄

Conclusion :

1- The particle size are decreased with increasing the gallium concentration in the system NiGaxFe2-xO4

2- Most of the Ga^{3+} ions occupy the A sites in the spinel Ni ferrite.

3- The assumed cation distribution seems to be close to the inverse one as it possible to interpret the magnetic properties of the investigated samples according to this distribution.

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Enhancement of Active Corrosion Protection of epoxy coating via Combination of Inhibitor-Loaded Halloysite Nanotubes

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Keywords: Corrosion Inhibitor, Nanocapsules, Surfactant, Halloysite Nanotubes, Paint Coating

Introduction:

Recent achievements in surface science open a new avenue for fabrication of environmentally friendly corrosion inhibitors directly into the coating, providing release of the inhibiting compound and termination of the corrosion propagation at already damaged corrosion defects. The main idea here is to develop nanocapsules, which can be sensitive to the external (e.g., mechanical damage) or internal (e.g., pH or temperature changes) corrosion trigger [1, 2]. The present work reports the fabrication of 5 types of nanocapsules by using halloysite nanotubes for the finding of low-cost nanocapsules. The interactive properties of fabricated nanocapsules are studied in 0.5 M NaCl solution. In addition, effect of developed nanocapsules used in active protective coating is investigated.

Experimental:

- To study the loading of different corrosion inhibitors, polyelectrolyte nanocapsules (PNC) were fabricated with loaded halloysite by salicylaldoxime (SAL), mercaptobenzimidazole (MBI), and benzotriazole (BTA) through layer by layer (lbl) assembly of poly(ethyleneimine) (PEI)/sodium poly(styrene sulfonate) (PSS) polyelectrolyte bilayers until the final Inhibitor/Halloysite/PEI/PSS nanocapsules were assembled.





- For formation of metal ion nanocapsules (MNC), BTA-loaded halloysite samples were exposed to the bulk aqueous solution containing $Al_2(SO4)_3$ to assemble Inhibitor/Halloysite/Al capsules.

- (MNC) were mixed with PEI polyelectrolyte solution for formation of metal ion and polyelectrolyte nanocapsules (MPNC) with Inhibitor/Halloysite/Al/PEI structure.

-As it seemed important to evaluate the effect of inexpensive methods of encapsulation on their inhibitor up-take and release behavior, the opening at the edges of BTA filled halloysites were became blocked with Hyamine and CTAP surfactants to obtain surfactant nanocapsules (SNC).

-Furthermore, to attain inexpensive nanocapsules with less release rate metal ion with surfactant nanocapsules (MSNC) were fabricated with mixing MNC through surfactant solution until the final Inhibitor/Halloysite/Al/Surfactant nanocapsules were assembled.

In order to provide a comparative study of the effect of the SMNC container on the corrosion protection of the paint coatings on AA 2024 aluminum alloy, two composite coatings were synthesized and doped with BTA loaded SMNC container and undoped epoxy painting.

Results and discussion:

The lbl assembly process of halloysite nanocapsules is characterized by SEM, ζ -potential and UV–vis spectrometry methods. In addition, UV spectrophotometry and potentiodynamic polarization results show that all of nanocapsules exhibit spontaneous release of the inhibitors by the time and to protect corrosion of aluminum. But the extent depended on the inhibitor and nanocapsules type. Also, effect of variation of solution parameters (pH, temperature) on the concentration of the released inhibitor and ability of these doped particles to maintain appropriate conditions for smart corrosion protection have been considered, Figure 1. The electrochemical impedance spectroscopy (EIS) measurements, Figure 2, show that developed nanocapsules have high potential to be used in new generations of active protective coatings.

1.08







Figure 1. Influence of pH and time on the concentration of released benzotriazole in 0.5 M NaCl solution containing MSNC.

Figure 2. EIS measurements of doped and undoped epoxy coating in 0.5 M Nacl after 72 hours.

Conclusions:

The results indicate that the release of inhibitors depends on the nanocapsules type. In addition, by increasing acidity and temperature, the concentration of inhibitor in solution increased.

The paint with the nanocapsules reveals enhanced long-term corrosion protection in comparison with the undoped paint.

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Thermodynamic properties of carbon chiral nanotubes and their dependence on molecular diameter

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Keywords : Carbon chiral nanotube - DFT calculation - Thermodynamic properties.

Introduction :

The study of the properties of nanotubes for physical and chemical applications has yielded many highly useful and effective results in different areas of science. The structure of a single-wall carbon nanotube is determined by the orientation of the hexagonal ring of carbon atoms in the honeycomb lattice relative to the nanotube's axis. In this study the relationship between some of thermodynamics properties such as thermal capacity (ΔC_v), entropy (ΔS), energy (ΔE), enthalpy(ΔH), Gibbs free energy (ΔG) of 14 different type of carbon chiral nanotubes in contrast to their diameter are presented [1-4].

Computational methods :

The first, ΔG , ΔH , ΔS , ΔC_v , ΔE of 14 different types of carbon chiral nanotubes are performed by density function theory method with (B₃LYP) on 6-31G basis set using the standard procedure in Gaussian 09, and also diameter of mentioned carbon chiral nanotubes are calculated, then relationships between diameter of carbon chiral nanutubes with the above mentioned thermodynamics properties is studied.

Results and discussions :

The data in Table. 1 are showed that the values of ΔS , ΔC_v , ΔG , ΔH , ΔE of 14 different type of carbon chiral nanotube (5, 4 to 11, 6) decrease by increasing the values of their diameter.





Dimensional diagrams is represented well-related of values of diameter with ΔC_v , ΔG , ΔH , ΔE , ΔS of 14 different type of used carbon chiral nanotube.

The following structure–property models are the most successful equations that relationship between thermodynamic properties with diameter of molecules are showed:

$\Delta E = -69303 d + 153797$	R2 = 0.9934 (1)
$\Delta H = -18574 d + 2886.1$	R2= 0.9869 (2)
$\Delta G = -18434 d + 2367.3$	R2=0.9863 (3)
$\Delta S = -1.2329 \text{ d} + 0.3753$	R2=0.9945 (4)
$\Delta C_v = -0.041 \text{ d} - 0.0263$	R2 = 0.9881 (5)

Conclusions:

The results are showed that there is good correlation between diameter of molecules and quantum chemical descriptors of carbon chiral nanotubes.

The most accurate QSPR models for carbon chiral nanotubes are ΔS , ΔE based on diameter (d), respectively.

In this report we presented a strategy for designing the QSPR based on structural index the instructive example was directed to the design of the structure property model for predicting some thermodynamics properties of carbon chiral nanotubes.

Regression was performed and the best model was taken as the one presenting the optimal value of prediction coefficient, taking into account the number of descriptor used (eques.1-5). The instructive example was directed to the design of the structure-property model for predicting the thermodynamic properties of the carbon chiral nanotubes which were discussed here.





Nanotube	D/nm	$\Delta E/kJmol^{-1}$	Δ H/kJmol ⁻¹	$\Delta Cv/kJmol^{-1}$	$\Delta S/kJmol^{-1}$	$\Delta G/kJmol^{-1}$
54	6.118	-4075055.567	-107184.763	-0.2725380	-7.0129794	-106400.5067
64	6.820	-4603747.402	-128372.5600	-0.3129252	-8.2075644	-127575.2014
73	6.963	-4692732.947	-126776.62	-0.3091704	-8.2219914	-125906.6569
65	7.470	-5003761.002	-133937.543	-0.3357858	-8.7430140	-132981.1968
83	7.710	-5215944.549	-142203.817	-0.3456978	-9.2100582	-141245.4311
75	8.179	-5519275.601	-143738.2810	-0.3625230	-9.5134368	-142621.4981
10 2	8.724	-5852689.443	-167145.783	-0.3820614	-10.6087674	-166181.9356
94	8.898	-6049998.343	-164625.8780	-0.3981852	-10.6933426	-163497.8704
86	9530	-6459467.328	-170328.659	-0.4217766	-11.2415814	-169028.4136
12 1	9.816	-6678780.866	-183653.853	-0.4211592	-11.8854940	-182447.2355
10 5	10.363	-6785513.854	-188419.906	-0.4425078	-12.1335522	-187208.3458
114	10.540	-7096403.621	-195460.189	-0.4414494	-12.6515888	-194163.1226
12 4	11.298	-7915012.958	-206541.435	-0.5013330	-13.7320050	-204923.5610
11 6	11.699	-7922844.378	-212333.6240	-0.5141052	-13.9314042	-210793.1920

Table. 1. The selected values of the ΔS , ΔC_V , ΔG , ΔH , ΔE of carbon chiral nanotube and their diameters.

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The relationship study of number of carbon and molecular diameter with quantum descriptors in some chairal carbon nanotubes

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Keywords: Chiral carbon nanotube; Quantum mechanic calculation; HOMO-LUMO gap band.

Introduction:

The study of the properties of carbon nanotubes and thair applications has yielded many highly useful and effective results in different areas of science. It was introduced by the chemist H. Wiener about 60 years ago to demonstrate correlations between the physico-chemical properties of organic compounds and the structures indices of their molecular graphs. Although many nano-scale materials occur regularly in applications, many nanotubes with well-defined characteristics have not yet been produced under controlled conditions. In this study the relationship between structural indices of chiral carbon nanotubes with the quantum descriptors are presented and discussed.

Computational methods:

In this study, the values of LUMO, HOMO levels energies for 13 different types of chiral carbon nanotubes (CNT's) such as (5 4, 6 4, 7 3, 6 5, 8 3, 7 5, 10 2, 9 4, 12 1, 10 5, 11 4, 12 4, 11 6) by use of the Gaussian 09 program with density function theory method (B3LYP) on 6-31G basis set are performed, and then the size of diameters in mention compounds are computed, Finally the relationship between the number of carbon and the diameter of molecules with their quantum indices has been studied.

Results and Discussion:





Table-1 has shown the values of the number of carbon atoms (C) and diameters (D) of CNT's versus the LUMO level energies in eV (1-13). The LUMO level energies has gotten decrease from -0.05402 eV to -0.12628 eV (for CNT's 1 to 13, respectively), in lieu of increasing diameter at the structures 1-13. The diameter size of CNT's (1-13) the expansion of the resonance field of the π -bonds have made decreasing LUMO levels from 1-13. Fig.1. has also shown a relationship between the diameter size versus the HOMO, LUMO gap in eV, of CNT's (1-13). The HOMO level energies has gotten increase from -0.15726 eV to -0.13740 eV (for 1-13, respectively), in lieu of increasing a couple of carbon atoms (C=C) at the structures 1-13. The diameter size of CNT'S the expansion of the resonance field of the π bonds have made increasing HOMO levels from 1-13. Fig.1. demonstrates the behavior of the relationships relevant to the diameters and the values of E_{HOMO}-E_{LUMO} bond gap for the CNT's of 1–13. The HOMO-LUMO energy gaps has gotten decrease from 0.10324 eV to 0.01112 eV (for 1 to 13), in lieu of increasing the number of carbon atoms at the structures 1-13. The structure size of CNT's the expansion of the resonance field of the π -bonds have made decreasing the HOMO-LUMO gaps from 1-13. The thermodynamic stability increased and the kinetic stability decreased by increasing the diameter size and/or the number of carbon atoms in the structures of 1-13.

Name	CNT	D/nm	С	LUMO	НОМО
1	5.4	6.118	39	-0.05402	-0.15726
2	64	6.820	44	-0.06420	-0.19404
3	73	6.963	45	-0.09360	-0.16436
4	65	7.470	48	-0.08311	-0.17689
5	83	7.710	50	-0.10712	-0.15749
6	7 5	8.179	53	-0.06822	-0.15740
7	10 2	8.724	56	-0.11632	-0.16637
8	94	8.898	58	-0.10715	-0.15764
9	12 1	9.816	64	-0.12424	-0.14773
10	10 5	10.363	65	-0.10011	-0.16716
11	114	10.540	68	-0.10859	-0.15612

Fable.1. The values of the diameter (!	D), number of carbon	(C), LUMO, HOMO	orbital energies of CNT' S.
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12	12 4	11.298	76	-0.12505	-0.13842
13	11 6	11.699	76	-0.12628	-0.13740

Fig. 1. The curve of the HOMO, LUMO versus the values of diameter of CNT'S.



Conclusions:

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play a dominant role in many chemical reactions. The HOMO–LUMO energy separation has been used as a simple and conventional indicator of kinetic stability. A large HOMO–LUMO gap (band gap) implies high kinetic stability and low chemical reactivity. The kinetic stability of chiral carbon nanotubes (CNT's) has previously been discussed in terms of the HOMO–LUMO energy gap. Recently, band gap in CNT's as a function of the size of the molecules has been studied. In this study, we have also determined frontier molecular orbital energies and gap bands for the 13 types of CNT's as a function of the size of diameter of molecules as well.

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Ultrasonic –assisted Synthesis and Characterization of a New Bulk and Micro Structure of Mixed – Ligand Zinc (II) Coordination Polymer

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Key Words: Coordination Polymer, Zinc (II), Mononuclear, Ligand.

Introduction:

Some of the materials scientists and chemists have been greatly fond of studying metal coordination polymers because of their particular structures and also their properties and their reactivities are never observed in mononuclear compounds. Nanometer and bulk sized particles of metal coordination polymers are very attractive to explore, as they have unique properties which are controlled by the large number of surface molecules [1-2]. Metal – coordination polymers are used widely in smart optoelectronic, magnetic, micro porous and biomimetic materials [3-4]. Several different synthetic approaches including slow diffusion of the reactants into a polymeric matrix, diffusion from the gas phase, evaporation of the solvent at ambient or reduced temperatures, precipitations or recrystallisation from a mixture of solvents, temperature controlled cooling and hydrothermal synthesis have been reported for the preparation of coordination polymers [5].

Materials and Methods:

In order to isolate single crystal of $[Zn (4-pyc)_3 (Br)]_n$, 4-Hpyc (1 mmol, 0.123 g), Zinc(II) nitrate hexahydrate (1mmol,0.279 g), potassium bromide (1mmol, 0.119 g) were placed in the main arm of a branched tube. After 2-3 weeks, colorless crystals deposited in the cooler arm were isolated, filtered off, washed with acetone and ether and air dried. To prepare the micro–structure of $[Zn(4-pyc)_3(Br)]_n$, a 15 ml of 0.1 M solution of Zinc(II) nitrate hexahydrate




in H_2O was positioned in a high density ultrasonic probe. The obtained precipitates were filtered off, washed with water and then dried in air.

Apparatus:

A multiwave ultrasonic generator (sonicator 3000; Hielscher), equipped with a converter and titanium oscillator (horn), 1.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 w, was used for the ultrasonic irradiation. IR spectra were recorded using Tensor 27 Bruker company spectrophotometers. X-ray powder diffraction measurements were performed using Bruker shart 1000 CCD.

Results and Discussion:

This article focuses on the simple synthetic preparation of both bulk and micro structures of a new mixed ligand Zinc (II) coordination polymer. Bulk and micro structure of a new Zinc (II) three –dimensional coordination polymer, $\{[Zn (4-pyc)_3(Br)]_n, 4-Hpyc = 4-$ Pyridine carboxylic acid $\}$ was synthesized by an ultrasonic- assisted method. The new structure was characterized by scanning electro microscopy, X-Ray powder diffraction, IR spectroscopy and elemental analyses. Also the synthesized compound was structurally characterized by single crystal x-ray diffraction and our findings showed three –dimensional polymeric units and proved that the coordination number is 4 for zinc (II) ions. The infra red spectra of a new zinc (II) coordination polymers showed that the band observed in the range 3025-3055 cm⁻¹ are due to the C-H vibrations of the aromatic cycles. The observed bands with diverse intensity in the range of 1400 -1600 cm⁻¹ were due to the vibrations of the pyridine units of ligand 4-Pyc in the complex.

Conclusion:

This study demonstrates that the coordination polymer may be suitable precursors for the preparation of nano –scale materials and dependent on their packing they may produce different and interesting morphologies. To the best of our knowledge, this is the first report of





a synthesis of nano-sized structures of the above compound from this type of coordination polymer.

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Preparation and evaluation of thermally stable nano-structured self-doped polythiophene coating for analysis of trace levels of phthalate esters

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Keywords: self-doped polythiophene; Solid-phase microextraction; phthalate esters; Nanostructure.

Introdoction:

Conducting polymer–based solid–phase microextraction (SPME) coatings such as polypyrrole, polyaniline and polythiophene (PT), are one the coating categories which have been successfully used for the extraction of various compounds [1]. Among them, PT and their derivatives [2] have been studied less than polypyrrole and polyaniline. It may be due to the low thermal stability of common PT i.e. 200 °C [3]. Nano–structured self–doped polythiophene (SPT) electrodeposited in the presence of fluorinated organic acid was applied as a thermally stable conductive polymer–based solid–phase microextraction (SPME) fiber candidate.

Phthalate esters (PAEs), are used primarily as plasticizers in polymeric materials to increase their flexibility through weak secondary molecular interactions with polymer chains.PAEs as well as their metabolites and degradation products can cause adverse effects on human health, especially on liver, kidney and testicles [4]

In this work we proposed a new strategy to increase the thermal stability of PT based on selfdoping of the polymer.

Materials and methods:

Thiophene was vacuum distilled and was kept under nitrogen atmosphere. Anhydrous fluorosulfonic acid (FSO₃H, triple–distilled, Aldrich) was used as sulfonation reagent. The





acetonitrile and sodium chloride were purchased from Merck (Darmstadt, Germany). LiClO₄ (Merck, Darmstadt, Germany) was used as electrolyte. Standard grade phthalate esters including dimethyl phthalate, diethyl phthalate, dibuthyl phthalate and diethylhexyl phthalate were purchased from Sigma–Aldrich (Madrid, Spain). A sample of mineral water, tap water and seawater (Caspian Sea) were used as real samples. Quantitative determination of trace levels of phthalate esters in water samples was carried out using this novel SPME fiber, coupling with gas chromatography–flame ionization detector (GC–FID).

Apparatus:

The SPME holder for manual sampling was purchased from Azar Electrode Co. (Urmia, Iran). A magnetic stirrer (IKA–Werke, Staufen, Germany) was employed for temperature control and solution stirring during extraction. Electrochemical measurements were carried out in a conventional three–electrode cell powered by a Potentiostat/Galvanostat, micro Autolab (GPES), type III, FRA 2 (The Netherlands). Morphological studies were carried out by a scanning electron microscope (SEM) S4160 Hitachi model (Tokyo, Japan). An Agilent 6890N gas chromatograph (Wilmington, DE, USA) was used in the measurements.

Results and discussion:

Properties of SPT consist of: a) Nano stracture (SEM studies: less than 100nm) b) High thermal stability (350 °C) and c) Good life time (up to 60 time). The extraction procedure was optimized by means of the Taguchi orthogonal array experimental design with an OA_{16} (4⁵) matrix including extraction temperature, extraction time, salt concentration, stirring rate and headspace volume. The detection limits were lower than 0.12 ng mL⁻¹ for phthalates.

Conclusions:

A new laboratory-made SPT fiber was prepared by a simple electrodeposition method and successfully applied for the detection of the trace levels of PAEs in the water samples. The proposed fiber has following merits: (a) High temperature and mechanical resistance; (b)





reproducible synthesis; (c) long life span; (d) high extraction efficiency. The method showed satisfactory accuracy, linearity, precision and detection limits.

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The Synthesis of TiO₂ Nanoparticles in order to Adsorption of Hg (II) From Aqueous Solutions

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Key words: Titanum dioxide nanocrystals, Hg (II) removal, Adsorption, Kinetics, Isotherm

Introduction:

Mercury is a very toxic and hazardous element to the human body and to the environment. Nano-sorbents have emerged as a new area of research with potential application, due to their large surface areas, in removal of heavy metal ions from liquid solutions. Among all nanoscale metal oxides, TiO₂ nanocrystals have high potential for environmental applications due to their physical and chemical stability [1]. In this study, we synthesized TiO₂ nanocrystals and investigated their application in the removal of Hg(II) from aqueous solutions in the absence of other metals , for the first time.

Materials and methods:

TiO₂ nanoparticles, were synthezied by the hydrolysis of TiCl₄ (99%, Merck) in HCl aqueous solution (ca. 37 wt.%, Merck) at low temperature. [2]. A stock solution (1000 mg/L) of Hg (II) was prepared by dissolving appropriate amounts of HgCl₂ (Merk) in double-distilled water. The PH adjusted with Phosphoric acid and sodium dihydrogen Phosphate buffers (0.1 M HCl and 0.1 M NaOH) in the range of 2.0–9. The adsorption experiment carried out by rotating 0.05 gr of nano-Tio₂ that suspended in 10 mL of Hg (II) solution with initial concentration 200 mg/L at PH 8 .The suspansion were mixed at 30 °C in thermostate shaiker bath at 150 rpm for 420 min .the mixture filtered and the concentrations of mercury ions were measured by an





atomic absorption spectrometer. The effects of pH, temperature, initial concentration of Hg^{2+} ion, and contact time between adsorbates and adsorbent were investigated.

Apparatus:

A Scanning electron microscope (SEM) equipped by energy dispersive X-ray analysis (EDAX), a BET-N₂ surface area analyzer, a X-ray diffraction (XRD) analysis and a FT–IR spectrophotometer were applied to characterize the Tio_2 nanocrystals before and after adsorption

Result and discussion:

The Textural properties of all the nanocrystaline TiO₂ are summarized inTable1. The SEM image of pure Tio₂, indicated that the particles are spherical and are agglomerated. Chemical composition of TiO₂ was obtained by EDX analysis. Data, confirmed the presence of Ti, oxygen, and residual Cl⁻ (leftover of HCl added in the synthesis step) in the sample before adsorption. Mercury was detected for TiO₂ samples after adsorption. Adsorption equilibrium was established in 420 min and the maximum adsorption of Hg(II) on the TiO₂ was observed to occur at pH 8.0. The adsorption data correlated with Freundlich, Langmuir, Dubinin–Radushkevich (D–R), and Temkin isotherms . The Freundlich isotherm showed the best fit to the equilibrium data. The Pseudo-first order and pseudo-second-order kinetic models were studied to analyze the kinetic data at three pH values 6,7,8. A second-order kinetic model fit the data with the (k₂ = 2.8126×10^{-3} g mg⁻¹min⁻¹, 303 K). The intraparticle diffusion models were applied to ascertain the rate-controlling step and the result shows that intraparticle diffusion is not the limiting step. The thermodynamic parameters (Δ G, Δ H, and Δ S) were calculated which showed adsorption process was spontaneous and endothermic in nature.

Material	Anatas%	Rutile%	Crystal size(nm)	Crystal	Speci c	Pore	Pore diameter,
			Anatas	size(nm)	surface	volume,	DP (BJH ADS)
				Rutile	area, SBET	VP (cm3 g1)	(nm)
					(m2g)		
TiO2	13.2	86.8	8.827	10.19	98.743	0.080099	3.2447

Table.1. Textural properties (S_{BET}, V_P, D_P) and TiO2 size(ϕ) of studied photo catalysts





Conclusion:

The results obtained confirmed that nano-TiO₂ can remove Hg(II) ions from aqueous solutions. The adsorption strongly depends on the parameters such as initial concentration of Hg (II), pH, contact tim and themprature . The percentage of Hg(II) removal by nano-TiO₂ is more than 96%. The data showed that the solution pH was a key factor affecting the adsorption characteristics. The adsorption process follows Freundlich isotherm which fits well heterogeneous surfaces. The equilibrium parameter (R_L), indicated that TiO₂ nanocrystals are useful for Hg(II) removal from aqueous solutions .

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Corrosion study of nanocomposite epoxy / poly aniline on copper electrode surface

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Introduction:

To exploit the full potential of the technological application of the composite material, it is important to characterize the nature of the association between the different components. Although the incorporation of gold, copper, platinum, and palladium nanoparticles in the conducting polymers has been reported by using chemical or electrochemical techniques, the synthesis of conducting polymer-metal nanoparticle composite materials having a nano fiber like morphology has not yet been undertaken [1]. Many investigations regarding the development of the techniques for incorporating the nanoparticles into a polymer matrix have been published [2-5].

Experimental:

In a typical reaction, 0.8 g DDS was dissolved in a magnetic stirred 25 ml of methanol in a 50 ml conical flask. After complete dissolution,100 ml dilute cupric sulfate solution (10⁻¹mol dm⁻³) was added drop wise. During this addition, a green colored turbidity developed. After addition of all of the cupric sulfate, the precipitated material collected at the bottom of the flask. This work accomplished for two solutions of nickel sulfate and silver nitrate that colloidal solutions observed white and milky colored.

Result and discussion:

The UV-vis spectrum, Figure 1, of the composite material shows three characteristic absorption bands at 320, 400 and 500 along with a shoulder at 600 nm. The absorption peak at 320 nm is due to the π - π * transition of the benzenoid rings. The peak at 420 nm results from





the polaron/bipolaron transition. A broad band with intense overlapping features is seen between 450 and 700 nm. A strong absorption peak at 500 nm and 600 nm has been observed when a very slow scanning condition has been applied. The band at 600–650 nm corresponds to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital, that is, a benzenoid to quinoid excitonic transition. A blue shift can be attributed to the lowering of the extent of conjugation caused by the steric repulsion between –CH3 and the adjacent phenyl ring hydrogen. In the present work, the UV–vis spectra revealed an intermediate absorption peak at ~500 nm along with a shoulder at 600 nm. This can be explained respectively in terms of the benzenoid to quinoid excitonic transition and the influence of –CH3 groups in the polyDDS backbone and the presence of a shoulder at ~600 nm can be explained as the plasma oscillation of the copper surface.



Figure 1. UV-vis spectrum of the metal-polymer composite material. (a) polymer-Cu.

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Corrosion study of nanocomposite epoxy / steel polyvinyl alcohol on the electrode surface

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Introduction:

Epoxy has several attractive properties, such as mechanical durability, hardness, toughness, and chemical inertness that complement the intrinsic characteristics of Polyaniline (PANI). Polyaniline (PANI) is considered a very interesting material for electrical or electronic applications, as it combines stability, conductivity and low cost.[1] A consequential drawback of the conductive form of PANI is its poor mechanical properties. To tackle this problem, researchers have intensively studied the blends of PANI with a variety of polymers.[2] Pud et al.[3] reviewed the different preparation methods of polyaniline blends and composites with organic polymers. Two general categories of processing methods can be defined as the following: a) synthetic methods, in which the polymerization of aniline takes place in the presence of the polymer matrix, and b) blending methods, in which PANI is mixed with the polymer matrix. Blending methods include the solution blending of PANI with polymers and dry blending.

Experimental:

Unless otherwise indicated, all chemicals used were of analytical grade and were used as received. The epoxy resin, Epon 828 (DGEBA), was obtained from Shell Chemicals. All aqueous solutions were prepared to use deionized water.

The DDS, TETA and methanol were purchased from Merck, and cupric sulfate, nickel sulfate and silver nitrate from Alderich. The stock solutions of cupric sulfate, nickel sulfate and silver nitrate $(10^{-1}, 10^{-1}, 2 \times 10^{-1} \text{ mol dm}^{-3})$ were prepared in distilled water.

Sodium Chloride (NaCl, 99%) was purchased from Merck (Darmstadt, Germany).





Result and discussion:

Figure 1 displays the conductivities of the polyDDS-metals/ DGEBA.TETA samples prepared using both the absorption-transferring and blending processes. As shown in Figure 1, the conductivity of the hybrid prepared using the absorption-transferring process was higher than that from the blending process regardless of the content of polyDDS-metals/ DGEBA.TETA. In addition, the percolation threshold was also lower because the polyDDS-metals particles aggregated readily during the latter process. In the absorption-transferring process, when the content of polyDDS-metals/ DGEBA.TETA reached a threshold, the conductivity of the hybrid increased thereafter because the polyDDS-metals composite aggregated into secondary particles. Not only did this process cause the polyDDS-metals chains to entangle readily, it also interrupted the conducting pathway.



Figure 3. Electrical conductivity of(a) polyDDS-Cu/ DGEBA.TETA (b) polyDDS-Ni/ DGEBA.TETA (c) polyDDS-Ag/ DGEBA.TETA.

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Electrochemical study of nano composite poly DDS / SiO2 nanoparticles on the surface of copper electrode

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Introduction:

Electrically conductive thermosetting materials, composite materials, such as anti static and conductive epoxy adhesives, contain metallic particles, fibers, flakes or other fillers, such as metal oxides, or carbon black. These materials are widely used in application fields, including automotive, aerospace, optical, medical and electronics. The desired conductivity of the materials determines the type and concentration of conductive fillers needed in a given resin system. The amount of metal loading usually ranges from 60 to 90 wt. % to reach a desired high conductivity level [1]. Although metals have a good electrical conductivity, some readily cover with inadequate conductivity stability on thermal cycling [2,3]. Furthermore, for charge dissipation the intermediate conductivity levels required are not readily achievable with carbon blacks [4,5].

Experimental:

Scanning electron microscopy (SEM) images are taken using a VEGA HV (high potential) 1500 V at various magnifications. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) attached to the SEM was used to determine the chemical composition of the samples. The remaining solution was filtered and a small portion of the remaining solid mass was dissolved in methanol and used for UV–vis spectrophotometry analysis. The UV–visible absorption spectrum is obtained ex situ at room temperature in the wavelength range 300–1100 nm using microprocessor controlled double beam UV–visible spectrophotometer (Hitachi, Model U2000). The next portion of the solid was dried under vacuum and used for IR spectral analysis. The FTIR transmission spectrum of polypyrrole coating is recorded in





horizontally attenuated total reflectance mode in the spectral range 3500–550 cm⁻¹ using a Bruker spectrometer, Vector Series 22, Germany.

Result and discussion:

Figure 1 is an EDS spectra derived from placing the electron beam directly on a nanoparticle in the polymer. This and other analyses confirmed that copper, nickel and silver were only found associated with the nanoparticles.



Figure 1. A typical EDS analysis of a nanoparticle (a) poly DDS-Cu.

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Electrochemical study of nanocomposite poly aniline / polyvinyl alcohol in an acid environment

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Introduction:

Several researchers have employed different post treatments after the synthesis of polymer films; however, there are no systematic studies on this aspect. On the other hand, when a polyaniline layer was deposited first and the electropolymerization was continued in a solution of poly aniline (PANI), a progressive transformation of the electrochemical behavior of the original polyaniline film has been observed. The polyaniline promotes the polymerization by providing electrocatalytic sites and nucleation centers. Thus, the conducting polyaniline surface is protected well and leads to better modification. Chemical polymerization of PANI also leads to newer polymers. Interestingly, both the newly

formed polymers are found to have nanostructure. The preparation of nanostructured conducting materials has become an important branch of materials research. [1-5]

Experimental:

The poly aniline (PANI), and poly vinyl alcohol (PVA) were purchased from Merck, and cupric sulfate, nickel sulfate and silver nitrate from Alderich. The stock solutions of cupric sulfate, nickel sulfate and silver nitrate $(10^{-1}, 10^{-1}, 2 \times 10^{-1} \text{ mol dm}^{-3})$ were prepared in distilled water.Sodium Chloride (NaCl, 99%) was purchased from Merck (Darmstadt, Germany).

Transmission electron microscopy (TEM) studies of the composite material were carried out at an accelerated voltage of 120 kV using a Philips CM200 TEM. Scanning electron microscopy (SEM) images are taken using a VEGA HV (high potential) 1500 V at various magnifications. The next portion of the solid was dried under vacuum and used for IR spectral analysis. The FTIR transmission spectrum of polypyrrole coating is recorded in horizontally attenuated total





reflectance mode in the spectral range 3500–550 cm⁻¹ using a Bruker spectrometer, Vector Series 22, Germany.

Result and discussion :

Figure 1 shows the XRD patterns of the pure poly aniline (PANI), and poly vinyl alcohol (PVA) and its nanocomposites reinforced with different poly aniline (PANI), and poly vinyl alcohol (PVA) nanocomposites loadings. The peaks at 17.5° and 40.0° were observed in the pure poly aniline (PANI), and poly vinyl alcohol (PVA). The first peak has a d-spacing of 0.454 nm, corresponding to the typical doublet reflection of the planes of the semi crystalline atactic poly aniline (PANI), and poly vinyl alcohol (PVA) The second peak is assigned to the plane of the poly aniline (PANI), and poly vinyl alcohol (PVA) The peak corresponding to the plane of the poly aniline (PANI), and poly vinyl alcohol (PVA) The peak corresponding to the plane of the poly aniline (PANI), and poly vinyl alcohol (PVA) becomes narrower and narrower as a function of the particle loading. The average particle size (L) was estimated from the Debye–Scherrer equation.

$$L = K\lambda/\beta(2\theta)\cos\theta \tag{1}$$

Where $\beta(2\theta)$ is the full width at half-maximum (FWHM), K is a constant taken as the normal value of 0.9, λ is the wavelength of X-ray wavelength (for copper, k = 1.5406 A^o), and h is the Bragg angle.







Figure 2. X-ray diffraction patterns of (a) poly aniline (PANI), and poly vinyl alcohol (PVA).

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Evaluation of corrosion rate of nanocomposite epoxy / polyvinyl alcohol -Poly aniline on the electrode surface iron

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Introduction:

Electrically conductive adhesives based on Nano polymer-metal composite /Epoxy. Tri Etyhlene Tetramine (DGEBA.TETA) system containing poly vinyl alcohol/epoxy and different metals (copper, nickel and silver) nanoparticles composite materials have been successfully developed and characterized. The blends were prepared by physical mixing of Nano poly vinyl alcohol/epoxy composite within poly vinyl alcohol/epoxy matrix. The physical mixing procedure contributes for the formation of a conducting pathway with the lower amount of poly vinyl alcohol/epoxy properties were achieved with these systems [1-4].

Experimental:

Measurements consisted in recording a change in the mass of copper specimens (99.99% Cu) as a result of spontaneous dissolution in solutions of known composition. The dimensions of the specimens were $0.5 \times 0.5 \times 0.5$ cm. Before immersing in a solution, each specimen was cleaned with emery paper (1200 and 2000 grade), rinsed with triple-distilled water, degreased in ethyl alcohol, and finally washed with water several times. After drying at room temperature and weighing, specimens were immersed in a 100 cm³ different solutions for different exposure periods of time. After exposure time each specimen was removed, rinsed, dried and weighed. Three specimens were used for each test. The average weight loss value was used to calculate the average corrosion and adsorption parameters of PolyDDS-PVA.

The electrical conductivities of the blend were measured by using a Keithley 6517A electrometer, a multimeter Minipa ET2907 and a homemade four probes device with a





medium distance between the probes of 0.171 ± 0.03 cm. The measurements were performed on a disk film with a thickness of 0. 5mm.

Result and discussion:

The spontaneous dissolution of copper in 0.5 M NaCl solutions of pH 3.0 containing different weight percent of polyDDS-PVA was studied by gravimetric measurements. The investigations were carried out in the open to air (non de-aerated solutions). Figure 1 shows the weight loss vs. time curves in the absence and in the presence of with 5% weight percent of polyDDS-Cu, polyDDS-Ni, polyDDS-Ag. It is clear that weight loss of specimens reduces with increasing the weight percent of polyDDS-metals. It can be observed that both inhibitors act identically.

The dissolution process of copper in corrosive mediums in the presence of the dissolved oxygen proceeds via a two-step reaction mechanism

$$2Cu + 1/2 O_2 + 2H^+ \leftrightarrow 2Cu^+ + H_2O$$
(1)

and

$$2Cu^{+} + 1/2 O_2 + 2H^{+} \leftrightarrow 2Cu^{2+} + H_2O$$
 (2)

It is interesting to observe that Δm decreased with an increase in the weight percent of polyDDS-metals (curves (c)–(a)). Thus it suggests that polyDDS-metals act as inhibitors of the spontaneous dissolution of copper in weak acidic chloride solutions.



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Figure6. Weight loss during spontaneous dissolution of copper in 0.5 M NaCl solutions containing in absence or presence of with different weight percent of (a) Cu uncoated.

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Methanol oxidation on the GC electrode surface modified with nanoparticles Fe₂O₃

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Introduction:

Chemical modified electrodes (CMEs) become a field of exiting research due to their unique electrode surfaces properties [1]. Many techniques were developed for preparation of modifie electrodes, such as covalent bonding and polymer film [2]. Deposit a film of conducting polymer was essential to work in a medium with an electrolyte that can protect the electrode surface from dissolution without impeding the electropolymerization process [3]. Polymeric films possess three-dimensional extensity, a large number of reactive sites, good stability and offer the possibility to be designed with particular redox active sites [4]. Electropolymerization is a good approach to immobilize polymer as adjusting the electrochemical parameters can control film thickness, permition and charge transport characteristics [5].

Experimental:

Electrochemical impedance spectroscopy (EIS) was performed with a frequency response detector EG&G model 1025 USA and Scanning electron microscopy (SEM) images were taken using a VEGA HV (high potential) 1500 V at various magnifications. A conventional three-electrode system was employed using working electrode (GCE), reference electrode (SCE) and countrer electrode (Pt). Phosphate buffer solutions (PBS) were prepared by 0.1M $NaH_2PO_4 - Na_2HPO_4$ The electropolymerization was carried out using the solution having 1.0×10^{-3} M (m-ABA) and 0.02 mgr nanosilica at pH 7.0 PBS. The impedance spectra were recorded in the frequency range 10 Hz to 65k Hz.

Result and discussion:





Figure 1 show the cyclic voltammograms (CVs) recorded during the oxidative polymerization of 1.0×10^{-3} M m-aminobenzoic acid in pH 7.0 phosphate buffer solution on GCE. In the frist scan, anodic current peak 1 was observed with current value at 180 μ A and potential value at 1.66 V, respectively. Then, larger peak were observed upon continuous scanning, reflecting the continuous growth of the film. It can also be observed that film growth was faster for the frist cycles than for the other cycles. From the seventh cycles, the film was hardly growth, the maximum of peak current was 600 μ A. It showed polymerization reached saturation. This fact indicated m-ABA was deposited on the surface of GCE by electropolymerization mode.



Figure1. Cyclic voltammograms of 1.0×10^{-3} M m-ABA in pH 7.0 PB solution. Terminal potential, 2.5 V, potential, -1.5 V; scan rate, 100 mV/sec, for 50 cycles at the GC electrode.

The SEM images of the electrodeposited poly(m-ABA) film and poly(m-ABA) using Fe_2O_3 are shown in Figure 2The polymer is formed by cyclic voltammetry mode for 25 cycle.







Figure2. SEM images of polymer coated GCE: (a) m-ABA.

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Electrocatalytic oxidation of L-cysteine at A nano-structured copper(II)– Schiff base complex multiwall carbon nanotube modified glassy carbon electrode

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Keywords: L-cysteine, Cu–Schiff base complex, Multiwall carbon nanotube, Electrocatalysis.

Introduction:

L-Cysteine [(R)-2-amino-3-mercaptopropanoic acid] is an important amino acid owing to its crucial roles in biological systems. For example, it can be used as a prospective radiation protector and cancer indicator, and its deficiency is associated with a number of clinical situations such as liver damage, skin lesions, slowed growth, and AIDS [1] The amino acid L-cysteine participates in a complex series of metabolic reactions and is incorporated in most proteins and glutathione. It is also a precursor of coenzyme A and can easily be oxidized to cystine; however, the intercellular cysteine/cystine ratio is very high [2].

Materials and Methods

Multiwall carbon nanotubes with purity 95% (10–20 nm diameters) and 1 μ m length were obtained appropriate amount Nanolab (Brighton, MA). Sodium hydroxide, ammonia, ethanol, K₂CO₃, DMSO, DMF, sodium acetate, ethanolamine, chloroform and hydrochloric acid were purchased from Fluka. All other chemicals were of analytical-reagent grade and used without further purification. Double distilled water was used thoroughly. All experiments were carried out at ambient temperature. Electrochemical experiments were performed via using an Autolab modular electrochemical system (Eco Chem. Utrecht, The Netherlands) equipped with PSTA 20 model and driven by GPES software (Eco Chem.)





Results and discussion:

Cyclic voltammograms of GCE, CNT/GCE, Cu-DES /GCE and Cu-DES CNT/GC electrode in 0.25 M acetate buffer solution at a scan rate of 50 mVs⁻¹ were recorded. No electrochemical response was observed at surface of GC and CNT/GC electrodes. One pair of well-defined redox peaks observed when Cu-DES /GC electrode was used. Modification of mentioned electrode by multiwall carbon nanotube on the bare GC electrode (Cu-DES /CNT/GC electrode) enhances the sensor response about 16 times. The presence of CNT supplied a larger surface area to allow more deposition of Cu-DES complex. To investigate the surface structure and morphology of the modified electrode, we performed SEM. Fig.1 shows the SEM images of bare GC electrode (A) and the nanostructure Cu-DES /CNT/GC electrode (B). The result indicated that the film has a globular structure with relatively homogeneous distribution in the range 65–105 nm. The presence of smaller nanoparticles leads to an increase in the surface coverage for adsorption of more L-cysteine.



Figure 1. Typical SEM image of, (A) bare glassy carbon electrode and (B) Cu-DES /CNT/GCE.

Conclusions:

We have demonstrated the suitability of Cu- DES /CNT/GCE as an ideal catalyst for lowpotential determination of L-cysteine with a high sensitivity. The experimental results reported above demonstrate that the Cu- DES nanoparticles can be firmly deposited on the CCE by an electrochemical method.

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Kinetics of Oxidation of Bio-ethanol in wastewater using nano CuO/ZnO Catalyst.

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Key word: Bio-ethanol, Nanocatalyst, Oxidation, Kinetics

Introduction:

In the last decades, the interest in the use of bio-ethanol as fuel has been widely developed in direct bio-ethanol Fuel Cells (DEFCs). Nowadays, the use of bio-fuels is becoming increasingly important. Among them, the bio-ethanol is an attractive alternative bio-fuel since it can be produced from biomass [1]. However, the release of these ethanolic wastewaters in the ecosystems is a dramatic source of eutrophication and perturbations in the aquatic ecosystems and also, killed good and bad microorganisms in soil.

In this study three models (Lagregern, Blanchard, Elovich) of kinetics rate equation is investigated for the optimum reaction [2].

Materials and methods:

CuO and ZnO nanocatalysts were prepared by the sol-gel auto combustion method, in both cases the mass ratio 2:9 is used for metal nitrate: urea composition. The mixture was dissolved in DI water and was warmed to 70 °C for 7 hr. the prepared gel was converted to powder on direct flame. Finally, Powder heated to 550 °C for 2 hr.

Maximum allowed concentration of bio-ethanol in aquatic media is 1000 ppm and catalytic oxidation of bio-ethanol from 10000 ppm bio-ethanol solution is investigated in this research.





Nano CuO/ZnO was added to bio-ethanol solution (250ml, 10000 ppm) and mixed for stirring for 120 minutes, sampling is done 20 minutes intervals and analyzed by gas chromatography technique. For the optimum reaction rate constant, then reaction order is calculated.

Result and discussion:

SEM and XRD techniques are used to qualitative evaluation of synthesized catalysts. Ratio of nano CuO/ZnO mixture is according to table 1. The effect of pH on degradation effect is shown in table 2.

Ratio of nano CuO	100	90	80	70	60	50	40	30	20	10	0
Ratio of nano ZnO	0	10	20	30	40	50	60	70	80	90	100
Removal percent	84	91	98	95	89	85	83	86	80	79	75

Table 1. Ratio of mixture of nano CuO/ZnO

Table 2. Efficiency of optimum pH

pН	3	5.5	7	9
Efficiency	61%	82%	90%	75%

Conclusion:

The optimum ratio of nano CuO:ZnO mixture was for 250 ml solution 7:3. The best and optimum of mass catalysts was 0.1 g. Optimum reaction condition in this study was in neutral pH so, it can be economic in large scales. Rate constant of optimum reaction calculated 0.1/mol.min.

The reaction was obey from lagersern rate equation and it was pseudo-second order reaction.

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Hydrogenic impurity effects on refractive index changes and absorption coefficients of a cylindrical quantum wire with a convex bottom in magnetic field

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Keywords: hydrogenic impurity, magnetic field, refractive index, absorption coefficient

Introduction:

Recent advances in crystal growth technique help us to fabricate semiconductor nanostructures such as quantum wells, wires and dots. In particular semiconductor quantum wires (QWs) have gained a great importance due to the possibility of tuning the size, shape, and number of bound electrons. The two-dimensional quantum confinement of electrons in these structures, leads to the formation of discrete energy levels and the drastic changes of the absorption spectra as well as many novel physical properties which had not been observed in the bulk materials [1,2]. So, the purpose of this paper is to investigate the effects of external magnetic field, geometrical size, convexity parameter and hydrogenic donor impurity on the linear, the third-order nonlinear and the total optical absorption coefficients and refractive index changes of the system. To this end, energy eigenvalues and eigenfunctions of a hydrogenic impurity confined in a cylindrical quantum wire have been obtained, using the matrix diagonalization method. Also, by means of the compact-density matrix approach the linear and nonlinear optical absorption coefficients have been calculated [3].

Materials and methods:

In the presence of an external magnetic field and hydrogenic impurity, the total Hamiltonian of the system is given by





$$H = \frac{1}{2m^*} (\vec{p} + e\vec{A})^2 + V(\rho) - \frac{e^2}{\varepsilon \sqrt{\rho^2 + z^2}}$$
(1)

Where the confinement potential inside the wire is $V(\rho) = u_0(1-\rho^2/R^2)$ and outside the wire is infinity (u_0 is the convexity parameter). Matrix diagonalization method is used to calculate energy eigenvalues and eigenfunctions of Eq. (1). After the energies and their corresponding wave functions are obtained, the linear, the third-order nonlinear and the total optical absorption coefficients (ACs) and refractive index (RI) changes for the intersubband transitions can be calculated by the density matrix approach and the perturbation expansion method.

Results and discussion:

We do our calculations for a typical GaAs quantum wire. The parameters used in this work are as follows: $m^* = 0.067m_e$, $n_r = 3.2$, $\varepsilon = 13.18$, $T = 0.2 \, ps$ and $\sigma_v = 5 \times 10^{24} \, m^{-3}$. To investigate the influence of an external magnetic field and hydrogenic impurity on the optical ACs of the system, we have presented the variations of the linear, the third-order nonlinear and the total optical ACs as a function of the photon energy and different values of the magnetic field strength with and without considering the impurity effect. The figure clearly shows that the impurity and external magnetic field strength increase the energy difference between the subbands and thus shift the absorption peaks to higher energies. Moreover, external magnetic field strength (hydrogenic impurity) enhances (diminishes) the overlap between the subbands. This leads to augment (reduce) maximum values of ACs.

Conclusion:

In conclusion, effects of an external magnetic field and hydrogenic impurity on the linear and nonlinear opyical ACs and RI changes of a quantum wire are investigated. Our results indicate that, the magnetic field strength, hydrogenic impurity the wire radius and the convexity





parameter have a great influence on the electronic structure and optical properties of the system.



Figure 1: The effect of magnetic field and hydrogen impurity on the index of absorption.

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Theoretical Study of Electron Transfer Process Between La₂@C₇₂(Adamantylidene Mono-Adducts) and Erythromycines

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Abstract:

Electron transfer between metallofullerenes and other molecules is thought to involve the transfer of electrons between molecules surrounding the fullerene cage. One class of electrontransfer molecules is the $[La_2(a)C_{72}(Adamantylidene Mono-Adducts)_n]$ (n=0,1). Macrolides are a broad spectrum of antibiotics that are commonly used in human pathologies as well as in veterinary medicine. In this study, the electron transfer process has been investigated between the structures of Erythromycin-A (EA) and the endohedral metallofullerenes (EMFs), which create [EA]. $[La_2@C_{72}(Adamantylidene Mono-Adducts)_n]$ (n=0,1). The free energies of electron transfer were assessed using the electron transfer (ET) equation for the complexes. The calculations are presented for Red.E1 to Red.E4 of the fullerenes. The results were used to $\Delta G_{et(1)}$ to $\Delta G_{et(4)}$ of complexes to for the metallofullerenes calculate the $[La_2@C_{72}(Adamantylidene Mono-Adducts)_n]$ (n=0,1). The first to forth free activation energies of electron transfer and the maximum wave length of the electron transfers, $\Delta G^{\#}_{et(n)}$ and λ_{et} (n=1-4), respectively, were calculated in this study and in accordance with the *Marcus* theory. The sign of wave function will change in photo-ET process, but in the thermal-ET the same sign would be performed for the metallofullerenes.

Keywords: Metallofullerenes; La₂@C₇₂(Adamantylidene Mono-Adducts); Non-IPR Carbon Cage; Electrochemical properties; Electron transfer properties; Activated free energies of electron transfer; Marcus Theory.







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Solid-state ion selective electrode based on modified nano conductive polymer

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Key Words:Pencil graphite electrode, Polypyrrole/sunset yellow,Cu(II)sensor, potentiometric sensor

Introduction:

Ion-selective electrode (ISE) is a potentiometric sensor having a potential response selectively to the specific ions in solutions. Compared with other methods, the ISE-based analysis can provide a fast, accurate, reliable, portable, convenient and inexpensive analytical technique. We chose pencil graphite as the material of the electrode because the pencil graphite electrode (PGE) has a larger active electrode surface area and is therefore able to detect low concentrations and/or volumes of the analyte [1,2].

Materials and methods:

All chemicals obtained were of analytical grade and were used without further purification, except for aniline and pyrrole which was distilled before use. All metal ion solutions were prepared in doubly-distilled water. The standard Cu (II) solution was prepared from CuSO₄.12H₂O as a 0.10 M solution and was diluted when necessary. Sunset yellow as carrier were purchased from Merck. The interfering cations were prepared from the respective metal chloride, nitrate and sulphate.

Apparatus:




Electrochemical synthesis of pyrrole was carried out with a SAMA 500 potentioscanner (Iran). The pH of the sample solutions was adjusted using HCl or NaOH solutions and monitored simultaneously with a Metrohm model 827 pH/mV meter). Measurements were performed according to the manufacturer's directions. A saturated calomel electrode (SCE, Metrohm) with a double junction was used as the reference electrode. EMF measurements were carried out using an accurate digital electronic voltmeter with high internal impedance to the nearest 0.10 mV.

Result and discussion:

A coated–pencil graphite ion selective electrode (PGE), which was selective and sensitive to Cu (II) ions, was developed using polypyrrole/sunset yellow (PGE/SY/PPy). When optimized, this electrode exhibits a linear Nernstian response over the range of 5.0×10^{-5} - 1.0×10^{-2} M of copper (II) ion, with a slope of 29.54 mV per decade. The proposed electrode has a response time between 20-50 s. The limit of detection is 7.4×10^{-6} M and a working pH range of 3-6. The effect of several parameters, such as content of ionophore in the membrane, pH of the sample solution was investigated. The preparation procedure of the electrode is very easy and inexpensive by potentiostatically method.

Conclusion:

The proposed electrode was applied as an indicator electrode in potentiometric titration of copper ion with EDTA solution. Although the value of the temperature coefficients of electrode was calculated (0.00168 V/°C) that is a small value which shows the thermal stability of the electrode response. The surface morphologies, approximate composition and the elemental map of polymer film were checked out by scanning electron microscopy(SEM) (Fig.1), fourier transform infrared (FTIR) and X-ray diffraction (XRD) that shows presence of SY and nanoparticles of polymer in surface of electrode.







Fig.1: SEM image of PPy film (a) particle size(65 nm) (b) thickness of film(2.275 μm)

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Application of a nano sized TD-TiO₂ in a sono assisted photo-catalytic process

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Keywords: Nano TD-TiO₂, Wastewater treatment, DR16, Thermal decomposition.

Introduction:

It has been revealed that, some of the drawbacks of individual techniques can be eliminated by some characteristics of other techniques [1]. In the present study application of a sono-assisted photo-catalytic degradation of an azo dye, Direct Red 16 (DR16), in aqueous solution was performed. The used photo-catalyst is nano titania particles synthesized via thermal decomposition method (TD-TiO₂) [2].

Material and methods:

The azo dye, direct red 16, $C_{26}H_{17}N_5Na_2O_8S_2$ (C.I. 27680, MW 637.26) was purchased from Alvan Sabet company (Iran), 99% pure. Sulfuric acid and sodium hydroxide used to adjust the pH of solutions and were all Merck products. Titanium tetraisopropoxide ((CH₃)₂CHO)₄Ti was used as precursor of titania and supplied by Aldrich (purity >97%).

In each run, a certain amount of the nano TD-TiO₂ powders was mixed with 1.0 L of the dye solution. The pH of the solutions was adjusted to the desired value and transferred to the reactor, and after adjusting temperature and well mixing using air bubbles and ultrasonic waves, the lamp was switched on to initiate the process (sono-assisted/UV/TiO₂). Samples (5 mL) were taken at regular time intervals and centrifuged (in two step) to separate the nanoparticles from the solutions for further analysis.





Catalyst preparation:

Titanium tetraisopropoxide (TTIP) under temperature of 95 °C was carried into a tubular electric furnace working under temperature of 900 °C by means of argon (4.3 L/min) and air (43 L/min) flows. An alumina tube (0.45 m in length and 0.02 m in diameter) was placed inside the electric furnace. A water cooled particle collection device was installed at downstream from the alumina tube, to collect the synthesized nano photo-catalysts.

Results and discussion



Fig. 1: TEM image of the synthesized nano TD-TiO₂ particles.



photo-catalyst process on the dye degradation efficiency; [TD-TiO₂]=63.4 mg/L, pH=8.5, [DR16]₀=30 mg/l , T=25 °C.

TEM image of the nano TD-TiO₂ (Fig. 1) shows that the diameter of the particles is less than 20 nm. Figure 2 indicates the effect of different component of the applied process on the degradation efficiency. It can be seen that simultaneous application of the ultrasonic waves and UV/nano TD-TiO₂ process can impressively improve the degradation efficiency. The reason is due to the fact that, the efficiency of the heterogeneous photo-catalytic process is hindered severely by two main factors: mass transfer limitations and fouling of the solid catalysts. In the presence of sonication, the rate of hydroxyl radical generation will be increased via raising in the catalyst surface expose to UV irradiation. Also mass transfer resistance will be eliminated due to the acoustic streaming and turbulence created by the





ultrasonic wave propagation. Moreover, the turbulence helps in cleaning of the catalyst surface, which leads to increase in degradation efficiency of the dye.

Conclusion:

The obtained results improved that the nano $TD-TiO_2$ particles are efficient in the photocatalytic treatment process and presence of ultrasonic waves in the media can improve efficiency of the combined process considerably.

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Alignment Independent 3D-QSAR Modeling of Fullerene (C₆₀) Solubility in Different Organic Solvents

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Abstract:

In this work, we have applied VolSurf and GRIND derived descriptors of Molecular Interaction Fields (MIFs), as Alignment independent three dimensional quantitative structure activity relationships (3D-QSAR) approaches, to prediction of C_{60} solubility in a diverse set of 132 organic solvents. GRIND methodology with fractional factorial design (FFD) and PLS analysis was carried out and yielded a highly descriptive and predictive model. Genetic algorithm (GA) and successive projection algorithm (SPA) applied to feature selection and extract more informative VolSurf descriptors. Support vector machine (SVM) were used to model construction and SPA-SVM based VolSurf descriptors showed excellent performance in predicting C_{60} solubility. Validation, reliability and robustness of obtained models checked by the prediction of external test sets, leave-one-out and progressive scrambling approach. The results confirmed that hydrophobic interactions besides steric effects are main factors influencing solubility of C_{60} in different organic solvents.

Keywords: Fullerene (C₆₀), Solubility, 3D-QSAR, GRIND, VolSurf





The effect of process factors on particle size of nanostructured lipid carriers containing beta carotene

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Keywords: Beta carotene, Nanostructured lipid carriers, Particle size, Mathematical model.

Introduction:

Beta carotene is one of the most important natural food colorants which is also the major source of vitamin A for most of the people in the world. Therefore, it is using as afunctional material in foods [1].

The nanostructured lipid carriers (NLC) based on mixture of solid lipids with spatially incompatible liquid lipidsare considered as thesecond-generation lipid nanoparticles. These new colloidal carriers combined the advantages and avoid the disadvantages of the other colloidal carriers [2].Application of the lipid nanoparticles (SLN and NLC) as potential delivery systems for functional materials in food have been recently investigated by many researchers in order to take the advantages of these systems in food industry such as increasing the bioavailability of functional food ingredients [3-4]. Thus, the aim of this study was to prepare the NLC containing beta carotene and to investigate the effect of liquid lipid content of lipid phase, lipid phase concentration, surfactant concentration and temperature on the particle size of drug loaded NLC. Additionally, a mathematical model was developed to predict the particle size of NLC.

Methods:





NLC containing beta carotenewere prepared using solvent diffusion method. Response surface methodology (RSM) was used to assess the effect of process factors on particle size of the NLC. A set of 30 experiments was designed using central composite design (CCD) experimental design. A second order polynomial equation was employed to express the particle size as a function of process factors. The fitted model was then statistically analyzed.

Apparatus:

A zetasizernanozs zen3600 (Malvern Instruments, Worcester, UK)instrument was employed to measure the particle size and the polydispersity index of the NLC. Statistical analysis was performed by Design-expert 7.0 software.

Results and discussion:

The high R^2 value of the fitted second order equation indicated that 95.5% of variation in particlesize was explained by the regression on process factors. Statistical analysis revealed that the lipid phase concentration, surfactant concentration and temperature had significant effect on particle size (p<0.05). However, the effect of liquid lipid content of lipid phase was insignificant (p>0.05). The particle size increased by increasing the temperature, while there were optimum values for lipid phase concentration and surfactant concentration in which particle size reached to a minimum point.

Conclusion:

Nanostructured lipid carries containing beta carotene was successfully prepared by solvent diffusion method using food grade materials. NLC systems with particle sizes of less than 50 nm were produced. Also, an appropriate mathematical model was developed to predict the particle size of NLC containing beta carotene. This research showed that NLC can be applied as potential delivery systems for beta carotene in food systems.

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Low temperature preparation of TiO₂/Activated carbon nanocomposites

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Key words: Nanocomposites, Sol-gel, Activated carbon, TiO₂

Introduction:

Titanium dioxide (TiO₂) has been investigated by many researcher because of their applications in many fields of chemical engineering,materials engineering,dye-sensetized cells,sensors and in the paint industry. TiO₂ exists in three different crystalline structure are stable : rutile,anatase and brookite [1]. Activated carbon (AC) is widely used as a support in gas and water remediation because of its good adsorption,and supported TiO₂ exhibits a synergism that has marked effects on the kinetics of disappearance of pollutants,each pollutant being more rapidly photodegraded. Adding activated carbon to TiO₂ can possibly increase its photocatalytic efficiency because of the large surface area of the whole composite catalyst,in which activated carbon can act as an efficient adsorption trap to the organic pollutant,which is then more efficiently transferred to TiO₂ surface,where it is immediately photocatalytically degraded [2,3].

In this work, activated carbon was selected as an adsorptive support a transparent TiO_2 nanosol was synthesized by hydrolysis titanium-n-butoxide. Some characterization techniques via,-X-ray diffraction analysis (XRD) and Scanning electron microscopy (SEM) were used to study the induced changes on the properties of TiO_2 -activated carbon (TiO_2/AC) nanocomposites.

Materials and Methods:





Anatase TiO_2 was prepared by a sol-gel method at low temperature by hydrolysis titanium-nbutoxide in acidic aqueous condition and subsequent reflux in 80 °C to enhance crystallization . Activated carbon was added into TiO_2 sol prepared . In order to make TiO_2/AC composites,mixture was then dispersed by ultrasonic for 30 min and then was dried into powders.

Result and discussion:

According to the XRD studies, TiO_2 particles possessed evident diffraction peak of anatase,which indicates that the TiO_2 particles were predominatly of the anatase crystal phase.. The XRD pattern reveal the crystal structure and present species of nano TiO_2 in TiO_2/AC composites. Scanning electron microscopy shows that the TiO_2 nanoparticles were deposited on the surface of activated carbon.

Conclusion:

Anatase nanocrystalline TiO_2 sol was prepared at low temperature. A TiO_2/AC nano composites with well-dispersed TiO_2 particles in the activated carbon. Results showed that the particles had formed anatase phase and the deposition of nano TiO_2 particles on activated carbon is uniform.

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Synthesis of SO₄²⁻/TiO₂ and SO₄²⁻/TiO₂/SiO₂ as nano-catalysts for Oacylation of phenol

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Key words: Solid acid, nano-catalyst, O-acylation of phenol

Introduction:

Acylation of phenol is one of the most important reactions in organic synthesis. The use of the solid acid catalysts such as clays, zeolites, ion exchange resins and metal oxides are gaining more attention in the chemical reactions. Since liquid acids such as H₂SO₄, HCl, H₃PO₄ and so on are highly corrosive, hazardous and polluting; recently, a number of organic synthesis have been conducted with solid acids [1,2]. The solid acids are less toxic and facilitate to recovery and recycling of the catalysts. They also can remain stable even at high temperature and in a solid-liquid system [3,4]. However, the SO₄²⁻/TiO₂ also have some disadvantage such as low surface areas and wide pore distributions. Compared with SO₄²⁻/TiO₂, SO₄²⁻/TiO₂/SiO₂ nanocatalyst had high specific surface area. In this paper, SO₄²⁻/TiO₂ and SO₄²⁻/TiO₂/SiO₂ nanocatalyst were prepared using the sol-gel method and were used for the O-acylation of phenol with acetic anhydride.

Materials and methods:

In this study, titanium iosopropoxide (TTIP) was used as titanium dioxide precursor. A solution of deionized distilled water (20 mL) and isopropanol (100 mL) was added gradually to a stirred solution of TTIP (13.5 mL) in isopropanol (100 mL). After stirring for one hour and evaporation of iso-propanol, 200 mL deionized water was added to the solution. Then nitric acid (1M) was added until the pH was adjusted to 1.5 at room temperature. To obtain a stable sol the slurry was heated in a flask equipped with a reflux condenser at 70°C for 24 h and then in an ultrasonic bath for 2 h. To obtain the TiO₂ nano powder, the sol was dried at





room temperature and calcined at 400°C for 3h. The TiO₂ and TiO₂/SiO₂ were sulfated via impregnation technique, where an aqueous ammonium sulfate solution, which contained 20 wt. % sulfate ions with respect to Ti, was used per gram of dried sols. The mixtures were dispersed under ultrasonic waves for 10 h at room temperature. The solids were decanted and dried at 70°C for 24 h. Then the sulfated TiO₂ and TiO₂/SiO₂ powders were calcined at 400 and 450 °C, respectively, for 3 h. The O-acylation was carried out under ultrasonic waves at room temperature in solvent-free conditions. Acetic anhydride was used as acylation agent.

Result and discussion:

The catalysts were characterized by means of XRD, FT-IR, BET, SEM and EDX methods. The XRD results show similar patterns and match well with the standard form of anatase crystalline phase. The specific surface area were indicated that the addition of the second metal oxide (SiO₂) has increased the specific surface area of SO_4^{2-}/TiO_2 (98 m²/g) to 239 m²/g for $SO_4^{2-}/TiO_2/SiO_2$ catalyst. The elemental contents of SO_4^{2-}/TiO_2 and $SO_4^{2-}/TiO_2/SiO_2$ were analyzed by EDX method for $SO_4^{2-}/TiO_2/SiO_2$, the Ti content is 34.36 wt.%, Si is 61.20 wt.% and S content of the sample is 4.43 wt.%.

Conclusion:

The results show that the $SO_4^{2^2}/TiO_2/SiO_2$ has high catalytic activity in the O-acylation of phenol. A high conversion yield (95.2%) was obtained at optimum conditions of 20 min, dosage 50 mg of catalyst, and phenol to acetic anhydride molar ratio of 1:0.5 at room temparture. This result is higher compared to the previous reported values. In conclusion, the $SO_4^{2^2}/TiO_2/SiO_2$ catalyst is a promising solid acid catalyst to conduct the O-acylation reaction of phenol with acetic anhydride.

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Template Extraction from Mesoporous MCM-41 Nano-Structredin Different Solvent in present of Ultrasound Wave

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Keywords: MCM-41, Ultrasound, Template extraction, different solvent

Introduction:

Mesoporous silica nano-structured materials of MCM-41 type are synthesized from the surfactant micellar template addition of an inorganic silica source. Quaternary alkylammonium bromides are most commonly used as a template. These mesoporoussilicas have many application in adsorption, catalysis, separation, and others because of its regular pore system, tunable pore size, high surface area, and pore volume. The micellar core is after synthesis removed and porous honeycomb like structure is created. Various method have been used for template removal. in most cases the as-synthesized samples are heat-treated in presence of oxygen or air above 773K. Main problem in this procedure is probable structure damage, shirinkage and dehydroxylation. Also burning and wasting of the template which could be collected is a problem.

In this work we have attempted to use ultrasound waves for removal of the organic template from the pores of mesoporous MCM-41 in different solvent.

Experiment:

1. MCM-41 preparation:

The surfactant-templated MCM-41 was synthesized by our common room temperature synthesis method [1]. We used tetraethlyleortheosilicate(TEOS, Merck, 800658) as a source of





silicon and cetyltrimethylammonium bromide (CTAB, Merck, 1.02342) as template for the preparation of mesoporous MCM-41.

2. Template removal procedure:

The ultrasound-assisted template removal was carried out in a 7500S ultrasonic device (SAIRAN Instrument Company, Iran)with an ultrasound frequencies of 28 kHz. MCM-41 was dispersed in different solvent (ethanol, methanol, methanol:n-Hexan) in a baker. Then, suspension was immersedinto water in the ultrasonic device, and irradiated for various timeattemperature of40°C.

3. Characterization:

A Philips PW1840 diffractometer with CuKα radiation was used to record the powder XRD patterns of the MCM-41 samples. Thermogravimetric analysis (TGA) was performed on a TGA (Polymer Laboratories 1500) to estimate the residual amount of the template in the MCM-41 samples. Specific surface area of the sonicated and the calcined MCM-41 was estimated based on the data provided by a Sibata Surface Area Apparatus 1100.

Results and discussion:

The influence of time sonication at organic solvent on the efficiency of the removal of cetyltrimethyl-ammonium (CTA) cations from the pores of mesoporous MCM-41 was investigated. The degree of template removal was verified by BET analysis and calculating the specific surface area of the sonicated sample. Results show thatthe majority (93%) of the surfactant molecules are removed outfrom the powder MCM-41 within a 15 min sonication at a moderate temperature of 40 °C. The XRD patterns show that ordered mesoporous structures are preserved for all the ultrasound-treated samples. Also particle size for sonicated sample was determined using sherrer equation and result of XRD pattern between 60-70 nm. To quantitatively determine the degree of surfactant removalfrom the sonicated MCM-41 materials, a thermogravimetric analysiswas employed. The amount of template can be estimated by the weight loss between 150 and 340 °C. This amount is approximately 57% and 7% for MCM-41 and sonicated MCM-41.





Conclusion:

Our work showed that ultrasound wave can be used for removal of organic template from MCM-41. There are several advantages for this efficient and mild method compared to calcination. The surfactant molecules are released into alcohol and can be recovered for reuse.

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Electrodeposition of silver on multi wall carbon nanotubes modified glassy carbon electrode for sensing and study of hydrogen peroxide decomposition

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Keywords: Carbon nanotube, Electrocatalyst, Nanosensor, Hydrogen peroxide, Kinetic study

Introduction:

In recent years, carbon nanotube (CNT) widely used in the construction of chemical sensors and biosensors, especially in the field of supporting materials due to their exceptional characters [1]. Meanwhile, silver used as electrochemical sensors have received much attention due to their excellent biocompatibility and unique catalytic properties [2]. The high surface area of CNT made it possible to load silver thin film with high catalytic activity. Fabricating CNT-supported silver thin film is thereby desirable since it combines both the advantages of CNT and silver thin film which may be helpful in widening the applications. Hydrogen peroxide is an essential mediator in many fields, such as food industries, clinical, and environmental analyses and it is crucial to detect H_2O_2 accurately and rapidly. In this paper, we fabricate Ag/MWCNT/GC electrode and further studied by electrochemical methods, which exhibited well-defined electrocatalytic activity towards H_2O_2 reduction.

Materials and methods:

 H_2O_2 (30% w/w, Rankem), MWCNTs (30-50nm in diameter, 20µm in length, Neutrino) and other reagents were of analytical reagent grade from Merck. All solutions were deaerated by bubbling nitrogen gas through them prior to the experiments. Electrochemical experiments were performed with a computer controlled µ-Autolab electrochemical system. For functionalization of the MWCNTs with hydroxyl groups typically 5mg of MWCNTs and





100mg of potassium hydroxide grained together for 3 h in a ruby, washed many times with methanol, dispersed in 5 ml absolute ethanol, and finally ultrasonicated for 2 h to get a uniform dispersion. The glassy carbon electrode (GCE) was polished with alumina, then 30 μ l of ethanol-MWCNTs solution (1mg/ml) was cast on the surface of GCE and dried in air to form a MWCNTs film at the electrode surface. The MWCNT/GC surface was modified by deposition of silver for 1 min at -0.2 V vs. Ag/AgCl from a 0.1 M KNO₃ solution containing 5.0 mM AgNO₃.

Result and discussion:

The cyclic voltammogram (CV) of AgNO₃ showed a cathodic peak at 0.11 V (Fig. 1), which resulted from the reduction of Ag⁺. The reduction potential adjusted to -0.2 V for taken effective reduction of Ag on MWCNT/GCE. The voltammetric behavior of hydrogen peroxide in phosphate buffer solutions (PBS) (pH 7, 0.1M) at different electrodes was investigated by cyclic voltammetry and the results are shown in Fig. 2. The results illustrated that the Ag/MWCNT/GCE could facilitate the reductive of hydrogen peroxide. So, the modified electrode could used to the directly determination of hydrogen peroxide. Fig. 3 shows the response of the Ag/MWCNT/GCE to additions of hydrogen peroxide. The current peak was found to increase linearly (inset of Fig. 3) with a determination coefficient of 0.996. The catalytic decomposition of H₂O₂ in present Ag/MWCNT/GCE was studied by CVs of 1mM H₂O₂ in PBS, cathodic peak current reduced with time (Fig. 4). The results showed that the reaction was first order with respect to H₂O₂ concentration (inset of Fig. 4). The rate constant (*k*) was calculated 0.013s⁻¹ by the expression ln(*a/a-x*)=*kt*, where *a* is the initial concentration of H₂O₂ at time *t*.



Fig. 1. CV of AgNO3 in KNO3, Scan rate 100mVs⁻¹.





Fig. 2. CVs of 1mM hydrogen peroxide at GCE (a); MWNT/GCE (b), Ag/GCE (c) and Ag/MWNT/GCE (d).

Fig. 3. CVs of Ag/MWNT/GCE after hydrogen peroxide addition, Inset: plot of calibration curve for Ag/MWNT/GCE toward H_2O_2 analysis.

Fig. 4. CVs of Ag/MWNT/GCE 1mM H_2O_2 versus time. Inset: the integrated first-order equation for H_2O_2 decomposition.

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DFT Studies of Interaction between Main Group Metals and B9N9 Nanocone using by Electron Paramagnetic Resonance (EPR)

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Keywords: ab initio calculations, chemical shift, Boron nitride, nanocone

Introduction:

Since the discovery of carbon nanotubes [1] tubular nanomaterial have been considerable attention for their unique physical, chemical, and mechanical properties as well as their potential for applications. The metal component can be a single atom, a metal cluster, or a planar metal surface. [2].Boron nitride nanotubes (BN), was another tubular nanomaterial which synthesized after the discovery of the carbon nanotubes.BN nanotubes have also many unique physical and mechanical properties,[10].

On the theoretical side, several studies on the filling the BN nanotubes with transition metals have been reported, wherein half-metallic behavior has been seen in some of these systems.[15]

Computational Methods:

All Density Functional Theory (DFT) and Hartree Fock quantum calculations were performed using Gaussian 98 program package [33] on structure of boron-nitride nanocone contain metals. The structures first optimized with Becke3,Lee-Yang-Parr (B3LYP) and Becke1,Lee-Yang-Parr (B1LYP) and Hartree Fock (HF)methods and LANL2DZ basis set and then Nuclear Magnetic Resonance (NMR) parameters at boron(B), nitrogen(N) and metals nuclei optimized structure calculated by these methods and LANL2DZ basis set





Results and Discussion:

Optimization for nanocone were performed using by B1LYP method with EPR2 and EPR3 basis sets but after transporting metals into nanocone the calculation were done with B1LYP, B3LYP and HF methods with LANL2DZ basis set.



In optimized structure we saw that with putting Li,Na,Be and Mg largest bond length belonged to N7-M and shortest bond length belonged to N9-M therefore maximum interaction was between these metals and N9 atom of nanocone and minimum interaction was belonged to N7 atom of nanocone and these metals. Also after located K and Ca in the center of nanocone shortest bond and maximum interaction don't change but largest bond and minimum interaction changed and was belonged to B5-M that is meant that the metal to be closed to entrance of nanocone.



In addition total atomic charges of atoms in B1LYP ,B3LYP and HF methods have been calculated Atom charge transfers have considered to full alternation B, N and metallic atoms in B9N9 nanocone. At direct interactions between indicated atoms have shown that the N atoms at nanocone had the most charge distribution in B1LYP ,B3LYP and HF methods with GIAO and CSGT approximates in presence of metals or in the absence of it. And most negative charge values in nanocone were belonged to N17 and N9 that after location of metal these most Negative values were shifted to N3 and N10; to be signified with putting metals the location of active sites in nanocone were changed.







Conclusion:

1. Interaction between K and Ca with nanocones atoms were different to compare of another metals such as Li, Na, Be and Mg .minimum interaction of K and Ca were with B5 atom in nanocone and for other metals were with N7 atom of nanocone.maximum interaction for all of metals with nanocone were the same and were belonged to N9.

3. The charge distribution values of N atoms are in agreement with structure coordinate.

4. The atom charge transfer values of atoms at nanocone had the same behavior inB1LYP, B3LYP and HF methods and according to these values it is found that the N3 and N10 at nanocone are active sites.

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Effect of Eu concentration on photoluminescent properties of sol gelderived nanocrystalline SrZn₂Si₂O₇ as a potential phosphor for solid state lighting

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Key words: Phosphor, Sol-gel, Concentration quenching, Light emitting diode.

Introduction:

White light-emitting diodes (LEDs) are anticipated to be the fourth generation light source following the incandescent filament lamps, fluorescent lamps and high-pressure discharge lamps, as a consequence of their high brightness, low power consumption, long lifetime and environment friendly situation existence [1-4]. Since UV LED can offer an efficient solid state light, more and more attention has been paid to the development of new phosphors that can be excited in the range of near-UV due to the essential efficiency improvement of white light emitting solid-state devices [5]. In recent years, silicate-based phosphors have attracted researcher's attention due to the advantages of stable crystal structure and high thermal stability [6, 7]. Among them, Eu-doped strontium silicate phosphor seems to have the potential for the application of various optical devices [8, 9]. These phosphors show interesting optical properties that are related to electronic transitions between the 4f ground state and the crystal field components of the 4f 5d excited state configuration [10]. Among the different methods to prepare precursors, the sol-gel route is one of the most important techniques for the synthesis of various functional materials. Many researchers are engaged in the luminescent property of Eu ions in different silicate compositions. But, there is high technological need for developing novel phosphors with high efficiency, stability and low cost.





Materials and methods:

A series of samples, $Sr_{1-x}Zn_2Si_2O_7$: xEu^{2+} (x= 0.02-0.1), were prepared by sol-gel method and then calcined at 1100 °C in a weak reductive atmosphere. First, Stoichiometric amounts of $Sr(NO_3)_2$, $Zn(NO_3)_2.6H_2O$ were dissolved in ethanol and water, thenSi(C₂H₅O)₄(SiO₂,28.4%) (TEOS) was added into mixture under stirring for 30 min. Afterwards, desired amount of europium nitrate (Eu(NO₃)₃.6H₂O) was added into the precursor solution and pH value was adjusted about 3.

Apparatus:

The resulting powders were analyzed by X-ray diffractometer (Bruker AXS: D8 ADVANCE), scanning electron microscope (SEM; Stereoscan S 360 Cambridge), transmission electron microscope (Hitachi H-800 electron microscope) and fluorescence spectrometer (Perkin-Elmer LS-55).

Result and discussion:

From XRD pattern, it can be concluded that crystallization of main phase ($SrZn_2Si_2O_7$)has occurred which corresponds to JCPDS file number 10-0051. Also, SEM and TEM micrograph show that particles have the approximately uniform size distribution (25-40 nm) and a spherical like shape.Photoluminescence (PL) results show that the phosphor can be efficiently excitedby NUV light from 345 to 390 nm, and exhibited bright blue emission (480 nm). Furthermore, the relative PL intensity increases with Eu²⁺-concentration increasing until a maximum intensity is reached (x=0.04), and then it decreases due to concentration quenching.

Conclusion:

In summary, a novel enhanced blue-emitting phosphors, $Sr_{1-x}Zn_2Si_2O_7$: xEu^{2+} were designed and synthesized for near UV LED applications by sol-gel route. Reducing atmosphere helped Eu^{3+} ions reduced to Eu^{2+} and $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} leaded to the strong emission peak at about 481 nm. The results declared that when the concentration of Eu is 0.04, the phosphor shows the highest PL intensity.





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Molecular Dynamics Simulation Study of Thermal Properties of the Au, Ni and AuNi₃ Nanowires

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The most important one-dimensional (1D) nanometer material, the metal nanowires have been expected to play an important role in future. A microscopic description of the melting behavior of nanowire is probably one of the most important problems in physical and material sciences. we have performed molecular dynamics based computations of the variation of the physical properties and the melting behavior of the nanowires Au, Ni and AuNi₃ with 3nm diameter. The quantum Sutton-Chen many-body interatomic potentials [1,2] have been used for these nanowires, and the standard mixing rule has been used to obtain the parameters of this potential for the alloy state. This molecular dynamics simulation was performed in the NPT ensemble. The standard Nose-Hoover thermostat [3,4] and Berendsen barostat[5] were used for temperature and pressure control, respectively. the simulation box was made up of 1008 particles arranged on the FCC structure. The simulation time step δt was set 0.7 fs. The nanowires first equilibrated for 2×10⁵ time steps at 250(K), and then the temperature was raised 1(K) at each time step, reaching melting temperature after many time steps. The MD simulation results are shown in figs1-4.





Fig1. Time variation of the Temperature and pressure for AuNi₃ during equilibration phase.

Fig2 Time variation of the Energy and volume for AuNi₃ during equilibration phase.







nanowires with temperature.

Fig4. Calculated radial distribution function of AuNi₃ at various Temperature.

Our study enabled us to predict the thermodynamic properties such as melting temperature, cohesive energy, latent heat, isobaric heat capacity as well as the lattice thermal expansion (Table1).

Thermal Properties		Au	Ni	AuNi ₃
$T_m(K)$	Nano	975	1220	1000
	Bulk	1340	1640	1225
$E(eV \mid atom)$	Nano	-3.63	-4.24	-3.96
0//	Bulk	-3.78	-4.53	-4.38
$L(eV \mid atom)$	Nano	0.06	0.09	0.065
11/2	Bulk	0.1	0.14	0.035
$\lambda_p imes 10^{-6}$	Nano	3.74	3.08	3.78
	Bulk	6.33	16.38	0.72
$C_p(j/mol.k)$	Nano	26.68	26.33	26.24
	Bulk	19.52	23.3	5.46

Table1: The thermal properties of the Au, Ni and AuNi₃.





Keywords: Thermal Properties, Nanowire, MD Simulation, Au-Ni

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The effects of process parameters on the photo-physical properties of a nanocrystalline blue-emitting phosphor

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Key words: Photoluminescence, Calcination, Nanocrystal, Sol-gel, Electronic transitions

Introduction:

Light emitting diodes (LEDs) as an important class of lighting devices show high potential for replacement of conventional lighting sources like incandescent and fluorescent lamps due to long lifetime, environmental-friendly affiliation and so on [1]. Phosphor is a key material for LEDs to generate desired light and process parameters during calcination of these advanced optical materials may greatly influence the crystallization, morphology and photo-physical properties. In this study, a series of Eu²⁺-doped SrZn₂Si₂O₇ phosphors were synthesized by sol-gel route in order to optimize the emission under a variety of calcination temperatures. In addition, a detailed investigation of the effect of atmosphere on photoluminescence properties was carried out.

Materials and methods:

A series of samples, $SrZn_2Si_2O_7$: 0.04Eu²⁺, were prepared by sol-gel method using metal nitrates and $Si(C_2H_5O)_4$ (TEOS) and then calcined at different temperatures in a weak reductive atmosphere (5% H₂+95% N₂) due to reduce Eu³⁺ \rightarrow Eu²⁺ for 1 h. Meantime, in order to investigate the effect of the atmosphere, the other sample was calcined at 1100°C for 1 h in air.





Apparatus:

The resulting powders were analyzed by X-ray diffraction (XRD; Bruker AXS: D8 Advance), scanning and transmission electron microscopy (SEM; Stereoscan S 360 Cambridge and TEM; Hitachi H-800 electron microscope) and fluorescence spectrophotometer (Perkin-Elmer LS-55, exciting source: near ultraviolet-Xenon lamp).

Result and discussion:

The obtained phosphors from reductive atmosphere show strong blue emission peaking at about 480 nm, which is attributed to a typical $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu²⁺. For the case of divalent Eu ions, the energy separation between the $4f^7$ and $4f^65d^1$ configurations will be large and these transitions are dipole-allowed that are about 10⁶ times stronger than the very frequently observed $4f \rightarrow 4f$ transitions in trivalent Eu ions [2]. Therefore, reducing atmosphere helps to reduce Eu³⁺ to Eu²⁺ ions to attain more blue emission intensity. On the other hand, the partial reduction phenomenon of Eu³⁺ \rightarrow Eu²⁺ in SrZn₂Si₂O₇: Eu prepared in air can be explained with a charge compensation model [3].

Conclusion:

The emission intensities markedly increased with the calcination temperature up to 1100 °C owing to an increase in the amount of $SrZn_2Si_2O_7$ phase and diffusion of dopant ions into host lattice. Furthermore, calcination temperature could convert morphological properties from flower-like to spherical shape. Under the near UV excitation, Eu^{2+} activated $SrZn_2Si_2O_7$ samples show strong blue emission centered at 481 nm. Eventually, the crystallite size of the optimum products was estimated about 25-40 nm.

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Dense coating of surface mounted CoWO₄ nanostructures on silk yarn, prepared by layer-by-layer method under sonicating

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Keywords: Ultrasound, Silk yarn, Nano, Antibacterial.

Introduction:

Metal tungstates nanoparticles have been of considerable interest by virtue of their unique physical and chemical properties. Transition metal nano-particles have a variety of applications ranging from pigments to electronics and in biological systems [1]. Cobalt cations have great significance in all industries, particularly in the electrical sector. In this paper, we report the preparation of silk fiber containing CoWO₄ nanoparticles by using the ultrasound technique. The sonochemical method has been used extensively to generate novel materials with unusual properties, since they form particles of a much smaller size and higher surface area than those reported by other methods [2].

Materials and Methods:

The samples were characterized with a scanning electron microscope (SEM, Philips XL 30) with gold coating. Ultrasonic generator was carried out on an Elma sonic p 60. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu K α radiation. The growth of CoWO₄ on silk yarn was achieved by sequential dipping in alternating bath of aqueous Co²⁺ and Na₂WO₄ in water under various conditions. Pristine silk fibers were dipped in alkaline solution. When negative silk was immersed in aqueous Co², cobalt ions were readily impregnated into the silk through the surface.





Results and discussion:

The effect of temperature, power of ultrasound irradiation and sequential dipping steps in growth of the CoWO₄ particles were studied. These systems depicted a decrease in the particles size accompanying a decrease in the power of ultrasound irradiation [2] as confirmed by the SEM images (Fig. 1). For the sake of investigating the role of sonicating, blank sample was performed without ultrasound irradiation. The average particle size for ultrasound method is around 95 nm, while, the average particle size for blank sample in similar conditions is over 195 nm. Particle sizes and morphology of nanoparticle are depending on temperature. An increase in temperature led to increase of particle size [3]. With the increasing of the particle size of CoWO₄, the fluorescence intensity of CoWO₄@silk decreased correspondingly, and it exhibits good linear relationship at low diameter of CoWO₄ (Fig. 1).



Figure 1. SEM photographs of the prepared samples under sonicating with emission fluorescence spectra.

Conclusions:

The CoWO₄ nanoparticles@silk fibers were prepared under ultrasound irradiation. XRD analyses indicated that the prepared CoWO4 nanoparticles@silk fibers were crystalline in structure. An increase in temperature led to increase of particle size. Results show a decrease in the particles size as the power of ultrasound irradiation decreased. The fiber containing CoWO₄ particles were tested for their antibacterial efficacy against *E. coli* and *S. aureus* and were found to possess significant antibacterial activity. Results show that that nano-sized CoWO₄ could be effectively utilized as a nano-sized highly sensitive fluorescence.





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Synthesis and Characterization of Ag Nanoparticle@Acrilic fiber Under Ultrasound Irradiation

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Keywords: Ultrasound, Acrylic, Nanoparticle, Silver, Antibacterial activity.

Introduction:

Metal nanoparticles have been of considerable interest by virtue of their unique physical and chemical properties. Silver metal has great significance in all industries, particularly in the electrical sector. Today silver is used in photography, medicine, electronic, magnetic, optical, catalytic properties [1]. Acrylic fiber is one of candidate materials for biomedical application, because it has good biocompatibility and minimal inflammatory reaction. The development of new clothing products based on the immobilization of nanophased materials on textile fibers has recently received growing interest from both academic and industrial sectors.

Materials and Methods:

The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating. Ultrasonic generator was carried out on an Elma sonic. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu K α radiation. This work consisted of preparing acrylic by coating its surface with Ag nanoparticles through the chemical reduction under sonicating. In this system, ethylene glycol (EG) served as a reduction reagent and protecting Ag nanoparticles from aggregation. Acrilic fiber was added to an Ag⁺ solution of EG and water in a sonication flask. The reaction mixture was then purged under Ar and irradiated under ultrasound irradiation. An aqueous solution of





ammonia was added to the reaction slurry during the first 10 min of sonication.

Results and discussion:

The effect of temperature, power of ultrasound irradiation and sequential dipping steps in growth of the Ag nanoparticles@fiber were studied. These systems depicted a decrease in the particles size accompanying a decrease in the power of ultrasound irradiation as confirmed by the SEM images (Fig. 1). For the sake of investigating the role of sonicating [2], blank sample was performed without ultrasound irradiation. The average particle size for ultrasound method is around 75 nm, while, the average particle size for blank sample in similar conditions is over 330 nm. Particle sizes and morphology of nanoparticle are depending on temperature. An increase in temperature led to increase of particle size [3]. The product containing Ag nanoparticles were tested for their antibacterial efficacy against *E. coli* and *S. aureus* and were found to possess significant antibacterial activity.



Figure 1. SEM photographs of the prepared samples under sonicating (left) and without sonicating (right).

Conclusions:

The sonicating effect and temperature of reaction were the parameters which were changed for reaching the optimized condition. XRD analyses indicated that the prepared Ag nanoparticles were crystalline in structure. An increase in temperature led to increase of particle size. Results show a decrease in the particles size as the power of ultrasound irradiation decreased. The advantage of using ultrasound radiation is that it does not need high temperatures during the reactions, using the surfactants is not necessary and it yields smaller particles.




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Electrosynthesis of polythiophene nanowires on Anodic Aluminum Oxide Template

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Keywords: polythiophene, nanowire arrays, conducting polymers, anodic aluminum oxide, electropolymerization

Introduction:

Conducting polymers, such as polythiophene, and its derivatives, are promising materials for synthesis of nanostructures. Because of their conjugated structures, conducting polymers have some unique electrical, chemical, and optical properties, and they are easily synthesized using chemical or electrochemical synthetic methods with low cost. Conducting polymers have electrical and optical properties similar to those of metals and semiconductors, while maintaining the flexibility and properties commonly associated with conventional polymer substances [1].

There are various methods for conducting polymer nanowires fabrication. The template method is one of them which have been widely used to fabricate 1D conducting polymer nanostructures such as nanowires and nanotubes because of its simplicity, versatility, and controllability. Generally, the template method has been classified into a hard-template method, which uses a nanopore film such as anodic aluminium oxide (AAO), and a soft-template method, which uses the self-assembly ability of molecules such as surfactants and DNA. In this study we used AAO template to fabricate well ordered polythiophene nanowires [2].





Materials and methods:

All the common chemicals were of analytical grade and were commercially available. Thiophene, acetonitrile (Merk), and tetrabutylammonim perchlorate (Aldrich), were used as received.

Conducting polythiophene nanowires were synthesized through electrochemical polymerization method using AAO nonoporous template which was purchased from Whatman Co. Tetrabutylammonium perchlorate was used as dopant and acetonitrile (CH3CN) as the solvent.

The electropolymerization synthesis of polythiophene nanowires was carried out using potentiostatic conditions two-electrode system.

Result and discussion:

The SEM images of polythiophene nanowires show uniform cylindrical nodules. A typical cross-sectional SEM micrograph of as prepared AAO is displayed in Fig. 1(a), which displays high aspect ratio parallel cylindrical nanopores.

Fig. 1(b) shows the SEM image of the polythiophene nanowires released from the AAO template. To release the nanowires from the AAO templates the electrodeposited membranes were dissolved in the solution containing 3 M NaOH. Nanowires are then washed several time by distilled water and dispersed in ethanol. The diameters of as-synthesized NWs are almost the same.



Fig. 1(a) SEM image of polythiophene nanowires



Fig. 1(b) SEM image of the NWs released from the AAO





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Tunnel magnetoresistance of the system of ferromagnetic electrode/ Diamantane/ferromagnetic electrode: A Greens function approach

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Key Words: Green's function, molecular spintronics, spin valves, Diamondoids

Introduction:

Molecular nanomagnets, often called single-molecule magnets (SMMs), have attracted much interest in recent years both from experimental and theoretical point of view. Besides, the synthetic chemistry produces controlled molecular structures at high yield and low cost. As a result, a wide range of SMMs systems incorporating transition metal and/or rare earth metal ions with tailored magnetic interactions have been discovered. In addition, the rich variety of quantum systems provided by the molecular magnetism field strongly motivates the use of SMMs for both quantum information storage and processing purposes. Diamondoids is deemed to be an excellent material for the next generation of electronics. Pure Diamantane(DIM), $C_{14}H_{18}$ has the same transmission and conductance for both spin up and down current. In this work, we report our green function studies of the quantum transport and electronic properties of Magnet DIM molecule.

Methodology:

We use a tight-binding (TB) Hamiltonian model within the framework of a generalized Green's function(GF) technique as the basis for studying the spin transport of this system. We assume that the system includes the DIM molecule which is bonded one-dimensional ferromagnetic electrodes. Hamiltonian system is described with: $\hat{\mathbf{H}} = \sum_{\alpha} (\epsilon_{\alpha} + e\phi_{\alpha} + e\phi_{\alpha})$





J) $|\alpha \rangle \langle \alpha| + \sum_{\alpha\beta} t_{\alpha\beta} |\alpha \rangle \langle \beta|$ the first term describes the states with energies ϵ_{α} , φ_{α} is the electrical potential, J is spin term and $t_{\alpha\beta}$ at the second term is hopping matrix element between states $|\alpha\rangle$ and $|\beta\rangle$ in TB model. GF of the molecule is coupled to two electrodes in the presence of bias voltage is to: $G(\epsilon) = [(\epsilon + i\eta)I - H_{DIM} - \Sigma_L - \Sigma_R]$ where $\Sigma_{i=L,R}$ is contact self-energy (left and right respectively), H_{DIM} Hamiltonian of DIM and η is an very small positive number. We used transmission function, $T(E) = Tr(\Gamma_L G^{\dagger}\Gamma_R G)$, that $\Gamma = i(\Sigma - \Sigma^{\dagger})$ and density of state, $Dos(E) = -\frac{1}{\pi}Im[Tr(G(\epsilon))]$, in our calculations.

Results and discussion:



Fig.1: a) transmission probability b) I-V for spin up and down

Using the above formalism we calculated the transmission and I-V for a Magnet DIM DIM•Co which is presented in Fig. 1(a),(b), respectively.

Conclusion:

Our calculations show that the presence of spin barer in Diamantine spread the transmission and I-V curves to spin up and down electrons current. (Figure 1)

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Effect of Magnetic Field on the Liquid-Liquid Extraction with Magnetic Nanofluids

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Key words: Magnetic nanofluid, Magnetic field, Liquid-liquid extraction

Introduction:

The potential application of nanofluids in mass transfer has not been much exploited yet. In fact, application of nanofluids promotes the rate of mass transfer¹. The objective of this paper is to investigate the effect of magnetic field on the mass transfer enhancement of acetic acid from toluene to aqueous continuous phase wile modified magnetite nanoparticles are present in organic phase. Two adjustable oscillating external electromagnetic fields have been employed. The magnetite nanoparticles used in the nanofluids were synthesis with co-precipitation method.

Materials and methods:

The chemical system of toluene-acetic acid-water was chosen. Fe_3O_4 (magnetite) nanoparticles were prepared by the chemical co-precipitation method. Magnetite nanofluid was prepared by dispersing pre-weighed quantities of Fe_3O_4 particles in toluene containing acetic acid. Different drop size forming was provided using a variety of glass nozzles in a glass extraction column. To study the effect of magnetic field, two external oscillating electromagnetic fields were used. The coils were similar and fixed located outside and just at the middle of the glass column height. The angle between coils axes was 90°. The intensity at center of the coils could be up to 2 tesla. The power supplier for electromagnetic fields could supply AC current with adjustable frequency and voltage. The experiments were conducted at 40 Hz.





Result and discussion:

The rate of mass transfer for a drop size, d, can be obtained with respect to the overall masstransfer coefficient concept. Considering mass transfer during the measured contact time, the overall dispersed phase mass transfer coefficient is calculated from equation $K_{od} = -\frac{d}{6t} \ln(1-E)$ where E is the extraction fraction, defined by $E = \frac{C_{di} - C_{df}}{C_{di} - C_{d}^{*}}$ where C_{di} ,

 C_{df} , and C_{d}^{*} are drop side initial, final and equilibrium solute concentrations, respectively.



Fig. 5. K_{ad} versus nanofluid concentration for different magnetic fields. **Fig.6.** Effect of the magnetic field on relative K_{ad} values. Fig.1 presents the variations of overall mass transfer coefficient, with nanoparticles concentration and magnetic field for typical nozzles that provide nearly the same drop sizes. The K_{od} variations can be discussed with the aid of the microconvection phenomenon induced by the Brownian motion. With magnetic field the root-mean-square velocity of a Brownian particle can be increased and velocity of particles would be more when magnetic field increased². Influence of magnetic field intensity on various concentrations nanoparticles is reflected in Fig. 2. The results indicate that using magnetic field can improve the rate of mass transfer up to 223%.

Conclusion:

This investigation is focused on the behavior of magnetic field intensity on magnetic nanofluid single drops in the liquid-liquid extraction process. The mass-transfer enhancement was





achieved with increasing magnetic field intensity. At higher concentrations, effect of magnetic field is more sensible. A maximum 223% enhancement can be achieved with this technique.

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The kinetic Study of polyaniline-alumina nanocomposite to sorption textile azo dye from aqueous media

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Key words: sorption, polyaniline-alumina, textile dye, kinetic.

Introduction:

Conducting polymers have attracted significant attention in the past two decades because of their potential applications in various fields such as microelectronics, composite materials, optics and biosensors [1] and as adsorbent [2,3]. Polyaniline (PANI) has been known as one of the most technologically important conducting polymers because of its easy preparation high electrical conductivity, environmental stability, easy producibility, and relatively low cost [4]. In this study, synthesis of polyaniline-alumina nanocomposite by situ chemical polymerization method using APS (ammonium peroxydisulfate) as an oxidant and its capacity for the removal of textile dye (azo dye) from aqueous solutions, was investigated.

Materials and Methods:

The precursor solutions for γ -Al₂O₃ nano particle were synthesized by sol–gel method using Al(OC₃H₇)₃, NH₄OH and CH₃OH (95%). The PAn/Al₂O₃ nanocomposite were synthesized by chemical polymerization in the presence of Al₂O₃ nanoparticles and H₂SO₄ as the dopant. A typical preparation process for PAn/Al₂O₃ composites was as follows: 0.2 g surfactant and 0.2 g of Al₂O₃ nanoparticles was stirred in 50 ml of distilled water for 15 min. Then 50 ml of H₂SO₄ 2.0 M and 2 g of APS added to solution. Finally 2.0 ml aniline monomer was injected to stirred aqueous solution. After 4 h nanocomposite was filtered. Product was washed several





times with acetone. Then the composites were dried at 80°C for 24 h under vacuum, until the total mass became constant. The adsorption experiments in this study were done for studying the effect of experimental conditions on dye removal. Kinetic evaluation were also conducted in this study.

Results and discussion:

The morphology and structures of product were analyzed by FE-SEM. Fig. 1 show the FE-SEM micrograph of nanocomposite prepared by chemical polymerization method. The average diameter was 15-35 nm. The effect of the dye solution's initial pH on sorption of azo dye was studied at pH values ranging from 2 to 12, under constant reaction time. For kinetic study effect of time was investigated and the results indicated that dye adsorption equilibrium time occurred in the 20 min.



Fig 1. FE-SEM micrograph of nanocomposite

Conclusion:

Polyaniline-alumina nanocomposite was prepared successfully in aqueous media by the chemical polymerization and the sorption of the azo dye on the producted adsorbent was studied in the aqueous media. Optimum condition for dye sorption occurred at pH 3 and time 20 min. The kinetics studies of azo dye on nanocomposite were based Pseudo-second-order and Morris-Weber equations. The data indicate that the adsorption kinetic of azo dye on





nanocomposite followed the Pseudo-second-order equation. The nanocomposite showed considerable potential for the removal of azo dye from aqueous media.

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sorption of Reactive Red 198 from aqueous solutions by Al₂O₃ nanoparticles; A kinetic study.

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Key words: sorption, Al₂O₃ nanoparticle, R-R198, kinetic.

Introduction:

Dye is the most significant identified contaminant amongst the various pollutants of wastewaters. Many industries, such as textile, tanning, printing, food, cosmetics, etc. use organic compounds as dyes to color their final products. Reactive azo dyes are the most commonly applied among more than 10000 dyes applied in textile processing industrie. The major environmental problem associated with the use of reactive dyes is their loss in the dyeing process since the fixation efficiency ranges from 60 to 90% [1]. There are several methods to synthesize nanoparticles such as condensation from the gas stage, by synthesis in vacuum, highly energetic reactive milling and by precipitation from solution (hydrothermal synthesis, sol-gel, reactions in aerosol-reactive spraying, electrochemical synthesis, sublimated drying) [2, 3]. In this work, preparation of γ -Al₂O₃ nanoparticles by Sol-gel method and its capacity for the removal of reactive red 198 dye from aqueous solutions, was investigated.

Materials and Methods:

The precursor solutions for γ -Al₂O₃ nano particle were synthesized by sol-gel method using Al(OC₃H₇)₃, NH₄OH and CH₃OH (95%). At first, NH₄OH was dissolved respectively in CH₃OH (95%) and stirred for 15 min. The aluminium isopropoxide solution was then added





dropwise (slowly for 45 min) to the vigorously stirred NH₄OH solution. The solution was then stirred using a magnetic stirrer at 60°C for 3 h to produce a transparent, gelatinous Al(OH)₃ precipitate. After 6 h, the obtained gel was filtrated, washed with acetone and dried at 60°C for 18 h. The dried gel was then calcined in a furnace at 500°C for 2 h and Al(OH)₃ was transformed into Al₂O₃ powder. The adsorption experiments in this work were done for studying the effect of experimental conditions on dye removal. Kinetic evaluation were also conducted in this study.

Results and discussion:

The morphology and structures of product were analyzed by FE-SEM. Fig. 1 show the FE-SEM micrograph of Al_2O_3 prepared by sol-gel method. The average diameter of particles was 35 nm.

To find a suitable pH for the effective adsorption of R-R198 dye by nanoparticle, experiments were performed over a pH range of 2–12. The maximum adsorption efficiency was 99.44 at pH 3 and the adsorption of dye decreased with further increase in pH. For kinetic study effect of time was investigated and the results indicated that dye equilibrium time occurred in the 40 min.



Fig 1. FE-SEM micrograph of nanoparticle

Conclusion:

Al₂O₃ nanoparticles was producted by sol-gel method and the sorption of the reactive dye R-R198 on the producted adsorbent was studied in the aqueous media. Optimum condition for





dye sorption occurred at pH 3 and time 40 min. The kinetics studies of R-R198 on alumina nanoparticles were based Pseudo-second-order and Lagergren equations. The data indicate that the adsorption kinetic of R-R198 on Al₂O₃ nanoparticles followed the Pseudo-second-order equation and. These studies showed that alumina nanoparticles is a good adsorbent for dye removal.

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Removal of reactive orange 12 by copper sulfide nano particle loaded on activated carbon: kinetic and isotherm study of removal process

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Key words: Reactive orange 12, Copper sulfide, Kinetic, Isotherm.

Introduction:

Use of dyes by many industries, such as textile, paper and plastics to color their products is a common activity. Since these industries also use substantial amount of water in their processes, this results in highly colored effluent of these industries which is generally colored due to the presence of these organic chemicals. Color in water is not only the first detectable contaminant in water; it also blocks sunlight which is essential for many photo-initiated chemical reactions which are necessary for aquatic life. Due to unique properties of nanoparticles in term of high ordered structure, high mechanical and thermal strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area recently focused on the application of this type of material especially metal-based nanoparticle. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and the improved performances make their potential application in many areas. The objective of the present work is synthesis, characterization of copper sulfide nano particle loaded on activated carbon (CUS-NP-AC) as new adsorbents and its efficient applications for removal of reactive orange 12(RO-12) following the optimization of variables the kinetic, thermodynamic and isotherm studied of adsorption process has been investigated, and respective values were calculated [1-3].

Materials and methods:





All chemicals including NaOH, HCl , KCl, RO-12 and activated carbon (AC) with the highest purity available are purchased from Merck. Stock RO-12 solution was prepared by dissolving its accurately weighted amount in double distilled water and the test solutions were prepared by diluting stock solution. The removal percentage of RO-12 was calculated using the following relationship: % RO-12 removal = $((C_0 - C_t)/C_0) \times 100$

Where C_0 (mg.L⁻¹) and C_t (mg.L⁻¹) is the dye concentration at initial and after time t respectively.

Apparatus:

During this study following pH optimization in all experiments, the RO-12 concentration was determined at 393 nm against a reagent blank. The pH measurements were done using pH/Ion meter model-686 (Metrohm) and absorption studies were carried out using Jusco UV-Visible spectrophotometer model 160-shimadzo.

Result and discussion:

in this work dye elimination on series of similar solution whit 50 ml volume in concentration of 20 mg.l⁻¹ in the various pH from 1 to 6 was investigated and showed that in pH=2, there is maximum percent of dye elimination.synthetic studies to determinate dye absorption effciency in optimum values namely solution with concentration of 20 mg.l⁻¹ in pH=2 in the 10 time with 0.015 gr absorbent with elovich synthetic models and inter particle diffusion was investigated and observed that dye absorption follows two-order synthetic. investigation of adsorption isotherms carried out in afew different concentration in 20 min with optimal condition of another parameters, and showed that dye absorption follow by langmuir isotherm.

Conclusion:

The copper sulfide nanoparticles loaded on active carbon have been synthesized and characterized with SEM, and then these new adsorbents have been applied for removal of RO-12. It was observed that batch sorption using CUS-NP-AC were dependent on parameters such as initial concentration of dye, time, pH, dose of adsorbent. Analysis of experimental data for





the Langmuir, Freundlich and Temkin isotherms were determined and the equilibrium data were best described by the Langmuir model. The kinetics process is can be successfully fitted to pseudo-second-order kinetic model respectively.

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The Evaluation of Research tools inventions patentability in nanobiotechnology

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Abstract:

Nanobiotechnology has become one of the key technologies of the 21st century. The rapid evolution of nanobiotechnological research has raised expectations of finding ever better treatment to an increased number of illnesses. Due to the complexity of nanobiotechnological research, researchers—scientists working in academia and in commercial enterprises alike—need access to numerous resources for their projects. In the domain of nanobiotechnology, a single basic patent often enables the patentee to exclusively manufacture more than one product or use more than one method. Access to research tools is a prerequisite to continuing scientific advancement in nanobiotechnology.

There is an ongoing debate about the ways in which patents impact on nanobiotechnology. Patents can have severe detrimental effects on innovation and indirectly on public health. DNA patents as a form of research tool patents are of particular concern. In particular, most patents for research tools are applicable to various purposes and are helpful in promoting research. However, at the same time, they are often less substitutable. If research tool patents are not easily available for research, the R&D process becomes stalled.

That is because of two main reasons. First, if individual patents are licensed on a restrictive basis, access to fundamental technology could be blocked and hence, hinder downstream research and development. Genes are discovered to be fundamental to life. Thus





genes have become the basis for exploring diseases and therefore, to develop new pharmaceuticals. Consequently patents on genes started to endanger innovation and impede research. Secondly, if it is required to negotiate licenses over multiple patents, the pace of innovation could be delayed and creating what is known as an anticommons.

Therefore, facilitating the use of research tool patents is an important challenge in the promotion of R&D activities in the life sciences and the creation of innovation from achievements in such activities especially in nanobiotechnology. Responding to these concerns, proposals have been made to facilitate access to the necessary inputs.

Universities, etc. and private businesses are expected to endeavor to establish practical operations in line with the recommendations and avoid disputes involving research tool patents, thereby facilitating the mutual use of research tool patents in research.

Key Words: Nanobiotechnology, Nanomedicine, Intellectual Property Rights, Research Tools, Patent, EPC, TRIPS Agreement.





Intellectual Property of Nanotechnology in Related International Documents

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Abstract:

With the emergence of any new technology, nanotechnology creates opportunities as well as challenges in adapting the patent regime to its particular context. There is some consensus that patenting nanotechnology innovations poses more problems than other technologies, owing to their multi-disciplinary character, cross-sectoral applications, broad claims as well as difficulties in fulfilling the patentability criteria. This is aggravated by the lack of a standardized terminology which impedes easy identification of nano-patents and also the fact that patent offices may not be well-equipped to handle nanotechnology. These problems are likely to be compounded for developing and least developed countries, which irrespective of their state of technological advancement, and capacity of the domestic regime, are obliged to confer IPR in the new technology.

In order to keep a desired level of in depth analysis this work will only contemplate the TRIPS Agreement. The paper finally arrives at certain recommendations, to help reconcile the need to incentivize innovation in the new technology, with the imperative of ensuring that the public interest is served and access to the patented knowledge is not hindered.

Keywords: Nanotechnology, Intellectual Property Law, TRIPS Agreement, patentability criteria, Challenges of patentability.





Selective adsorption of ascorbic acid on molecularly imprinted nanocomposits of mesoporous silica SBA-15/ polypyrrole

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Keywords: Molecular imprinting, nanoreactor, SBA-15, Polypyrrole, Ascorbic acid

Introduction:

Molecular imprinting is an attractive technique for preparing mimics of natural and biological receptors. Nevertheless, molecular imprinting for aqueous systems remains as a physicochemical challenge due to the hydrogen bonding between templates and functional monomers destroyed in the bulk water. The hydrogen bonding between templates and monomers are the most crucial factor governing recognition, particularly in non-covalent molecularly imprinted polymers (MIPs). Traditional MIPs have encountered many limitations including incomplete removal of the template, small binding capacity, slow mass transfer, and irregularity in the shape of materials (1). To overcome these problems, many attempts have been made to prepare the imprinted materials in the optimizing forms that control situation of templates at the surface or in the proximity of material surfaces (2). Using of mesoporous materials for molecular imprinting is an effective approach to overcome physicochemical barrier and to remove the limitations of the traditional molecularly imprinted polymers.

Materials and methods:

Three major steps can be imagined in the imprinting synthesis. First, monomer and template molecules diffused into the channels of SBA-15 because of the concentration gradient. Second, polymerization occurred and template molecules trapped into the PPy matrix and third, the template molecules were removed. The resulting nanocomposites were characterized





by fourier transform infrared (FT-IR) analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. All chromatographic measurements were performed using an Agilent 1100 high performance liquid chromatography with a UV/Vis and fluorescence detectors. To characterize the adsorption behaviors of the MIP and non-imprinted polymer (NIP), rebinding equilibrium and kinetic studies were accomplished. Batch rebinding tests were performed at different initial concentrations of ascorbic acid (AA) ranging from 0.05 to 0.8 mg mL⁻¹. The binding selectivity of the prepared MIP for its template and other structural analogues, including: dopamin (DA), paracetamol (PA) and epinephrine (EP) was determined. The equilibrium binding analysis was examined using both a non-competitive and competitive binding assay.

Result and discussion:

FT-IR results show that AA molecules could be adsorbed on the surface of SBA-15 in the first step of imprinting synthesis. SBA-15 is typically protecting interaction of template and monomer during formation of MIP against the solvent. TEM images shows that the pyrrole was polymerized not only inside the pores, but also along the outer surface of the SBA-15. Uniform spherical nanoparticles and similar morphologies can be seen for MIP and NIP SEM images. Fitting of the data on the Langmuir equation yielded a good fit for the MIP and NIP with the regression coefficient higher than 0.97. The estimated saturation capacity (q_m) and dissociate constant (K_d) were 83.3 mg g⁻¹ and 0.003 mg mL⁻¹ for the MIP, and 18.8 mg g⁻¹ and 0.016 mg mL⁻¹ for the NIP, respectively. It was shown that despite a display of significant molecular selectivity in the rebinding test, MIP had surprisingly slower kinetics (100 min) compared to the NIP (30 min). The imprinting factor (IF) for AA, DA, PA and EP in non-compatitive adsorption experiments were 3.2, 1.5, 1.4 and 1.3, respectively. It demonstrated that MIP is more selective for DA than PA due to the more structural similarity of DA to the AA than PA.





Conclusions:

In summary, a novel method for the preparation of SBA-15/PPy-based MIP for recognition of AA was developed. Using SBA-15, as a nanoreactor, for molecular imprinting is an effective approach to overcome the problem of imprinting in the aqueous systems which remained as a challenge.

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Synthesis of Fe₂O₃/polyaniline conducting nanocomposites

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Key words: Polyaniline, Nanocomposites, Fe₂O₃, Nano tech.

Introduction:

Polymer and metal oxides have been studied for many years for their independent electrical, optical, and mechanical properties. Recently, the combination of conducting and mechanical properties of conjugated polymers with the properties of metals or conducting inorganic particles has brought new prospects for applications [1, 2]. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis [3,4]. In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler, these materials are better described by the term nanofilled polymer composites. This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix [5].

Materials and methods:

Fe2O3 nanopartcles(Aldrich) – HCL - Aniline (merk).

Apparatus:

ultrasonic device - asetaier device - oven(shimazco.s made by Iran) - filter paper - Ice bath

Result and discussion:





In this investigation, we report a novel chemical synthesis of Fe_2O_3 -polyaniline conducting nanocomposite. Fe_2O_3 nano comparticles were incorporated in the nanocomposites to improve the ferromagnetic properties. new polyaniline nanocomposites derivatives in order to reaction of chemical activity by using reaction of Fe2o3 nanocomposites and HCL(1 M) with Ammonium Sulfate (as starter) in the ice bath for 3-4 hours.then put it in oven at 80^oC for 3 hours then filtered,washed and dried in air.The FT-IR,XRD,SEM spectra confirm the structure of compounds. This research work describes an efficient method to synthesize and characterization of polyaniline/Fe₂O₃ nanocomposites by one-step in situ polymerization.

Conclusion:

The obtained result from XRD, FT-IR, TGA, and SEM data confirmed that Fe_2O_3 nanoparticl are encapsulated by Polyaniline .Electrical conductivity measurement indicate that the conductivity of nanocomposites at low Fe_2O_3 content is much higher than of neat Fe_2O_3 .

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Simple hydrothermal synthesis and characterization of high surface area niobia

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Kywords: Niobium pentoxide, Hydrothermal, Nanoparticle, Mesopore, Surface area

Introduction:

Niobium pentoxide, or niobia (Nb₂O₅), possesses outstanding chemical and physical properties which make this oxide promising for application in catalysis and photoelectrochemical , ferroelectric , electrochromic devices. Recently, niobia-based systems have received special attention due to their catalytic application in several important chemical processes, particularly when high acidity and a water-tolerant property is required. The properties of Nb₂O₅ strongly depend on its synthesis procedure and the conditions of thermal treatment. It is crucial to develop methods of preparing niobium oxide with a high specific surface area and the preparation of well-ordered niobia nanocrystals, with high surface area and acidic surface characteristics still represents a challenge.

In this study niobium pentoxide (Nb₂O₅) nanoparticles with high surface area and pore volume have been prepared by simple hydrothermal method using least material (NbCl₅+H₂O₂) and low temperature and compared with commercial sample.[1-3]

Materials and methods:

5 g niobium pentachloride (NbCl₅) was added to 20 ml of a 30 wt% $H_2O_2(10 \text{ mol/mol of Nb})$ aqueous solution while stirring. The yellow solution was obtained which transferred into autoclave, and heat treated at constant temperature 140 °C for 10hours. During the hydrothermal treatment, the yellow solution became colorless with the release of gas, followed





by the precipitation of a white particulate material so called niobic acid, with the general formula of Nb₂O₅•*n*H₂O. The precipitated powder was centrifuged and washed. The resulting product was dried at 60 °C, for 180 min and calcined under flowing air at 300,400,450°C temperatures for 3 hours. Crystal structures, particle shape and product morphology, surface area and pore size distribution were characterized by various methods (XRD, BET, TG/DTG, SEM).

Results and discussion:

Comparison of XRD patterns of commercial and synthesized Nb₂O₅ samples showed successful synthesis of Single-phase (hexagonal phase) niobium pentoxide. Product was relatively amorphous at low calcination temperature (300°C), but crystallization ocurred at high temperatures followed by increasing of crystal size. The crystallite size of the samples (calculated using Scherrer's equation) which were calcined at 400 °C and 450 °C were at range 13.4 to 15.4 nm. Crystal size and spongy tissue of product with small particles were confirmed by SEM images. N₂ adsorption–desorption isotherms of synthetic samples exhibited typical type IV isotherm curves which suggest mesoporous product with uniform pore distribution. According to pore size distribution curves (BJH) of synthetic niobium pentoxide, increase in calcination temperature followed by increase in mean pore diameter (5.5nm) . Also synthetic niobia had high surface area (240 m^2/g) and pore volume(0.21 cm^3/g) more than commercial sample which make it superior, as support or active phase for catalytic application.

Conclusion:

Niobium pentoxide (niobia) nanoparticles have been prepared by hydrothermal method at low temperature and compared with commercial sample. Synthetic Nb_2O_5 showed distinct properties such as high surface area and pore volume. Mesoporous product with high surface area(240 m²/g) and uniform pore distribution was obtained at lower calcination temperature . Increasing in calcination temperature followed by decreasing in surface area and creates pores with great diameter (5.5nm) but decanter spout (ink bottel) .





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Synthesis of immobilized molybdenum on carbon nanotubes supported and study of its catalytic activity in the oxidation of methylphenyl sulfide

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Keywords: Carbon Nanotubes, Support for catalytic system, Molybdenum, oxidation of MethylPhenyl Sulfide

Introduction:

Oxidation and reduction of sulfur-based compounds are two fundamental chemical reactions, and both reactions have been intensively studied in recent years due to the biological, economic and environmental benefits. Among the variety of metal complexes that have been used for the deoxygenation of sulfoxides and oxygenation of sulfides, oxomolybdenum complexes have attracted considerable attention, because molybdenum is found in a class of enzymes that catalyze oxygen atom transfer to or from a physiological substrates. Transition metal complexes are well known for their catalytic activities in the oxidation as well as reduction of organic substrates and for the synthesis of fine chemicals. Their immobilisations on solid supports provide certain additional characteristic properties such as selectivity, thermal stability, and easy separation from the reaction mixture and recycle ability. Supports for catalytic systems can be inorganic or organic. Inorganic matrices have potential advantages of offering excellent chemical, thermal and mechanical stability. Highly dispersed inorganic materials with controlled particle dimension and pore diameter and dimension are commercially available. Some of the commonly used supports are molecular sieves, zeolites, clays, metal oxides, carbon, etc. Carbon nanotubes (CNTs) because of their exceptional surface structures, high electrical conductivities, relatively large surface areas, and high





mechanical, chemical and electrochemical stabilities, have been utilized as novel supports for metal catalysts [1-4].

Methods:

Multi-walled carbon nanotubes (MWCNT) used in this study as support is functionalized with carboxyl acid (1.23%-COOH). First, the carboxylic acid groups were converted to acyl chloride in order to increase the reactivity of MWCNT-COOH. In the next step, the modified MWCNT, EN-MWCNT, was prepared by covalent attachment of Ethylene Di-Amine (EN) to MWCNTCOCl via an amide inkage. The [Mo(O)2(acac)2-EN-MWCNT] catalyst was synthesized by the reaction of EN-MWCNT with a solution of Mo(O)2(acac)2 and methanol (MeOH) as solvent.

Result and discussion:

The ability of this heterogeneous catalytic system in the oxidation of methylphenyl sulfide to methylphenyl sulfoxide has been investigated. The optimum conditions for this new heterogeneous catalyst with over 90% yield in oxidation of methylphenyl sulfide with hydroxenperoxide (H_2O_2) as oxidant and Ethanol (C_2H_5OH) as solvent was 20mg catalyst, 2ml C_2H_5OH at room temperature after 150min.

The prepared catalysts were characterized by elemental analysis, scanning electron microscopy (SEM), FT-IR and diffuse reflectance UV-Vis spectroscopic and TG-TDA methods. The nitrogen content of catalyst was 0/74% (0.49mmol/g). The metal loading of [Mo(O)2 (acac)2@amines-MWCNT], which was measured by ICP, was 3.33 mmol/g.

Conclusion:

We immobilized Dioxobis (acetylacetonate) Molybdenum Complexes on MWCNTs modified by $NH_2CH_2CH_2NH_2$ (EN) and found that this supported catalyst was active in the oxidation of methylphenyl sulfides with H_2O_2 . The robust catalyst could be reused several times without loss of their catalytic activities.

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Preparation Functionalized Carbon nanotubes supported Dioxobis (acetylacetonate) Molybdenum Complexes and its catalytic application for the epoxidation of alkenes

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Keywords: Carbon Nanotubes, Heterogeneous Catalyst, Molybdenum, Epoxidation of Alkenes

Introduction:

The epoxidation of alkenes constitutes one of the most useful reactions in organic synthesis as the epoxide formation is a crucial step in the oxyfunctionalization of many molecules. Epoxides are commercially important intermediates used in the synthesis of a wide variety of fine chemicals. Reusable heterogeneous catalysts have attracted a great attention in organic laboratories and industries. Different approaches have been used for immobiliza-tion of molybdenum complexes on various supports to obtain heterogeneous catalysts. Several practical advantages over their homogeneous counterparts. In these systems, not only advantages of homogeneous catalysts such as high catalytic activity and selectivity are retained but also some properties like easier work-up, recyclability and stability of heterogeneous systems will be obtained. Molybdenum is an essential metal that is capable of forming complexes with many compounds of biological importance such as carbohydra- tes, amino acids, flavins and porphyrins. Although, molybdenum is not only much less toxic than many other metals of industrial importance but it is also an essential constituent of certain enzymes that catalyze reduction of molecular nitrogen and nitrate in plants and oxidation (hydroxylation) of xanthine and other purines and aldehydes in animals. Carbon nanotubes (CNTs) have attracted much attention in the synthesis, characterization, and other applications





because of their unique structural, mechanical, thermal, optical and elec-tronical properties. Since CNTs are insoluble in the most solvents, these materials can be used as catalysts support [1-4].

Methods:

Multi-walled carbon nanotubes (MWCNT) used in this study as support is functionalized with carboxyl acid (1.23%-COOH). First, the carboxylic acid groups were converted to acyl chloride in order to increase the reactivity of MWCNT-COOH. In the next step, the modified MWCNT, EN-MWCNT, was prepared by covalent attachment of Ethylene Di-Amine (EN) to MWCNT-COCl via an amide inkage. The $[Mo(O)_2(acac)_2$ -EN-MWCNT] catalyst was synthesized by the reaction of EN-MWCNT with a solution of $Mo(O)_2(acac)_2$ and methanol (MeOH) as solvent.

Result and discussion:

The ability of this heterogeneous catalytic system in the epoxida-tion of alkenes has been investigated. The optimum conditions for this new heterogeneous catalyst with over 98% yield in epoxidation of alkenes with tert-butyl hydroperoxide (tert-BuOOH) as oxidant and CCl₄ as solvent was 20mg catalyst, 3ml CCl₄ at 80C after 150min. The prepared catalysts were characterized by elemental analysis, scanning electron microscopy (SEM), FT-IR and diffuse reflectance UV-Vis spectroscopic and TG-TDA methods. The nitrogen content of catalyst was 0/74% (0.49mmol/g). The metal loading of [Mo(O)₂ (acac)₂@amines-MWCNT], which was measured by ICP, was 3.33 mmol/g.

Conclusion:

We immobilized Dioxobis (acetylacetonate) Molybdenum Complexes on MWCNTs modified by Ethylene Di-Amine and found that this supported catalyst was active in the epoxidation of alkenes with tert-BuOOH. This supported catalyst is highly reactive in the epoxidation of a wide range of alkenes such as linear and cyclic ones are. The robust catalyst could be reused several times without loss of their catalytic activities.





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Quantitative investigation of structural parameters contributions on anthraquinones solubility in SC-CO2 by QSAR coupled to ANFIS

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Abstract:

In 21st century, significant research is being done on finding new methods of particle synthesis or their application at nano scale. Many methods have been employed for synthesis of nanomaterials. In recent years supercritical fluids (SCFs) are finding wide application in nano materials systemization. Thus, many theoretical development, experimental and application studies have been done[1&2].

Quantitative structure–activity/property relationship (QSAR/QSPR) methods are common and rather successful techniques in chemistry. However, in cases of complex relationships, conventional QSAR/QSPR methods often lead to insufficient or misleading information because of nonlinear relationships within the data set [3].

We have applied structural parameters in uniqueness and binary combinations to calculate anthraquinones solubility in supercritical carbon dioxide. These structural parameters are computed by density functional theory: B3LYP / 6-31G. The selected calculation method is available, fast and reliable, so one can calculate aforementioned compounds solubility with high accuracy [4]. Applying improvements in SC-CO2-based synthesis of nanomaterials, best results are achieved. This paper proposes a new method, Adaptive Neuro-Fuzzy Inference System (ANFIS) to evaluate structural parameters of certain organic compounds for their appropriate solubility in terms of QSAR models with the aid of artificial neural network





(ANN) approach combined with the principle of fuzzy logic [5]. The ANFIS was utilized to predict solubility which accounts for non-linearities. A data set of 21 compounds was used [6]. The resulted 2 equations estimate solubility with acceptable error.

Keywords: QSAR, ANFIS, Fuzzy logic, Structural parameters, Nanomaterials synthesis.

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Application of modified nano-alumina as a solid phase extraction sorbent for the preconcentration and simultaneous separation of Cu, Cd and Zn in water to flame atomic absorption spectrometry determination

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Keywords: Solid phase extraction, Nano alumina, Preconcentration

Introduction:

nanometer-sized alumina has high surface area, high sorption capacity and high chemical activity, it could be successfully applied for the separation and preconcentration of trace metal ions in environmental samples. Chemical activation of the nanometer-sized alumina with functional groups containing N, S, and O atoms i s highly efficient for the sorption of several metal ions. Metal chelates could provide higher selectivity and high enrichment factors for such a preconcentration and separation. Recent studies on the use of surfactant-coated mineral oxide columns for SPE have demonstrated these new sorbent materials to be a promising tool for the extraction/preconcentration of organic compounds in a wide polarity range [1-3]. For these purposes, we have developed nano-sized alumina coated with SDS and new organic ligand (a), as a new and effective sorbent for the preconcentration and determination of Cd, Cu and Zn by FAAS in real samples with satisfactory results.







Methods:

The determination of Cu, Zn and Cd was carried out using the Spectra AA from Varian 220, equipped with an air-acetylene burner. Measurements were carried out in the peak area mode at 324.8 , 213.9 and 217.0 nm, using a spectral bandwidth of 0.7 for Cd, Cu and Zn, respectively.

Preparation of modified nano-alumina: Add 35 ml water in to 50 mg of SDS and The pH of solution was adjusted to 2-2.5 with 3 mol L⁻¹ HCl solutions, and then the flask was shaked mechanically for 15 min. Then 1g nano alumina add to flask and The pH of solution was adjusted to 7 with ammonia and add to flask 45mg of organic ligand and stired for 0.5 h.

Producer: A known volume of sample solution containing Cu(II), Zn(II) and Cd(II) in the range of 0.5–200 gL⁻¹ were prepared and the pH value was adjusted to 9 with 0.1 mol L⁻¹ HCl and ammonia. The solution was passed through the microcolumn packed with modified nano- -alumina sorbent at a flow rate of 3 mL min⁻¹ controlled by a peristaltic pump. Afterwards, the metal ions retained on the sorbent, were eluted using 5 mL o f 4 mol L⁻¹ HNO3 at a flow rate of 4 mLmin⁻¹. The analytes in the effluent were determined by FAAS. The nano-alumina could be modified repeatedly by SDS and organic ligand after each desorption step by acid.

Results and discussion:

The sorption of SDS on nano-sized alumina is highly dependent on the pH of solution. Max sorption of SDS on nano-alumina was achieved at pH 1–2.9 by shaking the solution containing SDS and nano-alumina for 15 min. The sorption behavior of Cu, Cd and Zn on the modified nano-alumina in water samples was studied in the pH range of 2.0–11.0. The pH of the solution was adjusted at the required value by the addition of ammonia and HCl. a quantitative recovery (>95%) was found for Cu, Cd and Zn at the pH range of 9 In order to preconcentrate ions simultaneously.

Choice of eluent: nitric acid could accomplish the quantitative elution of Cu, Cd and Zn from the modified nano-alumina. Thus, we selected 5.0 mL of 4.0 mol L^{-1} .





Conclusion:

A new sorbent of modified nano- alumina has been reported. It was found that the nanometer-sized alumina modified with SDSPAN in this study, is stable and has efficient analytical performance in preconcentrationCu, Cd and Zn samples. Samples. The simple, rapid and simultaneous determination of elements with high sensitivity and reproducibility are the advantages of modified nano-sized alumina. This methodology gives good accuracy, low limits of detection, excellent precision and relatively high kinetic sorption on the target analytes, which show its potentiality in trace analysis in various samples with complicated matrix.

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Synthesis of molecularly imprinted nanocomposits mesoporous silica SBA-15/polyaniline for 2,4-dinitrophenol

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In this work, we first proposed a simple surface molecular imprinting method to prepare molecularly imprinted polymers (MIPs) on the surface of mesoporous silica SBA-15 in water ,in which SBA-15nanoparticles were used as the support and also as nanoreactors for the fabrication of imprinting polymer nanostructures. Surface imprinting and adopting a nanosized physical form are two effective approaches to overcome the template transfer difficulty within molecularly imprinted polymers. We synthesized molecular imprinted SBA-15/polyaniline nanocomposites selective for 2,4-dinitrophenol based on positively charged anilinium ions on negatively charged SBA-15. The prepared nanocomposites were characterized by Fourier transform infrared (FT-IR), Transmission electron microscopy (TEM) and scanning electron microscopy (SEM).Characterizing this material by FT-IR and comparison between it and non-imprinted SBA-15/PANI approved the fabrication of template. A competitive adsorption of 2,4-DNP and other structurally similar compounds including: phenol, 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) was carried out in a mixture solution and distribution coefficient, $K_{d(2,4-DNP)}$, for imprinted and non-imprinted polymers were 301 and 101 mL g⁻¹.

Chemicals and apparatus:

Mesoporous silica SBA-15 was prepared following the procedure reported by Zhao et al.¹Aniline was provided by Merck (Darmstadt, Germany) and distilled under reduced pressure before use. Ammonium peroxydisulfate (APS) and 2,4-DNP were bought from Merck (Darmstadt, Germany). All chromatographic measurements were performed using an Agilent





1100 High performance liquid chromatography (Santa Clara, CA, USA) with a UV/Vis detector. A C18 column (250 mm \times 4.6 mm i.d., 5 µm) from Agilent was used as the analytical column.

Preparation of 2,4-DNP-MIP/SBA-15:

SBA-15 was synthesized as described by Zhao et al.¹ To prepare the 2,4-DNP-MIP based on mesoporous silica SBA-15 nanocomposites, 0.2 g of the SBA-15 were dispersed in 30 mL Milli-Q water uniformly. 0.3 mL of aniline (distilled under vacuum) and 110 mg of 2,4-DNP were added to the dispersion solution, which were then continuously stirred at room temperature for 2 h. After that, the pH of the dispersion was adjusted to 3 with an aqueous HCl solution (36 wt%), and then the mixture was stirred for 4 h. Ammonium persulfate (APS) of 0.38 g was dissolved in 1 mL Milli-Q water which was then added to the solution. The polymerization was carried out at room temperature for 20 h under stirring. Then, the MIP prepared were isolated by centrifugation, washed with Milli-Q water several times and dried in vacuum at 40 °C for 24 h. By comparison, the non-imprinted polymer (NIP) was also prepared as a blank in parallel but without the addition of 2,4-DNP.² MIP particles were washed with the mixture solution of methanol/acetic acid (90:10, v/v) using soxhlet extraction to remove the template molecules. Then, polymers were washed with methanol to remove acetic acid and dried at 60°C.

Result and discussion:

The binding assays were carried out in aqueous solution. 10.0 mg washed and dried MIPs were added into 5mL 2,4-DNP at different concentrations. Then the suspensions were mechanically shaken for 2 h at room temperature to ensure equilibration. After centrifugation at 3500 rpm, the concentration of free 2,4-DNP in the supernatant was detected with HPLC. The amount of 2,4-DNP bound to the polymer was calculated by subtracting the concentration of free 2,4-DNP from the initial concentration. The maximum amount Q_{max} was estimated to be 55 ± 0.8 mg g⁻¹ and 19.3±1.2 mg g⁻¹ for MIP and NIP, respectively. The static adsorption capacity of the 2,4-DNP imprinted polymers was about two times of non-imprinted polymers.





The results showed that the 2,4-DNP imprinted polymers had a higher adsorption capacity for 2,4-DNP.

Conclusions:

Based on the negatively charged SBA-15 internal hexagonal pores surface and positively charged anilinium ions in a pH 3 solution, a facile and effective method has been developed to fabricate SBA-15/MIP nanocomposites via chemical polymerization. In the proposed method, SBA-15 was not just as a support but also was as a cage. Monomer (Aniline) and template (2,4-DNP) diffuse into the channel of SBA-15 and trapped, then the polymerization accrued on the surface and into the channels of SBA-15.

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Interactions of Doxorobocin Anticancer Agent with Different Sites of Graphene by Using Quantum Chemical Methods

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Keyword: Graphite, Doxorobocin, Adsorption, Density Functional Theory

Introduction:

There is growing interest in two-dimensional (2D) materials for vast variety of applications. In this respect, graphene is a source of exciting new physics. Graphene is a single layer of graphite, and has been extensively studied during the past decade because of its astonishing properties, which are mostly attributed to quantum phenomena from two-dimensional confinement effects [1]. In a perfect graphene, each carbon atom forms σ -bonds with its three nearest neighbors (sp² hybridization). Since 2008, increasing numbers of reports have explored the potential of graphene for different biomedical applications [2,3]. Sharing a similar chemical structure with CNTs, graphene can also be used as a drug delivery carrier. Similar to the drug loading on CNTs, the graphene surface with delocalized π electrons can be utilized for effective loading of aromatic anticancer drugs such as doxorubicin.

In the present study we investigate the changes in electronic structure of graphene when loaded with doxorubicin anticancer drug by the density functional theory calculations.

Methods:

Density functional theory (DFT) calculations by Gaussian09 were performed in order to optimize both doxorubicin and one-layer graphene plate for structures and energies using the hybrid B3LYP functional with 6-31 g basis set without any symmetry restrictions in the singlet ground state. Calculated vibrational frequencies without imaginary frequencies ensure





the stable structures. Boys-Bernardi's counterpoise procedure (CP) to correct for the basis set superposition error (BSSE) was indicated that the so-called overcorrection of the BSSE by the counterpoise method is not large.

Results and Discusions:

Binding energies were calculated via the difference in energy of graphene/doxorubicin complexes from those of isolated fragments at different positions (see Figure 1), where all fragments were fully optimised at the B3LYP/6-31G level. In the most stable structure the graphene sheet separate from doxorubicin on average by about 3 Å. The results show that doxorubicin interacts more strongly with middle atoms of graphene sheet particularly at 13, 14 and 15 positions. The HOMO-LUMO Gap (HLG) is shown for each sites in Figure 2. For a small graphite model plate, the band gap is located nearer to the zero energy, and thus in the stable form [1].



Figure 1: The optimized gas phase structure of graphene obtained at B3LYP/6-31G level of theory. Lables are different positions of drug with respect to sheet.



Figure 2: HLG for each site.

Conclusions:

From these and more detailed considerations, it can be concluded that Graphene nano sheet could be used as a carrier for doxorubicin anti-cancer agents. The interactions of doxorubicin





with middle atoms is stronger than the atoms in the edge of the sheet. Particularly, The band gap indicates that the relative stability of the system in 13.14 and 15 positions are higher.

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Density Functional Study of Doxorobocin Adsorption on Boron Nitride Nano Sheet

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Keyword: Boron nitride, Doxorobocin, Adsorption, Density Functional Theory

Introduction:

Recent developments in graphene research [1] have stimulated intense interest in the study of other two-dimensional materials such as boron nitride (BN). Boron nitride is important material from both fundamental point of view and applications. BN can form in numerous structures analogous to carbon. The main reason is because boron and nitrogen can have different hybridizations of chemical bonding, i.e., sp2 and sp3. Bulk BN can form in hexagonal-BN [2] and cubic-BN [3] structures, which can be considered analogous to graphite and diamond in the carbon system. Monolayer BN (1-BN) is formed by sp² bonds and is structurally similar to graphene, with the B-N bond only 1.7% larger than the C-C bond in graphene. The electronic properties of 1-BN, on the other hand, differ significantly from those of graphene. The purpose of present study is the investigation of changes in electronic structure of 1-BN when loaded with doxorubicin anticancer drug.

Methods:

Ab initio calculations were carried out, using the density functional theory (DFT) and the hybrid B3LYP functional with 6-31 G basis set without any symmetry restrictions in the singlet ground state, in order to optimize both doxorubicin and one-layer BN plate for structures and energies. Calculated vibrational frequencies without imaginary frequencies





ensure the stable structures. Boys-Bernardi's counterpoise procedure (CP) to correct for the basis set superposition error (BSSE) was used.

Results and Discusions:

Binding energies were calculated via the difference in energy of BN/doxorubicin complexes from those of isolated fragments (see Figure 1), where all fragments were fully optimised at the B3LYP/6-31G level. The most stable structure is the structure that the BN sheet separate from doxorubicin on average by about 3 Å. The results show that doxorubicin interacts more strongly with edge atoms of BN sheet particularly at 7,8,14, and 15 positions. The HOMO-LUMO Gaps (HLG) are shown for each sites in Figure 2 and could be used for the same conclusion.



Figure 2: HLG versus for each site.

Conclusions:

From these and more detailed considerations, it can be concluded that BN nano sheet could be used as a carrier for doxorubicin anti-cancer agents. The interactions of doxorubicin with edge atoms is stronger than the atoms in the middle of the sheet.





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Effect Improving nail and screw withdrawal strengths of oriented strand board (OSB) made from underutilized low quality paulownia (*paulownia fortunie*) wood employing nano-SiO₂

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Key words: Nail and screw withdrawal strengths, Oriented strand board (OSB), Nano-SiO₂.

Introduction:

The social and economical developments of human beings are depending on better utilization of available resources [1]. Forests, the major sources of wood supply are declining at the alarming rate of 13.0 million ha each year in developing countries [2].

Fillers have modifying effects on urea formaldehyde resin not only by decreasing resin viscosity and controlling its penetration into the wood tissue and improving bonding but also economically [3]. Nano-size particles give superior properties compared to micro-size particles [4]. Substantial improvement of physical and mechanical properties as a in situ reinforcement with silicates has been reported for various thermosets and thermoplastics at low concentrations [4].

The initial objective of this study was to investigate the suitability of paulowina wood for OSB manufacturing. In addition, the influence of nano-Sio2 on screw and nail withdrawal strengths of resulting panels.

Materials and methods:

Strands for OSB panels were manufactured from paulownia (Paulownia fortunei) logs. The resin was UF which had been produced by a local plant. Ammonium chloride (NH4Cl) was



added as a hardener. The commercial Na+ montmorillonite (NaMMT) nanoclay used with a cation exchange capacity (CEC) value of 92.6 mequiv/100 g was purchased from Southern Clay Products Co., USA. It was added to the resin at four levels of 0, 1, 3 and 5%. Experimental design is given in Table 1.

Board type	Press time (min)	Strand (wt*. %)	UF (%)	Nanosilica (%)
A_1B_1	7	90	10	0
$A_1B_2 \\$	7	90	10	1
$A_1B_3 \\$	7	90	10	3
$A_1B_4 \\$	7	90	10	5
A_2B_1	10	90	10	0
A_2B_2	10	90	10	1
A_2B_3	10	90	10	3
A_2B_4	10	90	10	5

 Table 1. The experimental design



Apparatus:

A circular saw; A laboratory scale hydraulic hot press (OTT, Germany); A laboratory stirrer; A spray machine; A Bruker X-ray diffractometer (D8 Advanced, Germany); A Philips (Model EM 208, Netherland) transmission electron microscope (TEM)

Result and discussion:

The highest screw and nail withdrawal strength values of 132 and 14 N/mm was obtained for the OSBs made with UF resin containing 3% nano-Sio2 pressed for 10 min (Fig. 1). Nano-Sio2 by decreasing the UF resins viscosity could prevent too much of adhesive from filtering into the wood to create the phenomena of permeation or inadequate bonding [5]. The improvement of mechanical and physical properties up to 3 wt% nano-sio2 content may be attributed to the high aspect ratio of stiff silicate layers in the polymeric matrix that result in a higher extent of interaction with the polymer chains [6] and good interfacial adhesion between





the nanoparticles and the UF matrix, so that the mobility of polymer chains is restricted under loading [4]. Nevertheless, with further increase in nano-sio2 loading from 3 to 5 wt%, a decrease in the mechanical and physical properties of composites was observed. One possible reason for this kind of behavior may be attributed to the agglomeration of the nanofillers or the filler-filler interaction, resulting in induced local stress concentration in the composites [7]. The intermolecular interactions between UF and silica are H-bonding [4].

Conclusion:

In this study, the potential of underutilized low quality paulownia wood as a bio-resource in OSB manufacturing was studied. Based on initial findings of this study, it can be concluded that underutilized paulownia wood could be used in manufacturing OSB. The addition of small percentage (3%) of nano-Sio2 into UF resins appeared to improve considerably the scre and nail withdrawal strengths of the resulting panels. The results of XRD and TEM approved the improvement of the properties by addition of small quantities of the nanoparticles.

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Effect of nanoclay on screw and nail withdrawal of strengths of oriented strand board (OSB) made from underutilized low quality paulownia (*Paulownia fortunei*) wood

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Key words: Screw and nail withdrawal strengths, Oriented strand board (OSB), Nanoclay.

Introduction:

Paulownia is an extremely fast-growing deciduous tree species with vegetative propagation and tolerance to different soil and climate conditions and is original of China and its natural distribution ranges from tropical through to cool temperate climates [1].

Oriented strand board (OSB) is a reconstituted flat pressed wood based panel composed of oriented wood strands bonded by hot-pressing by using thermosetting adhesive resins [2].

Using organo-modified montmorillonite (MMT) (commonly called "Nanoclay") to reinforce polymer-based composites have raised great attention to academic and industrial sectors since the addition of small amount of nanoclay could substantially enhance the mechanical properties of pristine polymers [3].

The initial objective of this study was to investigate the influence of nanoclay and press cycle time on the mechanical, physical and formaldehyde emission of the resulting panels and to determine if such fiber resource employing nanoclay could be used to produce OSB with acceptable properties.

Materials and methods:





Strands for OSB panels were manufactured from paulownia (Paulownia fortunei) logs. The resin was UF which had been produced by a local plant. Ammonium chloride (NH4Cl) was added as a hardener to UF resin at a level of 1% based on oven-dry weight of resin. The commercial Na+ montmorillonite (NaMMT) nanoclay used with a cation exchange capacity (CEC) value of 92.6 mequiv/100 g was purchased from Southern Clay Products Co., USA. It was added to the resin at four levels of 0%, 1%, 3% and 5% based on oven-dry weight of resin. Experimental design is given in Table 1.

Table 1. The experimental design							
Board	Press time	Strand	UF	Nanoclay			
type	(min)	(wt.%)	(%)	(%)			
A_1B_1	7	90	10	0			
$A_1B_2 \\$	7	90	10	1			
$A_1B_3 \\$	7	90	10	3			
$A_1B_4 \\$	7	90	10	5			
A_2B_1	10	90	10	0			
A_2B_2	10	90	10	1			
A_2B_3	10	90	10	3			
A_2B_4	10	90	10	5			





Apparatus:

A circular saw; A laboratory scale hydraulic hot press (OTT, Germany); A laboratory stirrer; A spray machine; A Bruker X-ray diffractometer (D8 Advanced, Germany); A Philips (Model EM 208, Netherland) transmission electron microscope (TEM)

Result and discussion:

Screw and nail withdrawal strength

According to the results, the screw and nail withdrawal strength was affected by nanoclay and press time at 99% and 95% confidence level respectively. In case of screw and nail withdrawal





strength, the highest screw and nail withdrawal strength values of 135 and 18 N/mm was obtained for the OSBs made with UF resin containing 5% nanoclay (Fig 1).

NaMMT exfoliates in UF resin and urea formaldehyde molecules could penetrate the galleries between clay layers.

In fact, the organoclay could improve the barrier performance of composites based on the simple "tortuous path" model [4]. NaMMT is exfoliated in UF resin and urea formaldehyde molecules could penetrate the galleries between clay layers and exfoliate the clay. Due to extremely high aspect ratio, specific surface area, small size effects for its insufficient surface atoms and high reactivity, nanoclay could easily cross with the active groups of pure resins and improve bonding strength of the modified resin [5].

Conclusion:

In this study, the potential of underutilized low quality paulownia wood as a bio-resource in OSB manufacturing was studied. Based on initial findings of this study, it can be concluded that underutilized paulownia wood could be used in manufacturing OSB. The addition of small percentage (5%) of nanoclay into UF resins appeared to improve considerably the screw and nail withdrawal strengths of the resulting panels. XRD characterization indicated that nanoclay completely exfoliated when mixed with UF and TEM images approved the results. Finding this type of new application area for underutilized paulownia wood can lead to decreasing the pressure on the forests and alleviating raw material shortage in wood industry in developing countries.

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Synthesis Nano sizeMetastable tetragonal Zirconium Oxide

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Key words: Zirconia, Precipitation, Milling, Crystallite size.

Introduction:

Zirconia is an important ceramic material and is used in medical and industry for a variety of applications. It is known that the main crystal phases of ZrO_2 are cubic (c), tetragonal (t) and monoclinic (m).

The monoclinic phase is thermodynamically stable up to 1100 °C, the tetragonal phase exists in the temperature range 1100–2370 °C and the cubic phase is found above 2370 °C [2].

Zirconia has some unique properties such as high ionic conductivity, fracture toughness, strength and low thermal conductivity. These attractive properties are due to the stabilization of tetragonal and cubic phases at room temperature.

Materials and methods:

In this investigation we synthesis nanoparticles of zirconia and stabilization tetragonal phase of zirconia at room temperature by three different methods such as precipitation method, wet milling method, dry milling method. In thismethods zirconia powder and yttria powder are as starting materials. yttria use as stabilizations agent.

In precipitation and wet milling methods starting material added to ethanoland this precipitation solventmixed Inprecipitationmethod by magnetic mixture but In wet milling methoditmixed by planetary mill with alumina balls for 5h. In both methodsprecipitation solventdriedwith microwave.





In dry milling methodstarting material milling whit planetary mill in Teflon jar with alumina balls. The ball to powder mass ratio of 10:1 and 20 h milling time was used in this study. The heat treatment in all the prepared powders was applied at air atmosphere with 4 h holding time at 420°c.

Apparatus:

The tools has been applied for this work contain aelectrical oven CARBOLITE, microwaveLG, absorbance spectra recorded by UV SHIMADZU(Model:1800), XRD patterns were recorded using a B8 advance (BRUKER)x-ray diffractometerand for milling a special design planetary mill made by Nano sharghabzaretoos Company.

Results and discussion:

The samples prepared characteristic with XRD and UV.The XRD and UV patterns showed that tetragonal phase of zirconia existed in all samples.The XRD patterns of the specimens showed that insample that prepared with dry milling; widthof picks is larger than other samples, and this showed the crystallite size in this sample is smaller than other samples. The crystallite size of the tetragonal phase in this samples, calculated by the Debye-Scherrer formula, does not exceed 30nm.



Conclusion:

Nano particles of zirconia can be synthesis by mechanochemical method and powder material can be use as starting material. with increase time of milling size of particles decrease.





This powders can be used for produce bioactive nanocomposite.

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pH Affect on the Structural and Morphological Properties of Barium Hexaferrite Nanoparticles Synthesized by Co-precipitation Method

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Key words: Barium Hexaferrite; Co-precipitation; Magnetic Nanoparticles; Permanent Magnets.

Introduction:

Hexagonal ferrites are a wide family of ferromagnetic oxides, with peculiar and useful properties. The crystal structure of the different known types of hexagonal ferrites (M, W, X, Y, Z and U) is very complex and can be considered as a superposition of R and S blocks along the hexagonal c axis, RSR*S* for M-type [1]. Barium hexaferrite (BaFe₁₂O₁₉) is a famous permanent magnetic material due to its high coercivity and fairly large crystal anisotropy [2]. Several chemical methods have been used to prepare barium ferrite, including co-precipitation [3], sol–gel technique [4], hydrothermal method [5] and etc. Among these methods, co-precipitation is one of the simplest techniques.

In the present work barium hexaferrite powder has been prepared by co-precipitation method using metallic nitrates of barium and iron as precursors and studied by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

Materials and methods:

Nano-sized powder of magnetic barium hexaferrite was prepared by co-precipitation method using barium nitrate $Ba(NO_3)_2$ (99%, Merck), ferric nitrate nonahydrated $Fe(NO_3).9H_2O$ (99%, Merck) and sodium hydroxide as starting materials. The ratio between Fe and Ba was kept at 10:1. The salt solution was added drop wise to the base solution until the pH reached to 8, 10 and 12 for each system, respectively. The red precipitates was washed and filtered





repeatedly with distilled water. This process took about 6 to 7 hours. The sample was then dried in an oven keeping temperature at 80°C for 3 hours. After attaining the powder by pestle, calcinations process was carried out at 1000°C for 2 hours to get the final product of barium hexaferrite.

Result and discussion:

The phase identification of the nanopowders was recorded by X-ray diffraction with $Cu-K\alpha$ radiation. The crystallite powders size was also measured by X-ray line broadening technique using the Scherrer formula indicated in Equation (1):

(Eq. 1)
$$D = (0.9)\lambda/\beta \cos\theta$$

where *D* is the grain diameter, β is half-intensity width of the relevant diffraction, λ is X-ray wavelength and θ the diffraction angle.

The effect of pH on the average size and percent crystallinity of nanoparticles is summarized in Table 1.

Sample	Ba:Fe	nН	Phases	Particles size	Percent Crystallinity
		pm		(nm)	(%)
C ₁	1:10	8	Fe ₂ O ₃ , BaFe ₁₂ O ₁₉	35.58	49.45
Ca	1.10	10	Fe ₂ O ₃ , BaFe ₂ O ₄ ,	39.25	57.83
02	1.10		BaFe ₁₂ O ₁₉	57.20	0,.00
C ₃	1:10	12	BaFe ₁₂ O ₁₉	44.28	58.80

Table 1. Crystallinity percent, particle size and phases of samples prepare in different pH

The results revealed that the number of phases, particle size and percent cristallinity of $BaFe_{12}O_{19}$ hexagonal structures are influenced by changing pH. XRD pattern shows that hexagonal structures at selected pH 8, 10, and 12 is the main structure. Number of phases decrease with the pH rising. The morphology of the obtained samples was investigated by using scanning electron microscopy (SEM). It is observed that $BaFe_{12}O_{19}$ nanoparticles were clearly shaped in hexagonal with increase pH.





Conclusion:

The structural and morphological properties of barium hexaferrite nanopowders prepared by the co-precipitation method were compared at three different pH. It is interesting to note that different phases were formed at different pH during the co-precipitation steps. The XRD patterns show a pure phase at the high pH. Also, the size of nanoparticles and percent crystallinity increased at pH of 12.

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Leaching of copper 0xide nano particles from recycling sources

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Abstract:

In this nickel metal hydride cells were used to recover copper content. According to XRD analysis, spent cells contain CuO (6.44%), NiO (47.5%), MgO(5.46%), k2O(0.30%). The recovery of copper from spent sources carried out by leaching. According to the preliminary results, leaching optimization includes hydrochloric acid (6M), the process lasts for two hours at 95°C. However, nano copper oxide from spent copper tubes underwent leaching by using HCl (6M) at 120°C for 2 hours. Neutralization of copper sulfate (0.5M) solution carried out by using Na2CO3 (0.5M),the insoluble solid product was heated at 750C for 2 hours to obtained nano copper oxide particles. SEM images and XRF analysis of the final nano particles of copper II oxide are in good agreement with the experimental results.

Key words: Copper II Oxide, Nano-particles, Recycling, Spent source, Copper tube

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Synthesis and Characterization of Sol-gel derived SiO2-CaO-P2O5-ZnO Bioglass

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Keywords: "bioglass", "sol-gel", "SBF"

Introduction:

Bioactive glass has been used extensively because of the good bioactivity, osteoconductivity and biodegradability [1]. It was found that the bioactivity of sol-gel derived bioactive glass is better than of the melt-derived materials [2]. A variety of sol-gel derived bioglass incorporating modifiers such as magnesium, cerium, boron, strontium and calcium have been reported [3]. Zn is an essential trace element which is playing an important role in body growth and development [3]. The effect of 5%mol ZnO on the chemical and physical characteristics of bioglass is the main subject of this report.

Experimental:

The sol-gel synthesis of the glass of composition SiO2-CaO-P2O5-ZnO was performed as follows: initially, tetraethoxysilane was added to 0.1 M nitric acid and the mixture was allowed to react for 60 min for the acid hydrolysis of TEOS. Then a series of reagents were added in the following sequence, allowing 45 min for each reagent to react completely: Triethylphosphite, calcium nitrate tetrahydrate, and zinc nitrate hexahydrate..The result solution was kept in a sealed container for 6 days at ambient temperature to allow gelation to occure. After 6 days, the gel was heated at 60°C for 3 days. Then, gel was heated at 120 °C for 2 days to remove all free water. After grinding and sieving, the dry powder was heated for 12





hr at 500°C for nitrate elimination and stabilization. The bioglass samples were characterized using XRD, EDXA, SEM, TEM, TGA and DTA.

Results and Discussion:

The results from the TGA, DTA and XRD allowed us to set the temperature of 500°C for calcination of sample. Also, the XRD pattern of prepared glass after heating at 500°C for 12hr indicated relatively amorphous nature of this material. Taking into account SEM and TEM Fig1), MAP and EDAX results, the bioglass powder contained Micro size SiO2 (region A in Fig1) and Nano size Calcium Zinc Phosphate and Calcium Zinc Silicate compounds (B region in Fig1). As shown in EDAX results area A had high content of Si and area B showed high amount of Zn, P, Ca, Si. The pH value (after soaking in SBF) has been found to be stabilized at 8.2. Eventually, due to formation of Zinc hydroxide in the SBF [3].

Fig1. SEM (a) TEM (b) images of bioglass powder



Conclusion:

The SiO2-CaO-P2O5-ZnO bioglass has been successfully synthesized by the sol-gel technique. The obtained results in this work suggested that incorporation of Zn into bioglass system is beneficial for stabilized of pH in SBF.





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Investigating the effect of nanosilica particles on mechanical properties of OCC fiber-HDPE Composite

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Keywords: Composite, OCC fiber, HDPE, Nanosilica, Mechanical properties

Introduction:

In recent yearscomposites reinforced with nanoparticles have caught the attention of many researchers and engineers. In nanocompositematerials, the particles are dispersed through the polymer matrix in the nanometer range at least in one dimension. In polymer composites, nanosilica is one of the widely used fillers. In recent years, there have been many publications dedicated exclusivelyto the effect of nanosilica on mechanical properties of thermoplastic composite, however there are not many reports related to the effect of nanosilica particles on practical properties of wood plastic composite [1-6]. In this study, the effect of nanosilica particles on practical properties of wood plastic composite made of high density polyethylene and OCC fiber were investigated. To achieve this aim, OCC fiber were mixed with high density polyethylene at 30% by weight, and nanosilica with 0, 1and 3% respectively, also 2% of MAPE was used as the coupling agent in allformulation. Then samples were made in injection molding and mechanical properties weretested according to ASTM standard. Results indicated flexural strength, tensile strength, flexural modulus, tensile modulus, elongation at break, and hardness increased with nanosilica loading, however impact strength was decreased by increasing of nanosilica particles.

Materials and methods:

High density polyethylene (HDPE) was supplied by Tabriz Petrochemical Company, Iran, with grade of HD-5218UA. It had a density of 0.952 gr/cm³ and a MFI of 18 gr/10 min at





190°C. OCC fibers were prepared from municipal waste stream in Karaj, Iran. Maleic anhydride grafted polyethylene (PE-g-MA) provided by Karangin Company, Iran, with trade name of KARABOND EHM anddensity of 0.935 gr/cm³ (MFI=1.1gr/10 min) was used as coupling agent. Fumed silica (Nanosilica) was supplied by Degussa AG (Hanau, Germany) under the trade name AEROSIL 12000. The average primary particle size was 12 nm, the specific surface area 230 m²/g and the SiO₂ content >99.8%.

Composite preparation:

The components of each sample (HDPE, MAPE, and OCC fiber) were pre-mixed to prepare homogeneous compounds and were blended in a counter-rotating twin-screw extruder (Collin, Germany) at a screw speed of 80 rpm with profiles at 152-150-162-160-165-170°C. The mix was removed from the mixing bowl, cooled in water, and granulated into pellets. The pellets were dried at 80°C for 24h before injection molding. Finally, the pellets were injection molded (Imen Machine Co., Iran) at 160°C.

Result and discussion:

Figure 1 shows the values of the tensile strength and modulus in the studied nanocomposites. It can be seen that the strength and modulus values of the nanocompositesincrease in samples with 3% nanosilica. The interaction between nanosilica, polymerand fiber would restrict the movement of the polymer chains and as a result the tensile properties would be improved. This is consistent with the results reported by most authors[7-9].



Figure 1. Effect of nanosilica content on tensile strength and modulus 2858





Conclusion:

The tensile modulus and tensile strength of the HDPE/OCC fiber composites increased with increasing nanosilica content, however the impact strength of the composites decreased with increasing the nanosilica loading. This project has shown that the composites treated with nanosilica will be desirable as building materials due to their improved stability and strength properties.

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Synthesis of $TiO_2 - \gamma - Al_2O_3 / SO_4^{2-}$ solid acid nanocatalyst with impregnation method and its catalytic property

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Key words: solid acid nanocatalyst, TiO₂ $-\gamma$ -Al₂O₃/SO₄²⁻, Esterification, Acetic acid

Introduction:

Esters are one of the most important classess in organic compounds, sience they are used in production of a wide range of products such as cosmetics, perfumes, food preservatives and so on. Among thesis products, isoamyl acetate is one of the most employed esters in chemicals, heteropolyacid, and solid acid were applicable for synthesis of isoamyl acetate. Among them, the solid acid catalyst SO_4^{2-}/TiO_2 was more noticeable due to its high activity at high reaction temperature and recovery compared with ion – exchange resin, zeolite and protonic acids. So it has been widely used in many organic reactions such as esterification, acylation, alkylation, and so on. However, the SO_4^{2-}/TiO_2 also have some disadvantage such as low surface areas and wide pore distributions. Compared with SO_4^{2-}/TiO_2 , $TiO_2 - \gamma -Al_2O_3/SO_4^{2-}$ nanocatalyst had high specific surface area. In this paper, first nanosized TiO₂ was synthesized by sol-gel method using titanium tetra isopropoxide (TTIP) as a precursor. Then $TiO_2 - \gamma -Al_2O_3/SO_4^{2-}$ solid acid nanocatalysts was prepared by impregnation method [1-6].

Materials and methods:

The reagents used in this study such as titanium isopropoxide (TTIP, 98%), γ -Al₂O₃ (purity > 99.5 %), iso-propanol, tuloene, n-heptane, acetic acid, iso amyl alcohol, nitric acid, concentrated sulfuric acid (H₂SO₄), were purchased from Merck Co (Germany). TiO₂ powder was prepared by sol-gel method. 60 ml of a mixture of distilled water (10ml) and iso-propanol





(50ml) was added to a round-bottom flask. After vigorous stirring for 60 min, to this solution was added 56.62 ml of titanium tetraisopropoxide (TTIP) solution in iso-propanol. The pH of the solution was adjusted with nitric acid at a value of 1.5 at room temperature. Then, the solution was refluxed at 70°C with constant stirring for 24 h and was dried at room temperature for 48 h. The TiO₂ – Al₂O₃ (3:7 weight ratio) mixed oxide was prepared by impregnation method. 1.4 g of the γ -Al₂O₃ powder was dispersed in 23 ml of the sol of TiO₂ containing 0.6 g of TiO₂ powder. Then, the TiO₂ – Al₂O₃ suspension was placed under ultrasonic treatment for 3h to loading TiO₂ on the surface γ -Al₂O₃. Then the prepared sample was dried at 90 °C in a water bath and calcined at 723 K for 4h. After time, the sulfation was carried out with a solution of sulfuric acid by impregnation method. In this method 0.736 ml of a solution of sulfuric acid (0.5mol/L) was added drop wise under vigorous stirring to 0.5g of the synthesized TiO₂ – Al₂O₃. Then the suspension was kept in an ultrasonic bath at room temperature for 10h. The prepared catalyst was dried at 343 K for 24 h and calcined at 723 K for 4 h.

Result and discussion:

The catalysts were characterized by means of XRD, FT-IR, BET, BJH, SEM and EDX methods. The XRD, FT-IR and EDX analyzing results showed that the TiO₂ was well placed on the surface of Al₂O₃. XRD showed both anatas of TiO₂ and γ - Al₂O₃ phases. The esterification of acetic acid with isoamyl alcohol was used as model reaction to test the catalytic activity of the catalyst. The results show that the TiO₂ – Al₂O₃/ SO₄²⁻ has high catalytic activity.

Conclusion:

The results show that the TiO₂ – Al₂O₃/SO₄²⁻ has high catalytic activity. A high conversion yield (99%) was obtained at optimum conditions of 130 °C, 5 h, and dosage catalyst of 3 wt% of acetic acid, and alcohol to acid molar ratio of 1:6.9. This result is higher compared to the previous reported values. In conclusion, the TiO₂ – γ -Al₂O₃/SO₄²⁻ nanocatalyst is a promising solid acid catalyst to conduct the esterification reaction of acetic acid.





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Using Gold nanoparticles as a solid carrier for luminant molecules as a biocompatible label

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Key words: gold nanoparticles, chemiluminescence, luminol, hepatitis B surface antigen

Gold nanoparticles (GNPs) are very attractive labels due to their special physical and chemical properties such as ease of synthesis, simplicity of conjugation and excellent biocompatibility [1]. Their unique optical properties in having very low photobleaching and blinking make them ideal carriers for optical biosensors. Two approaches have been developed for GNPs based chemiluminescent biosensors. GNPs can be used as chemiluminescent labels to amplify the detection of proteins and DNA[2]. Also, they can be used as solid carrier for chemiluminescent molecules to amplify the detection of biomolecules[3].

Gold nanoparticles were synthesis by reducing gold ions into solid gold. This was done by using hydrogen tetrachloroaurate (HAuCl4) as source of gold ions and trisodium citrate (Na3C6H5O7) as reduction agent.Luminol and secondary antibody were immobilized after carboxylation of the GNPs surface.

In the present work, by co-immobilization of luminol and a secondary antibody on GNPs we established a labeled antibody for detection of hepatitis B surface antigen in human serum. In the presence of hydrogen peroxide as an oxidant, a stable and efficient chemiluminescent signal was obtained when luminol molecules and secondary antibodies were co-immobilized on the GNP. Limit of detection in this system is 14 pg/ml. The process used in this report seems to be promising a new approach for establishment of a nanoparticle based biosensor.

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Synthesis Platinum-Polymer Nanocomposite by using Microemulsion System

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Key words: Nanoparticle, Nanocomposite, Reverse micelle, Microemulsion, Surfactant.

Introduction:

Water-in-oil microemulsions are isotropic and thermodynamically stable mixtures consisting of nano-sized aqueous droplets surrounded by a monolayer of surfactant molecules dispersed in a continuous non-polar organic medium [1-2]. In this study, we synthesized nanoparticles of platinum that dispersed in methylmetacrylate polymer by using microemulsion system.

Materials:

Methyl methacrylate 99% (MMA) was obtained from Merck. Triton X-100 (Acros) as the surfactant. Platinum salt (K_2PtCl_6) were purchased from Aldrich. benzoil peroxide from Alfa Aesar and deionized water were used and hydrazine hydrate (80.0%), was used as reducing agent.

Apparatus:

The UV spectra were recorded using a Perkin-Elmer model lambda 15 system. The scanning electron microscope used is a Philips operating at 10 kV.

Polymerizations:

Polymerization was carried out in an oven at 60-65 °C for 10 hours. In all of the reactions 0.2 M Triton X-100 was dissolved in MMA and water was added to yield a water-to-surfactant mole ratio (w) of 5. The amount of benzoyl peroxide used was 0.3% of the total weight of monomer.





Synthesis of Pt nanoparticles in Reverse Micelles:

The microemulsions were prepared by mixing the same volume of aqueous solution of platinum salt (0.02 M) and hydrazine hydrate (0.06 M) to the 0.2 M Triton X-100/ MMA solution. The molar concentrations of platinum salt and hydrazine hydrate were 4×10^{-4} and 12×10^{-4} M, respectively. The molar ratio of hydrazine hydrate and platinum salt was held constant for all experiments at a value of 4. The water-to-Triton X-100 molar ratio was kept the same in all cases and was equal to 5. The microemulsion containing hydrazine hydrate was added into another microemulsion containing metal ion drop by drop while the solution that containing metal ion was stirred. After all the hydrazine hydrate microemulsion was added, the vigorous magnetic stirring was maintained for 1.5 h, the resulting microemulsion mixtures changed to a stable dark yellow color after the reaction, indicating the formation of Pt nanoparticles.

Result and discussion:

Upon mixing of the two inverse micellar solutions of Pt^{2+} and hydrazine, the resulting solution instantaneously became dark yellow and the intensity of the coloration was increasing slowly with time, indicating the reduction of platinum ion into its metal form. Fig.1 show the UV–vis absorption spectra of the platinum nanoparticles formed in the Triton X-100 microemulsion. At the initial stage of reaction, a characteristic absorption band centered at approximately 296 nm was detected for platinum nanoparticles. The morphology and structure of PMMA/ Triton X-100/Pt nanocomposite was analyzed by SEM. Figs.2 show that nanoparticles were formed.



Fig. 1. UV absorption of platinum nanoparticles after 30 minutes.



Fig. 2. SEM image of PMMA/ Triton x-100/Pt nanoparticles.





Conclusion:

In this method, reverse microemulsions are used to control the generation of the metal particles with the aid of surfactant. The continuous phase was pure monomer during reduce of the metal ion; the monomer is polymerized by radical polymerization. Thus, particle generation and microemulsion polymerization are combined in a single-step synthesis. Because of entrapping nanoparticles in polymer matrix, particle agglomeration is significantly reduced.

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Study Contact angle of water droplet with the surface of graphene oxide

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Key words: Graphene oxide, Hummers method, Contact angle, hydrophilic.

Introduction:

Graphene oxide is a two-dimensional material which consists of only one single atomic layer of carbon, oxygen, and hydrogen. In recent years this material has become the most exciting topics. Graphene has attracted much attention from researchers due to its interesting mechanical, electrochemical, and electronic properties. It has many potential applications such as polymer filter, sensor, energy conversion, energy storage devices and the medical field. Graphene oxide is a chemical intermediate for the manufacture of graphene, another twodimensional material but only consists of a single atomic layer of carbon. In this study graphene oxide was obtained through Hummers method. The material was then sonicated for exfoliation. The obtained materials were characterized by FTIR, XRD, SEM, TGA and the percentage purity of the synthesized material was investigated with EDX. Significant effort has been dedicated to both theoretical and experimental investigation of water on graphitic surfaces. In general, the hydrophobic nature of the graphene is commonly observed and revealed on the macro scale as a large contact angle, i.e. up to 93°, between a water droplet (~1 µl) and graphene surface. against graphene, graphene oxide with a high hydrophilic property that is. However, being hydrophilic, graphene oxide disperses readily in water, breaking up into macroscopic flakes, mostly one layer thick .We do this while large scale synthesis graphene oxide experiments designed to Hummers method with hydrophilic properties of this substance is also paid to review. In this work we study the water contact angle with the surface of graphene oxide paid. The results indicate that the hydrophilic properties of this material is.





Materials and methods:

by acid oxidation of graphite powder according to the modified Hummers's method. 1 g graphite

powder ,0.5 g of sodium nitrate and 3 g of KMnO₄ were added to 70 mL of sulfuric acid (98%). The reaction was performed for 2 hours .After the synthesis of grapheme oxide In several experiments with different concentrations of materials was. Then use the appropriate software to

to study the contact angle of water drops with the surface of paid.

Result and discussion:

Contact angle of water droplet Was obtained 52.51° that showed a high hydrophilic property of the material ,and The product yield was above 50%. Spectra show Synthesis of graphene oxide.





IR spectrum is one important tool to identify the chemical modification proposed in the reaction scheme. As shown in Fig, GO powder sample exhibits the following characteristic





signals: O–H stretching of the C–OH at 3458.33 cm_1C=O stretching of the –COOH at 1719 cm_1, O–H vibration of the C–OH groups at 1381 cm_1, C–O vibration of the C–OH at 1173 cm_1, and epoxy vibration at 1055 cm_1One band at 1627 cm_1 was attributed to the deformation vibration of the water, which illustrated that there was a small quantity of water left in GO.Contant angle images of graphene oxide

Conclusion:

with several design Experiments high value obtained for graphene oxide and were characterized by FTIR, XRD, SEM, TGA and Study Contact angle of water droplet with the surface of graphene oxide showed a high hydrophilic property of the material.

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Electropolymerization and characterization of poly (aniline-co-Nmethylaniline)/ silver nanocomposite

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Keywords: nanocomposite, Electropolymerization, poly (aniline-co-N-methylaniline)/ silver, electrochemical impedance spectroscopy, scanning electron microscopy (SEM). BSE

Introduction:

Among the whole conducting polymers, polyaniline (PANI) has a specific situation because of its simply synthesis, environmental stability, and doping with protonic acids [1]. Polyaniline (PANI) is a very popular conductive polymer which has been re-discovered in recent years. Electrochemical or chemical homopolymerization of aniline derivatives [2] and copolymerization of aniline with ring or N-substituted aniline derivatives [3] have also been employed successfully to improve properties of PANI. The most studied ones are alkyl, alkoxy anilines, with the substituent groups in the ortho or meta position. The development of inorganic/organic composites has recently received increasing attention due to their wide range of potential uses. Composites of conducting polymers and inorganic nanoparticles have received a lot of attention because of their usefulness in several applications [4].

Materials and methods:

All reagents and solvents were analytical grade from Aldrich, Fluka or Merck and were used as received and all aqueous solutions were prepared from distilled deionized water.

The electropolymerization was carried out in a conventional three electrode electrochemical cell. Either Au disc electrode was used as the working electrode (WE). A Ag/AgCl electrode and a pt electerod as the reference electrode (RE) and counter electrodes (CE), respectively. The polymers and nanocomposites film was synthesized by the Cyclic voltammetry (CV)





using cell from 0.01 M AgNO₃ + 0.2 M monomer + 1.0M HNO₃ solution at room temperature.

Apparatus:

Morphology of the sample studied by a SEM (TESCAN _ VEGAU Π LMU) on Au substrate. FTIR is recorded with a FTIR- Equinox55 instrument in theregion of 400–4000cm–1 using KBr pellet. UV–vis spectroscopy was done on Shimadzu SHIMADZU - 1650PC system from 275 nm to 800 nm wavelength. Optical path length of the quartzcuvette is 1.0cm.

Result and discussion:

In this present study, copolymers of aniline (ANI) with N-methylaniline (NMANI) were prepared using Cyclic voltammetry (CV). The electropolymerization of nanocomposite of poly (aniline co N-methylaniline)/ silver were prepared by in-situ oxidative polymerization of NMANI monomer and Anilin monomer in the presence of AgNO₃. The formation of polymer and nanocomposite was characterized by FTIR and UV–vis spectroscopy. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of copolymer and nanocomposite owing to the aggregation effect The cyclic voltammetry results show that the nanocomposite film considerably higher electroactivity compared with copolymer film. The surface morphology of the coating was determined by scanning electron microscopy (SEM) and EDX. From the SEM image, it is observed that nanoparticles are well dispersed in the copolymer matrix.

Data obtained in this project can be concluded that for applications that require more conductivity can be electropolymerization in the presence of silver nitrate did and nanocomposite copolymer / silver won. That a simple, rapid and inexpensive and it can be to build sensors, rechargeable cell and fuel cell used.

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Electropolymerization and characterization of poly (aniline-co-Nmethylaniline)/ silver nanocomposite

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Keywords: nanocomposite, Electropolymerization, poly (aniline-co-N-methylaniline)/ silver, electrochemical impedance spectroscopy, scanning electron microscopy (SEM). BSE

Among the whole conducting polymers, polyaniline (PANI) has a specific situation because of its simply synthesis, environmental stability, and doping with protonic acids [1]. Polyaniline (PANI) is a very popular conductive polymer which has been re-discovered in recent years. Electrochemical or chemical homopolymerization of aniline derivatives [2] and copolymerization of aniline with ring or N-substituted aniline derivatives [3] have also been employed successfully to improve properties of PANI. The most studied ones are alkyl, alkoxy anilines, with the substituent groups in the ortho or meta position. The development of inorganic/organic composites has recently received increasing attention due to their wide range of potential uses. Composites of conducting polymers and inorganic nanoparticles have received a lot of attention because of their usefulness in several applications [4].

In this present study, copolymers of aniline (ANI) with N-methylaniline (NMANI) were prepared using Cyclic voltammetry (CV). The electropolymerization of nanocomposite of poly (aniline co N-methylaniline)/ silver were prepared by in-situ oxidative polymerization of NMANI monomer and Anilin monomer in the presence of AgNO₃. The formation of polymer and nanocomposite was characterized by FTIR and UV–vis spectroscopy. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of copolymer and nanocomposite owing to the aggregation effect



The cyclic voltammetry results show that the nanocomposite film considerably higher electroactivity compared with copolymer film. The surface morphology of the coating was determined by scanning electron microscopy (SEM) and EDX. From the SEM image, it is observed that nanoparticles are well dispersed in the copolymer matrix.

Data obtained in this project can be concluded that for applications that require more conductivity can be electropolymerization in the presence of silver nitrate did and nanocomposite copolymer / silver won. That a simple, rapid and inexpensive and it can be to build sensors, rechargeable cell and fuel cell used.





Figure1. EDX nanocomposite of poly (aniline-co-N-methylaniline)/ silver

References

[1] Franco Cataldo , On the action of ozone on undoped and doped alkyl and N-alkyl-substituted polyanilines, Polymer Degradation and Stability, NO. 75(2002) PP. 99–106
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Electrochemical study and characterization of copolyaniline/Ag nanocomposites as conducting polymer in fuel cells

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Keywords: cyclic voltammetry, copolyaniline/Ag, electrochemical impedance spectroscopy (EIS), nanocomposites, SEM, DSC

Introduction:

Among the whole conducting polymers, polyaniline (PANI) has a specific situation because of it's simply synthesis, environmental stability, and doping with protonic acids [1]. Polyaniline (PANI) is a very popular conductive polymer which has been re-discovered in recent years. Deep studies have better clarified its chemical structure with different oxidation states which can assume under different conditions [2]. Recently, the synthesis of electrically conducting polymers such as polyaniline (PANI) and its derivatives has received a considerable attention owing to their various technological applications . The composites of conducting polymers, such as polyaniline (PANI), with noble metals find applications in electrocatalysis, catalysis, design of fuel-cell electrodes, sensors, conducting printing inks, recovery of noble metals, etc. The first method has only been used exceptionally for modifying silver nanoparticles with PANI or substituted PANI. Composites of silver and PANI have been prepared by the second technique, by the direct reduction of silver nitrate with PANI or PANI derivatives. The incorporation of metal nanoparticles could effectively improve the electrical, optical and dielectric properties of the polyaniline composites [3].

Materials and methods:

All reagents and solvents were analytical grade from Aldrich, Fluka or Merck and were used as received and all aqueous solutions were prepared from distilled deionized water.





The electropolymerization

was carried out in a conventional three electrode electrochemical cell. Either Au disc electrode was used as the working electrode (WE). A Ag/AgCl electrode and a pt electerod as the reference electrode (RE) and counter electrodes (CE), respectively. The polymers and nanocomposites film was synthesized by the Cyclic voltammetry (CV) using cell from 0.01 M AgNO₃ + 0.2 M monomer + 1.0M HNO₃ solution at room temperature.

Apparatus:

Morphology of the sample studied by a SEM (TESCAN _ VEGAU II LMU) on Au substrate. FTIR is recorded with a FTIR- Equinox55 instrument in theregion of 400–4000cm–1 using KBr pellet. UV–vis spectroscopy was done on Shimadzu SHIMADZU - 1650PC system from 275 nm to 800 nm wavelength. Optical path length of the quartzcuvette is 1.0cm. DSC analysis is carried out in DSC- Perkin Elmer Pyris 1-537N0042401 LTI05 temperature range of (-200–250) °C.

Result and discussion:

Polymerization was accomplished by voltammetric method (cyclic voltammeter) in the following conditions (with a fixed concentration of monomer in an aqueous solution of nitric acid). Silver- polymer nanocomposites were prepared by cyclice voltammeteric method in the presence of silver nitrate. The properties of polyaniline, its derivatives and its nanocomposites were determined by cyclic voltammetery (CV), potentiometerice method, EIS, TGA, DSC, FTIR spectrometry, UV-vis spectrometry. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of polymers and nanocomposite film considerably higher electroactivity compared with polymer film. Also, its morphology was determined by SEM. The results showed that the response of aniline derivatives to pH and their sensitivity to pH has been reduced and by synchronous synthesis of nanosilver particles, improved the sensitivity of nano composites.





SEM images of the nanocomposites nanocomposite powders show non-agglomerated uniformly packed silver particles.

Conclusion:

Here, we have tried to improve the dependence of electrochemical activity of polyaniline on pH in order that we can make use of it to build sensors, fuel cells and rechargeable cells. The surface morphology of the coating was determined by scanning electron microscopy (SEM) and EDX. From the SEM image, it is observed that nanoparticles are well dispersed in the copolymer matrix.

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Hydrothermal and Sonochemical Synthesize of nano TiO₂ by Acid Leaching

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Keywords: Sonochemical, Hydrothermal, Ilmenite, TiO₂

Introduction:

Titanium dioxide is widely used in the manufacture of paints, varnishes, lacquer, paper, paperboard, printing inks, rubber, floor covering, and ceramics and so on. White titanium dioxide pigment has been produced by two main processes. The sulfate and the chloride processes. Each of these two routes requires a different feedstock. However, economic and environmental pressures are shifting the world balance of titanium dioxide production away from sulphate based manufacture towards the more cost effective and cleaner chloride route. This so-called chloride process has been reported by several researchers [1,4].

Materials and methods:

The ilmenite concentrate was received from Kahnooj/Iran processing plant (Iran) mine. The chemical composition of the representative sample is presented in Table 1. XRF results (detected by an ARLX⁺) show FeTiO3 as the major composition.

Leaching experiments were carried out under sulfuric acid leaching process. 0.5 mgr TiFeO3 was added to 20 mL pure H2SO4 (merck,germany) with 120 c heat. After 30 min the mixture was filtered, and then H2O was added to precipitate in ultra sounding bath(BANDELIN-SONOREX DIGITEC) at 50 c for 15 min.





Leaching experiments were carried out under Hydrocholoric acid leaching process. 0.5 mgr TiFeO3 was added to 100 mL pure HCl (merck,germany) with 95c heat. After 6 hour the mixture was filtered, and then HCl was added to wash the precipitate.

Particle size distribution of the produced nano particles (rutile) was determined using ZEN 3600 Zeta Sizer(Malvern).

Conclusion :

This research reveals nano size of TiO_2 that produced by hydrothermal and sonochemical process. Synthesized TiO_2 obtained from hydrochloric and sulfuric acid leaching. Zeta sizer and SEM analyzer confirmed that the size of nano particles is 85 nm.

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Adsorption Isotherm Study of Ketotifen on Multi -Walled Carbon Nanotube

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Key words: Isotherm, Adsorption, Multi – Walled Carbon nano-tubes, Ketotifen

Introduction:

Carbon nanotubes (CNT) discovery by Iijima in 1991^[1]. Carbon nanotubes (CNTs) are hollow cylinders of graphite carbon atoms .These tubes are on the nano scale (10^{-9} m) . Carbon nanotubes are a new form of carbon with unique electrical and mechanical properties .They can be considered as the result of folding graphite layers into carbon cylinders .These cylinders may be composed of single (MWCNTs).Due to the variety of extraordinary properties exhibited by CNTs , a large number of possible applications have been proposed. ^[2]Ketotifen is a second-generation H₁-antihistamine and mast cell stabilizer. It is most commonly sold in as a salt of fumaric acid, ketotifen fumarate, and is available in two forms. In its ophthalmic form, it is used to treat allergic conjunctivitis, or the itchy red eyes caused by allergies. In its oral form, it is used to prevent asthma attacks. Side effects include drowsiness, weight gain, dry mouth, irritability, and increased nosebleeds. ^[3]

Materials and methods:

Distilled water as solvent , Ketotifen and Adsorbent Carbon nano-tubes with a diameter of the outer surface 5-10 nm space 40-600 m²/gr and high purity merk95% of the company . At first, stock solution of Ketotifen was prepared in distilled water (50 mg/l). Then , from stock solution of Ketotifen, five standard solutions in concentration of 1,2,3,4,and 5ppm were prepared . 0.01 gr carbon nano-tube have been added as absorbent to 100 mL glasses





containing 10 mL Ketotifen solution, then it was stirred by mixer for 24 hours . After mixing process then the solution should be put into 10000 rpm speed for 20 minutes. Ketotifen concentration was measured before and also after adsorption by spectrophotometer.

Result and discussion:

Table 1 shown the adsorption of Ketotifen on 0.01 grams of Carbon nano tubes(mgg^{-1}). Calculated parameters based on isothermic equations are shown in table 2. The results showed that the absorbance of Ketotifen on absorbent is in conformance with Langmuir isotherm.

Table 1: The adsorbance of Ketotifen on 0.01 grams of carbon nano-tubes (mg.g⁻¹)

concentration	Adsorption on0.01 gr carbon nanotube (mg.g ⁻¹)
1	0.783
2	1.339
3	1.626
4	1.605
5	2.15

Table 2: Isotherm parameters calculated for models

	Freundlich	Langmuir	Temkin
Ketotifen	R ² =0.918	R ² =0.934	R ² =0.885
	1/n=0.340	$1/q_m = 0.451$	B=0.443
	lnk _f =0.334	$1/q_{mb} = 0.209$	BlnA=1.474

Conclusion :

In this research has studied equilibrium adsorption isotherms of Ketotifen on carbon nanotube. And also results of experiments through Freundlich, Temkin and Langmuir models have been studied and it has found different parameters of these models for carbon nano tube absorbent. According to the error rate for each model, we obtained a good agreement between these data which it showed the best agreement by Langmuir model Experimental result showed that by increasing concentrations of Ketotifen therefore absorption rate will increase too. The highest absorption rate is for 5 ppm concentration of Ketotifen.





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Adsorption Isotherm Study of Loratadine on Multi -Walled Carbon Nanotube

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Key words: Isotherm, Adsorption, Multi – Walled Carbon nano-tubes, Loratadine

Introduction:

Carbon nanotubes (CNT)discovery by Iijima in 1991^[1]. Carbon nanotubes (CNTs) are hollow cylinders of graphite carbon atoms .These tubes are on the nano scale (10^{-9} m) . Carbon nanotubes are a new form of carbon with unique electrical and mechanical properties .They can be considered as the result of folding graphite layers into carbon cylinders .These cylinders may be composed of single shell single wall Carbon nano-tubes (SWCNTs), or of several shells multi-wall Carbon nanotubes (MWCNTs). Due to the variety of extraordinary properties exhibited by CNTs , a large number of possible applications have been proposed. ^[2] Loratadine is a white to off-white powder not soluble in water. It has a molecular weight of 382.89, and empirical formula of $C_{22}H_{23}CIN_2O_2$. Loratadine is a second-generation H₁ histamine antagonist drug used to treat allergies. Structurally, it is closely related to tricyclic antidepressants, such as imipramine .^[3]

Materials and methods:

Ethanol (Purity %96) as solvent, Loratadine. Adsorbent Carbon nano-tubes with a diameter of the outer surface 5-10 nm space 40-600 m²/gr and high purity merk95% of the company . At first, stock solution of Loratadine was prepared in ethanol (50 mg/l). Then , from stock solution of Loratadine, four standard solutions in concentration of 2,3,4,and 5ppm were prepared . 0.01 g of carbon nano-tube have been added as absorbent to 100 mL glasses





containing 10 mL Loratadine solution, then it was stirred by mixer for 24 hours . After mixing process then the solution should be put into 10000 rpm speed for 20 minutes. Loratadine concentration was measured before and also after adsorption by spectrophotometer.

Result and discussion:

table 1 shown the adsorption of Lortadine on 0.01 grams of Carbon nano tubes(mgg⁻¹). Calculated parameters based on isothermic equations are shown in table 2. The results showed that the absorbance of Loratadine on absorbent is in conformance with Langmuir isotherm.

concentration	Adsorption on 0.01 gr carbon nanotube ($mg.g^{-1}$)
2	1.94
3	2.83
4	3.42
5	4.13

Table 1: The adsorbance of loratadine on 0.01 grams of carbon nano-tubes (mg.g⁻¹)

Table 2: Isotherm parameters calculated for models

	Freundlich	Langmuir	Temkin
Loratadine	$R^2 = 0.968$	$R^2 = 0.984$	$R^2 = 0.964$
	1/n=0.259	$1/q_m = 0.228$	B=0.744
	lnk _f =1.431	$1/q_{mb} = 0.021$	BlnA=4.066

Conclusion :

In this research has studied equilibrium adsorption isotherms of Loratadine on carbon nanotube. And also results of experiments through Freundlich, Temkin and Langmuir models have been studied and it has found different parameters of these models for carbon nano tube absorbent. According to the error rate for each model, we obtained a good agreement between these data which it showed the best agreement by Langmuir model Experimental result showed that by increasing concentrations of Loratadine therefore absorption rate will increase too. The highest absorption rate is for 5 ppm concentration of Loratadine.





Refrences:

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Influence of Organoclay on Compatibility of Different Ratio of Immiscible (SBR/NBR) Rubber Blend

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Introduction:

Blending of polymers has become a useful technique to produce and develop material with properties superior to those of individual constituents [1]. However, most polymer blends are thermodynamically immiscible and phase separated upon blending [2]. This phenomenon during blending causes poorer properties than their individual constituents, therefore a third component which is called compatibilizers have been used to prevent this phenomenon. Recently Nanoparticles are being used as a compatibilizer to reduce interfacial tension and improve final properties by locating at the interface [3].

In this study nanocomposites based on styrene butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR) and different ratio (SBR/NBR: 80/20, 20/80) of their blend were prepared by melt mixing. Then the structure and compatibility of the prepared compounds were investigated. Mechanical properties of the prepared samples were also determined and compared with each other.

Materials and methods:

Acrylonitrile butadiene copolymer ,(NBR6240, LG chem. Korea)with 34% acrylonitrile bound content, and Mooney viscosity of: ML (1+4,100°c) =41 , styrene butadiene rubber (SBR1502, Bandare Emam Iran)with 23.5 % styrene content, and Mooney viscosity of: ML (1+4,100°c) =55, dicumyl peroxide(DCP 99%, Shenyang Chem. Co), and organo-modified layered nanosilicates(C30B and C15A, Southern Clay) were used to prepare the samples.





The formulation of the compounds are shown in table 1 and are given by the name of X/Y which X shows the SBR phr in SBR/NBR and Y shows the kind of cloisites and the amount of cloisites (phr) (Y=A5 indicates 5phr C15A and Y=B5 indicates 5phr C30B).

Apparatus:

X-ray diffraction (XRD) analysis were performed at room temperature by using Philips model X'Pert with Cu K α radiation (λ =1.78897A°) at 40Kv and 30mA at a rate of 0.02°/sec.

Tensile strength and elongation at break were measured according to ASTM D 412 method by using a Galdabini-Sun 2500(Italy) tensile tester at a strain rate of 500 mm/min. The clay particles dispersion of freeze-fractured and coated by gold samples was observed by field emission scanning electron microscopy (FE-SEM; Hitachi S-4160) under an acceleration voltage of 15 kV. Differential Scanning Calorimetry (DSC) was used to study compatibility of the samples. DSC measurements were performed under a nitrogen atmosphere on the samples using a DSC1 star system (Mettler model) apparatus at a scan rate of 10 °C/min.

Result and discussion:

XRD results showed more intercalation of SBR chains into the C30B and C15A compared to correspond NBR based compounds which was due to higher Mooney viscosity of the used SBR with respect to NBR. XRD results also indicated more intercalation of NBR macromolecule chains into the C30B (in 0/5B compound) than that of C15A (in 0/A5 compound) was due to higher interaction between NBR and C30B respect to NBR and C15A. FE-SEM images of fracture surfaces of the 0/5B and 0/5A nanocomposites shows that the cloisites aggregation can barely be seen within the matrix by using C15A or C30B[4].

DSC thermograms revealed the incompatibility between NBR and SBR in their neat blends meanwhile filled blends showed decrease in the difference between glasses transitions of blend constituents due to organoclays compatibilizing effect. Finally presence of nanoparticles resulted in improvement of tensile properties which was attributed to increasing the compatibility between, SBR and NBR, the constituents of the blends.





Conclusion:

According to the XRD and FE-SEM results, it can be concluded that the nanoparticles-rubber affinity and rubber Mooney viscosity play an important role in the final inter layer distance of the nanoparticles. Curing characteristic and DSC results showed that presence of nanoparticles in the blends exhibited a higher compatibility and thereby increasing the mechanical properties.

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Fabrication of NanocrystallineLa_{0.6}Ca_{0.4}MnO₃manganitesby sol-gel method and study of Magnetocaloric effect from indirect measurements

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Key words: Magnetocaloric, Perovskite, Nanocrystalline powder, Magnetic Entropy

Introduction:

Magnetic refrigeration technology based on the magnetocaloric effect shows advantages over traditional gas compression technologyand may be considered as a promising alternative[1]. When an external magnetic field is applied to a material, the magnetic spins in the material attempt to align with the magnetic field, thereby reducing the magnetic entropy of the spin system. If this process is performed adiabatically, the reduction in spin entropy is offset by an increase in lattice entropy, and the temperature of the specimen will rise[2]. This temperature variation is known as the magnetocaloric effect[3]. Magneticentropy change is known to achieve relatively high valuesat the parato ferromagnetic transition. The transition temperature ofmanganites may be varied mainly by a chemical composition.

Samples:

NanocrystallineLa_{0.6}Ca_{0.4}MnO₃manganites were prepared by citratesol–gel method in Ferdowsi University Microelectronic laboratory. Stoichiometric amounts of CaCO₃,La₂O₃ and MnO were dissolved in nitric acid. Citric acid (CA) andEthylene glycol (EG) were added to the solution of metal nitratesin the molar ratio metals: CA: EG = 1:5:5. The resultant solution was evaporated on an oil bath at90 °C until a viscous gel-like productformed. The gels were decomposed by slow heating in air upto 400 °C. Nanocrystalline powder La_{0.6}Ca_{0.4}MnO₃was obtained bycalcination of the citrate precursor at 750 °C for 6 h.X-ray diffractionusing Bruker





D8 advance instrument with Cu_{ka} (λ =1.54 Å), shows orthorhombic structure (s.g.Pnma) at roomtemperature. Unit cell parameters equal to: a=0.5427nm, b=0.76782 nm, c=0.53981 nm.

Magnetic measurements:

Magnetic characterization using Physical Properties Measurement System (PPMS; Quantum Design) in University of Wollongong,was made by measurements of the temperature dependence of the magnetization with a DC magnetic field of 100 Oe in field cooledand zero field cooled conditions. Magnetization isotherms up to 5 T have been carried out between 160 and 310 K.

Magnetocaloric effect:

The magnetic entropy change ΔS_M was numerically calculated from magnetization isotherms according to the formula[4]: $|\Delta S_M| = \sum_i \frac{(M_i - M_{i+1})}{(T_{i+1} - T_i)} \Delta H_i$.

Result and Conclusion:

Magnetic characterization in NanocrystallineLa_{0.6}Ca_{0.4}MnO₃ manganite prepared by the citrate sol-gel method, shows that the transition temperature of a material is defined as the temperature at which $\partial M / \partial T$ curve shows a minimum and is fixed at 268 K. The maximum magnetic entropy change value obtained for a variation of almost 5 T in the magnetic field is 8.387 J/kg K.In conclusion, the results show thatLa_{0.6}Ca_{0.4}MnO₃materials are candidates formagnetic refrigerant working in sub-room temperaturerange, because of: (1) a well-defined transitiontemperature; (2) a modest magnetic entropy changeupon application/removal of a low magnetic field;(3) easily controllable magnetic entropy in the presence of a modest magnetic field; (4) goodchemical stability, and (5) the possibility of beingmanufactured at a low price[2].



Figure 7Magnetic Entropy Change



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Dependence of magnetic properties of cobalt ferrite nanoparticles on ball milling time

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Key words: Cobalt ferrite, Nanoparticles, Ball milling, Magnetization, Coercivity.

Introduction:

Cobalt ferrite nanoparticles (CoFe₂O₄), including magnetic materials have spinel ferrite structure show interesting properties [1].CoFe₂O₄ structure is a ferrimagnet oxide with partial inverse spinel structure that its degree of inversion depends on the preparation method and heat treatment [2]. This kind of ferrite was an interesting matter for research [1,2,3,4]. Because of high saturation magnetization, field coercivity, high physical and chemical stability cobalt ferrite is attractive for researchers[4]. It has many applications including ferrofluid, the recording magnetic and targeted drug delivery [4]. In this work, cobalt ferrite nanoparticles by combustion method were generated and then were ball milled on two different times.

Methods:

 $CoFe_2O_4$ sample is prepared according to the following method. Firstly, powders of $Fe(No_3)_3.9H_2O$, $Co(No_3)_2.6H2O$ and glycine ($C_2H_5NO_2$) on appropriate molar ratio and high purity were mixed, distilled water. In the next step solution was obtained from this material with using a magnetic stirring. After evaporation of its water, spontaneous combustion occurs and ferrite cobalt can be raised. Then we divided the sample into three parts. Two parts of them were milled on 90 and 150 minutes, by planetary mill of ~250 rpm. In order to identify the crystal structure from X-ray diffraction analysis (XRD) was used (Holland Philips X'pert). Existence of bonds was investigated using FTIR analysis (Thermo Nicolet). The magnetic





hysteresis measurements were performed on the samples using vibrating sample magnetometer (VSM).

Results and discussion:

XRD spectra of the samples are given on figure 1. Diffraction pattern shows that the first peaks observed in all three cases are corresponding to the after composition of spinel ferrite, secondly, the peaks widths after the ball milling were broad. It shows crystallites have smaller sizes. Average sizes of grains were calculated for samples before ball milling and after 1.5 h and 2.5 h ball milling using Debye Scherrer formula $D=0.9\lambda/\beta cos\theta$.

They were 50.41, 39.70 and 33.86 nm respectively. It was seen that after ball milling the crystalline structure of the samples was maintained.



Figure1. X-ray diffraction pattern of sample CoFe₂O₄, before, after 1.5h and 2.5 h ball milling.

The magnetization curves of the samples, for before ball milling and after 1.5 h and 2.5 h of ball milling are shown in Figure 2 respectively. As it can be seen increasing of the ball milling time leads to reducing of saturation magnetization and arising of coercivity. These effects may be due to reducing the size of crystalline as well as arising of bonds strengths.






Figure2. Cobalt ferrite hysteresis loops before, after 1.5 h and 2.5 h ball milling.

Conclusions:

We conclude that using ball milling leads to smaller sizes of crystalline. The crystal structure of the nanoparticles was nearly unchanged and magnetic properties such as magnetization and coercivity undergo considerable changes.

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Selective acetylation of alcohols and phenols with recoverable nanocatalyst

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Key words: Fe₃O₄ nanoparticles, Acetylation, Heterogeneous catalyst, Nanocatalyst, Protection

Introduction:

Selective protection of alcohols and phenols has received attention in recent years for their role in multistep synthesis [1]. Numerous homogeneous catalytic systems are available for this transformation [2,3], but most of them are non-reusable, and they often have other disadvantages. The employment of heterogeneous catalysis in organic synthesis makes the reaction handling easier. Many examples of selective protection of multifunctional molecules using heterogeneous catalysts have been reported by Sartori in a review [4]. An attractive advantage of magnetic Fe_3O_4 nanoparticles (MNPs) is its easy separation using external magnets, which minimizes the loss of catalyst during separation. The direct use of MNPs without modification as magnetically recoverable catalysts for organic reactions is very scarce. Therefore, we were prepared MNPs by arc discharge (AD-MNPs) and co-precipitation (CP-MNPs) methods and their catalytic activities for acetylating of alcohols and phenols were compared. We carried out all our reactions in the presents of CaCl₂ co-catalyst and acetic anhydride, under solvent free conditions at room temperature.

Materials and methods:

Synthesis of AD-MNPs was carried out by passing Currents of 50 A through thin iron wires in the open air. In the formation of the CP-MNPs, $FeCl_3 \cdot 6H_2O$ and $FeSO_4.7H_2O$ with the molar ratio of (Fe^{3+} : $Fe^{2+}= 2:1$) were dissolved in deionized water. Then, NaOH was added to the solution with vigorous stirring at room temperature. CP-MNPs immediately formed. In order





to acetylation reaction, to a solution of alcohol or phenol (1 mmol) and acetic anhydride (2 mmol) was added nano-Fe₃O₄ (20 mg) and CaCl₂ (10 mg) at room temperature and stirred.

Results and discussion:

According to SEM images, AD-MNPs and CP-MNPs were prepared with sizes of 53nm and 28 nm, respectively (Fig. 1). Also, the average AD-MNPs and CP-MNPs core diameters were calculated to be 7 nm and 17 nm from the XRD (Fig. 2). In AD-MNPs the presence of Fe_3O_4 was shown in FT-IR by two strong absorption bands at around 579.10 and 400.34 cm⁻¹(Fig. 3a). Similarly, CP-MNPs show two absorption peaks at 600.08 and 437.55 cm⁻¹ (Fig. 3b). We investigated catalytic activity of AD-MNPs as a heterogeneous catalyst in acetylation reactions and compared with CP-MNPs (Table 1). The effects of some organic solvents were also probed. The best result was achieved when the reaction was carried out without solvent.



Fig. 1. SEM images of (a) AD-MNPs and (b) CP-MNPs.



and (b) CP-MNPs.



(c) AD-MNPs after usage.

Table 1. Acetylation of alcohols with acetic anhydride over AD-MNPs.

Alcohol	Yield (%)	Alcohol	Yield (%)	Yield (%) Alcohol	
Benzyl alcohol	100	4-Methoxyphenol	0	2-Naphthol	100
4-Nitrophenol	phenol1002,4-Dinitrophenolrozol01,4-Cyclohexanediol		100	100 3-Piperidinol	
Metacrozol			55	Phenol	75
2-Aminophenol	0	1-Naphthol	100	4-Iodophenol	58





Conclusions:

Fe₃O₄ nanoparticles prepared by the arc discharge method (AD-MNPs) were successfully used as an efficient and recyclable heterogeneous catalyst for the acetylation of alcohols, and phenols under solvent-free conditions. Among the various substrates, acetylation of benzyl alcohol and phenols with electron withdrawing groups proceeded most efficiently due to the high acidic character of their phenolic OH. Nano-Fe₃O₄ catalyst was also prepared by the coprecipitation method (CP-MNPs) and showed less catalytic activity than AD-MNPs.

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A ZnO-nanoparticle-promoted synthesis of oxazole derivatives

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Keywords: Zinc oxide, Zinc oxide, oxazole

Introduction:

Zinc oxide nanoparticles (ZnO NPs) have great potential for use as a catalyst for a variety of organic and inorganic reactions due to their high surface-to-volume ratio [1]. Also, since ZnO NPs are often recovered easily by simple workups, which prevents contamination of products, they may be considered as a promising safe and reusable catalyst. Zinc oxide nanoparticles are used as an effective and reusable catalyst for one-pot, three-component couplings of ammonium thiocyanate, acylchloride and phenacylbromide to produce oxazole derivatives at room temperature. Compared with other methods, satisfactory results are obtained with high yields, short reaction times, and simplicity in the experimental procedure. The catalyst could easily be recycled and reused four times without noticeable decrease in catalytic activity.

Materiala and methods:

We first prepared ZnO NPs through a solid-state reaction method. The X-ray diffraction (XRD) patterns of the ZnO NPs could be indexed to the hexagonal wurtzite structure (space group: P63mc; $a = 3.249 \text{ A}^{\circ}$, $c = 5.206 \text{ A}^{\circ}$, JCPDS card no. 36-1451). No impurities were involved in the synthesized ZnO NPs sample, for which an average size of 21 nm was estimated by Scherrer's equation, Dh,k,l = kk/b cosh, where k is a constant (generally considered as 0.89 for ZnO), k is the wavelength of Cu Ka (1.54 A $^{\circ}$), b is the corrected diffraction line full-width at half-maximum (FWHM), and h is Bragg's angle [2]. The morphology and grain size of the ZnO NPs were investigated by Transmission electron microscopy (TEM). They had spherical and hexagonal morphology with a narrow size





distribution from 18 to 36 nm and a mean grain size of 21 nm, confirming the results calculated from Scherrer's equation. The presence of some larger particles should be attributed to aggregating or overlapping of smaller particles. The selected-area electron diffraction (SAED) pattern of ZnO NPs clearly shows the crystalline nature of the product, indexed to (100) (002), (101), (102),(110), and (103), respectively, for the diffraction rings, in accordance with similar peaks in the XRD pattern.

Result and discussion:

We have used zinc oxide nanoparticles as an effective and reusable catalyst for one-pot, threecomponent couplings of ammonium thiocyanate, acylchloride and phenacyl bromide to produce oxazole derivatives at room temperature. In comparison with other methods, satisfactory results are obtained with high yields, short reaction times, and simplicity in the experimental procedure. The catalyst could easily be recycled and reused four times without noticeable decrease in catalytic activity.

Conclusions:

In conclusion, the present three-component, one-pot condensation for the synthesis of oxazole by ZnO NPs catalysis provides an efficient, facile, and environmentally acceptable method for this reaction. This method offers several advantages including high yields, short reaction times, a simple work-up procedure under solvent-free conditions, ease of separation, and recyclability of the catalyst, as well as the ability to tolerate a wide variety of substituents in all the multi components.

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Effect of nano zinc oxide on the hind limb bud NMRI mouse embryos at in vivo conditions

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Abstract:

Materials in nano size have a very different properties from the same materials in mass form. These materials can transport easily from the placenta. Therefore, in this study experiments were performed on effects of nano zinc oxide on hind limb bud development in NMRI mice embryos.

In this work in vivo technique was applied. Experimental groups of pregnant mice on day 11 of pregnancy, received single injection of zinc oxide in doses of 0.5gr/kgr, 1gr/kgr and 1.5gr/kgr intraperitoneally. On day 15 of pregnancy the fetuses were extruded the hind limb buds, were separated from their bodies and after the morphological studies preparation, were applied, for histological and statistical analysis. In three regions of foot including toes, legs and thigh, number of mesenchymal cells, chondrocyt (cartilage), atrophied, and muscle , hypertrophied, resting, dividing and degenerated cells, bone and red blood cells were counted. Fetuses in experimental group1 (0.5gr/kgr nano zinc oxide), were aborted and statistical results obtained from cell counts in all three regions. The experimental group2 received 1gr/kgr and group3 received 1.5gr/kgr of nano zinc oxide, showed significant changes (P<0.05 , P< 0.01, P< 0.001) in the number of mesenchymal cells, cartilage, atrophied, and muscle, hypertrophy, dividing, degenerated bone and red blood cells compared with control and sham groups. Therefore nano zinc oxide, showed significant effect on hind limb buds development in NMRI mice fetus.

Key words: nano zinc oxide, hind limb bud development, in vivo technique.





Advanced Isoconversional and Master Plot Analyses on Thermal Degradation Kinetics of Nanocamposite Reinforced with Octasilane Polyhedral Oligomeric Silsesquioxanes

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Keywords: Thermal Degradation, Nanocamposite, Activation Energy

Introduction:

Research in thermal degradation of epoxy systems is of great interest because these materials are widely used as structural adhesives, coatings and as matrices in fiber reinforced composites [1]. In polymer science, thermal methods of analysis have found important applications and among them, the determination of the kinetic parameters is crucial. For this purpose, thermogravimetric analysis (TGA) [2-3] is a common technique that widely applied to study polymer degradation kinetics.

Materials and methods:

The epoxyresinsystemusedinthisstudywasdiglycidyl ether ofbisphenolA,D.E.R.332, from Sigma–AldrichCompany with anepoxyequivalent weight (EEW) 185 g.eq⁻¹.3,3'- diaminodiphenylsulfone with a molecular weight 248.30 g.mol⁻¹ was utilized ascuring agent. The diamine and Octasilane POSS nanoparticles were purchased from Aldrich.

Apparatus:

The thermal degradation of the epoxy system containing different concentrations of polyhedral oligomeric silsesquioxanes (POSS) nanoparticles was studied by thermogravimetric analysis in order to determine the influence of both, the POSS concentration and the curing cycle on





the degradation process and to compare it with the results for the non modified system. Glass transition temperatures for the same systems were also determined by differential scanning calorimetry (DSC).TGAtestswerecarried out usingaThermogravimetryAnalyzer (TGA-50, Shimadzu, Japan)in the temperature range $25 - 650^{\circ C}$.

Result and discussion:

The DTG curves showed one stage of decomposition reaction in Epoxy/DDS/POSS systems (Figure 1).The kinetic parameters were determined by using Kissinger and Flynn–Wall–Ozawa methods. The activation energy values obtained by Kissinger and Flynn–Wall–Ozawa methods, are 155.8 kJ/mol and 158 kJ/mol respectively. The results showed that the activation energy obtained from Kissinger method was in good agreement with the value obtained using Flynn-Wall-Ozawa method.



Figure 1: TGA and DTGdynamic thermograms of DGEBA/DDS systemA) TGA thermogramsB) DTG thermograms.

Coatse-Redfern, Van-Krevelen, Horowits-Metzeger and Criado methods were also used to discuss the probable degradation mechanisms. The homogeneous dispersion of POSS cages in the polymer matrix was evidenced by SEM and XRD.

Conclusion:

The thermograms showed that a single reaction mechanism is operative for the both systems. By comparing the results, it has been concluded that the best fitting is corresponded to an A_2 (Avrami–Erofeev) kinetic model. Images from SEM measurements revealed that the used dispersion method was reliable. The obtained results indicated that a relatively low concentration of Octasilane POSS led to an impressive improvement of thermo-physical





properties of epoxy resin. Since the main application of epoxy materials in industry is in the production of different types of protective coating and knowing that the Octasilane POSS have anticorrosion properties; therefore, epoxy resin containing Octasilane POSS can be used in high performance coating systems.

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Oxidized multiwalled carbon nanotubes as efficient adsorbent for 2-(4,5-Diphenyl- 1-H-Imidazol- 2-yle)4- Nitrophenol

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In this work, an efficient adsorption system for the removal of 2-(4,5-Diphenyl- 1-H-Imidazol-2-yle)4- Nitrophenol from an aqueous solution using oxidized multiwalled carbon nanotubes(MWCNTs) has been described. The influence of effective variables suchas solution pH, contact time, initial 2-(4,5-Diphenyl- 1-H-Imidazol- 2-yle)4- Nitrophenol concentration, amount of MWCNTs, and temperature on the adsorption efficiency in batch system was examined while 2-(4,5-Diphenyl- 1-H-Imidazol- 2-yle)4- Nitrophenol content was determined via UV-Vis spectrophotometer.

Among different kinetic models (pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich model), experimental data of the removal process well fitted with the pseudo-second-order kinetic model with a high correlation coefficient. Evaluating the fitness of experimental equilibrium data by various conventional isotherm models including the Langmuir, Freundlich, and Tempkin models (based on considering R2 value as criterion) show the applicability of the Langmuir model for the interpretation of experimental data with a maximum adsorption capacity of 60 mgg_1 of adsorbent. Thermodynamic parameters (Gibb's free energy, entropy and enthalpy) of adsorption show that the adsorption process has endothermic nature.

Keywords: adsorption; *2-(4,5-Diphenyl- 1-H-Imidazol- 2-yle)4- Nitrophenol*; multiwalled carbon nanotubes; adsorption isotherm; thermodynamics and kinetics of adsorption.





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Theoretical study of structural and electronic properties of single walled pure Silicon and Boron-Silicon nanotubes

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Key words: Density functional theory, Siliconnanotube, Boron-Silicon nanotube, Band gap.

Introduction:

Due to the unique physical properties (elasticity, stiffness and deformation) and the application in various materials (semiconducting, H_2 , storage) and the probes of nanotubes, they have attracted considerable attention. In order to investigate the physical properties of single walled nanotubes, it seems that theoretical analysis are necessary to determining the real nature of single walled nanotubes and specify their properties [1].

The geometrical structure of single walled silicon and boron-silicon nanotubes is a rolling up 2-D-semigraphite sheet as a hollow cylindrical shape [2]. According to the geometrical analysis, there exist armchair, zigzag and chiral tubular structures. Single walled nanotubes are π -bonded aromatic molecular that can be either semi conducting or metallic depending upon the tubular diameter and chirality.

In this study the electronic and structural properties of single walled silicon nanotubes (n,0) zigzag for $7 \le n \le 10$ and (n,n) armchair for $5 \le n \le 8$ and single walled boron-silicon nanotubes (n,0) zigzag for $4 \le n \le 10$ and (n,n) armchair for $4 \le n \le 8$ with dangling bonds that saturated by hydrogen atoms have been investigated using density functional theory.

Methods:

In the present study, the DFT method with $3-21G^*$ and $6-31G^*$ basis sets, used to generate the geometry-optimized structure, E_g of nanotubes types with different tubular diameters and





finite tubular length up to 10 nm. Calculated E_g of nanotubes allow us to predict some physical properties of nanotubes.

Results:

The results show that an increase in diameter of nanotubes will enhance the stability energy. The phenomena might be a consequence of an increment in bond length which leads to more stability of 2-D planar lattice of nanotube.

Theoretically, boron-silicon nanotubes have a considerable stability and a dipole moment, unlike the pure silicon nanotubes, that induces some different properties. In both categoryof nanotubes, H-L gap reduces with an increase in the diameter of nanotubes which results an enhancement for electrical conductivity.

Conclusion:

In accordance with considerable stability of boron-silicon nanotubes it seems that experimental synthesis of these compounds is possible.

It is noticeable that existence of dipole moment property in boron-silicon nanotubes leads to use of these materials in some instruments such as: Sensors, SEM etc. The conductivity is a function of the diameter of nanotubes. Thus, it is possible to have a specific conductivity with controlling the average diameter of nanotubes.

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Low temperaturesolvothermal synthesis of TiO2nanocrystallite: Effect of precursor concentration on photocatalytic activity

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Keywords: "Solvothermal", "precursor concentration", "Photocatalytic", "Anatase"

Introduction:

The interest in the investigation of the photocatalyticactivity of nanocrystalline materials is associated with the promising outlook of their application in solving important ecological problems such as air and water purification from organic contaminants. Titania has been widely studied for itshigh photocatalytic properties, such as photoactivity, photochemicalstability, suitable band-gap energy, and so on. TiO₂ powders havethree common polymorphs: rutile, brookite, and anatase. Amongthem, rutile phase has the thermodynamically most stable modification of TiO₂[1]. Theanatase phase, on the other hand, has higher photocatalytic activity than the others, thus is suitable for photocatalysts. Over recent years, solvo thermal method allows the preparation of individual and multicomponentoxides with a specified composition and micromorphologyat relatively low temperatures. This can be achieved by variation of solvothermalparameters. It has found ever-expanding application for thepreparation of nanocrystalline oxide materials, amongthem are titanium dioxide-based photocatalysts.Particle morphology, crystalline phase, and surface chemistry of the solvothermal-derived TiO₂ can be easily controlled by regulating precursorcomposition and concentration, reaction temperature and time, pressure and solvent properties [2].In our previous work, effects of synthesis temperature, time and aging on photocatalyticactivity of





nano-TiO2 by solvothermalmethod were studied, but no considerable distinct in photocatalyticbehaviour for different conditions have been observed[3].

Materials and methods:

A solution of tetrabutyltitanate, TBOT, (Merck, 98%) in Ethanol (99.7%) was used as starting precursor of TiO₂. Solutions with concentrations precursor of .1M, .2M, .3M, .4M and 0.5M prepared in Ethanol solvent. HNO3 added drop wisefor pH adjusted at 1.5 in solution. Then the solswere transferred into 100 mL teflon-inner-liner stainless steelautoclaves. The autoclave was kept at 140° C for 8 h forsolvothermal process. Finally the precipitate gained waswashed by distilled water, dried at 80° C for 6 h.

Apparatus:

Structure and microstructure analysis of samples were performed using XRD (Unisantis XMD400), FE-SEM (HITACHI, S4160) techniques, TEM (HITACHI-H7100), respectively. The photocatalytic activity of the products was evaluated by the photodegradation of aqueous methyl orange solution in a self-assembled apparatus under UV light. Then absorbencies of the samples were checked on PG UV–Vis spectrophotometer (UV-T 80) after centrifugation.

Result and discussion:

In this study,nanocrystalliteanatase particles were synthesized by solvothermal process using tetrabutyltitanate (TBOT) in pure ethanol as starting material. Various parameters such as, solvothermal temperature, reaction time and precursor concentration were studied. The results show increasing reaction temperature and holding time led to increase in the average crystallite size of TiO_2 powders. As shown in fig.1 thebest photocatalytic yield was related to the sample synthesized using precursor concentration of 0.3M.







Fig1. Photocatalytic activity of TiO2 powders verus irradiation time for different precursor concentration

Conclusion:

Concentration of starting materials shows considerable influence on photocatalyticactivites of nanocrystallitetitania. It is due to strong difference of crystallite size, morphology and agglomeration tendency of obtained powders.

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Evaluation of a Coupling Strategy to Obtain Biofunctional-Magnetic Nanoparticle for Biodetection

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Keywords: "Magnetic Capture Hybridization, Iron Oxide Nanoparticle, Oligonucleotide Probe, Diagnostic"

Introduction:

Rapid and sensitive determination of pathogenic bacteria is extremely important in biotechnology, medical diagnosis and the current fight against bioterrorism [1]. It is possible to capture and detect biomolecules by the movement of magnetic nanoparticles under an external magnetic field. There are various methods to synthesize magnetic nanoparticles Among these methods, co-precipitation is a general and simple technique for synthesis of magnetic nanoparticles. Different chemical groups (carboxyl, amino, aldehyde, etc.) on the surface of nanoparticles can be used to covalently immobilize oligonucleotide probes to increase affinity of nanoparticles to the desired target.

Materials and methods:

In this work, Magnetic nanoparticles were synthesized by a co-precipitation method[1] using FeCl3.6H2O/FeCl2.4H2O and aqueous solution of NH3. Nanoparticles size distribution was determined using scanning electron microscope (SEM). The sizes of uncoated nanoparticles were in the range of 10-35 nm, whereas those of coated nanoparticles were from 10 to 50 nm Fig.2.

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P: :





Figure 2: Width distribution histograms of uncoated (A) and coated (B) nanoparticles obtained by measuring the width on SEM micrographs.

Synthesized nanoparticles were functionalized with aldehyde groups[3], Brady's test confirmed the presence of aldehyde groups on the nanoparticles[4]. NH2 modified probes were then covalently immobilized on the surface of modified particles. Ethanolamine blocker reagent was used to reduce nonspecific adsorption of the oligonucleotide on the nanoparticles. A FAM-labeled complementary oligonucleotide probe verified immobilization step. A considerable fluorescence intensity obtained after adding the probe demonstrated the ability of modified particles to capture DNA targets Table I.

	Type of	Fluorescence Intensity	Excitation		
	particles	(a. u.)	Wavelength(nm)		
4	OMNP	573.64	495		
	CNP-1	101.62	495		
	CNP-2	5.08	495		

Result and discussion:

The results showed that the oligonucleotide-functionalized magnetic nanoparticles could be used as a potential diagnostic kit in the field of medical diagnostic. The used particle coating method is a one-step and fast procedure to obtain functionalized particles that have high





affinity to NH2-labaled probes the complementary fluorescence labeled probes were captured by synthesized particles.

Conclusion:

The obtained oligonucleotide-magnetic nanoparticle conjugate has the potential of rapid, sensitive and specific detection of target complementary oligonucleotides.

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XRD evaluation of nickel-phosphorus nanoparticles lattice tensions in various thermal annealing conditions

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Keywords: Nickel nanoparticles, thermal annealing, XRD, lattice tension

Introduction:

In many production processes of nanoparticles, their controlled growth has important rule. These materials widely used in production of magnets, catalysts and surfactants and ...[1]. In this article we will investigate the heat treatment conditions of nickel-phosphorus nanoparticles. Knowing these conditions will result saving the time and have economical benefits. In the first, we produced nickel phosphorous nanoparticles and then seek to investigate heat treatment conditions [2,3].

Materials and methods:

Certain amount of nickel sulfate dissolved in distilled water. This solution slowly added to a solution of sodium hypophosphite that its pH fixed to 9 and the temperature must be 90 to 95 °C. Reaction time is 45 to 50 minutes. produced NiP nanoparticles annealed under argon gas at temperatures 110, 150, 250, 450 °C, each at 1, 2 and 3 h.

Results and discussion:

By XRD data and use of Scherrer equation, $D=k\lambda/(\delta w \cos\theta)$; we determined the approximate size of particles. Lattice tensions in samples calculated by [4], $e = (d_0 - d)/d_0$. Diffraction angle (θ), full width at half maximum (δw), the average particle size (D), the distance between the plates of crystalline samples (d) and of the standard blank (d_0) and finally, crystal tension (e)





is given in table 1. In its column one, and in Fig. 1, TA, symbolized to thermal annealing, and then, the tow numbers show temperature and time of annealing, respectively. NA is our sample that has, no heat treatment.

During the heat treatment, the XRD parameters show that crystals tensions decreased by 250 to 450 °C and 1 h. the times more than this, can affect on grain size to lower and increase lattice tension to higher values. Moreover at higher temperatures and also times, we have some compounds, that growth beside together.

Sample	2θ(°)	δw (°)	D (nm)	d (Å)	$d_{0}\left(\mathring{A} ight)$	e			
NA	45.176	5.874	1.44165	2.00188	2.020	0.0098			
TA – 110 - 1	45.012	5.975	1.44086	2.01682	2.020	0.0015			
TA – 110 - 3	45.012	5.312	1.44089	2.01161	2.020	0.0041			
TA – 150 - 3	45.463	5.507	1.65167	2.00321	2.020	0.0081			
TA – 250 - 3	47.687	0.435	20.0834	1.90636	1.9080	0.0017			
TA – 450 - 1	40.918	0.275	31.3676	2.20375	2.2100	0.0028			
		0.040							

 Table 1-XRD parameters of samples



Figure 1 - XRD spectrum of Ni-P nanoparticles.

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Impregnation of Porcelain Pots with Silver Nanoparticles via Pervaporation and Study of the Effects on Pathogens (*Escherichia coli, Staphylococcus aureus*) in the Contacted Broth

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Abstract:

Growth of Pathogenic microorganisms is one of the major challenges in food industry. An innovative method has been introduced for impregnating porcelain pots with antimicrobial silver nanoparticles. Silver nanoparticles were produced by reducing silver nitrate with hydrazine. Particles were then impregnated in porcelain pottery using a pervaporation technique. The resulting pots were characterized using SEM, EDX, XRD and AFM analyses. Antibacterial properties of the pottery were confirmed by the exposure to broth containing *Escherichia coli* and *Staphylococcus aureus*, however the beneficial effects of the pots on gram-negative (*Escherichia coli*) bacteria, compared to gram-positive (Staphylococcus aureus) bacteria, were observed. This finding is attributed to the thicker *Staphylococcus aureus* membrane compared to thinner membrane of Escherichia coli. Moreover, the higher silver particle content of the samples led to a stronger antibacterial property.

Keywords: Silver nanoparticles, Pervaporation, Escherichia coli, Staphylococcus aureus

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Synthesis and Photoluminescence Properties of Silica Capped ZnO Quantum Dots

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Keywords: Quantum Dots, Sol Gel, Photoluminescence, ZnO

Introduction:

ZnO Quantum Dots (QDs) can potentially be used as photoluminescence (PL) materials because of their wide direct band gap, easy availability, and cost effectiveness. Recently, these materials have been shown to be applicable in the manufacture of Light Emitting Diodes (LEDs), optical devices, and biological cell labeling applications [1].

In this work, ZnO quantum dots were synthesized by using a sol gel method and the effect of base catalysis (LiOH) concentration and reaction temperature on the PL and absorption spectra of samples were examined. To stabilize photoluminescence, Silica (SiO₂) were used as a matrix for ZnO QDs because it is chemically stable except in a strong acid or base, and has a low refractive index, which can contribute to effective excitation by ultraviolet light[2,3].

Materials and methods:

ZnO QDs were formed through precipitation from zinc acetate, in the presence of the base LiOH and ethanol. Four different sizes (denoted by Z1, Z2, Z3 and Z4) of ZnO-QDs were synthesized, under the molar ratio of [LiOH] / $[Zn^{2+}]$ with a value of 3.5 (Z1) and 4.5(Z3) at the mixing temperature of 40°C while Z2 and Z4 were under the molar ratio of 3. 5 and 4.5 at 70°C. TEOS was used to form a silica layer on the ZnO QDs during the coating process. Morphology and optical properties of samples were studied with XRD pattern, absorption and photoluminescence spectra.





Result and discussion:

Broad XRD peaks show formation of nanosized Wurtzite particles in all the samples.

By using the Debey Scherrer formula, the average sizes of ZnO crystals is estimated to be around 5.6, 8.2, 4.9 and 7.8 nm for Z1, Z2, Z3, Z4 respectively.

The UV-Visible absorption spectra (Figure1.(a)) of the ZnO QDs show the blue shift in absorption edge as the LiOH concentration increased while they show the red shift as the reaction temperature increased.

In The PL emission spectra (Figure1.(b)) of the ZnO QDs, the relative emission intensity was decreased as the reaction temperature increased and the emission pick maxima were shifted to lower wavelengths with increasing LiOH concentration. In higher temperature this effect was more significant.



Figure1. (a) UV-vis absorbance, and (b) PL spectra of ZnO-QDs in Ethanol solution under the excitation of UV light at λ =350nm.

Conclusions:

In summary, we have successfully synthesized stable ZnO QDs of different sizes showing strong bluish green luminescence. The stability of such QDs is achieved by using silica as the capping agent. Sizes and The PL properties of QDs have been tuned by varying the reaction temperature and LiOH concentration.





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Fabrication of TiO₂ Nanofibers via Electrospinning as High Potential Photocatalyst

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Abstract:

Polyvinyl acetate (PVAc)/TiO₂ hybrid nanofibers were fabricated electrospinning technique, which consisted of PVAc as organic segment and TiO₂ as inorganic part. SEM images revealed that the nanofibrous structure was formed. FTIR analysis indicated the newly formed associated hydrogen bond because of the hybrid effect, between PVAc and TiO₂ sol. Finally, the photo-oxidative decomposition of MO by using the TiO₂ nanofibers as photocatalyst was examined and discussed.

Keywords: Nanofibers; TiO₂; PVAc; Electrospinning; Photocatalysis

Introduction:

Since photocatalytic reactions mainly take place on the surface of the catalyst, a high surfaceto-volume ratio is of great significance for increasing the decomposition rate [1]. In general, most of the studies have been carried out with spherical TiO_2 nanoparticles, which show higher photocatalytic efficiency subsequent to a reduction in the particle size, resulting in a large surface-to-volume ratio [2]. TiO_2 -based fibers with large aspect ratio can be easily separated from solution, and thereby the disadvantages arising due to the use of spherical TiO_2 catalysts can be overcome. In addition, nanofibers are continuous and easy to fabricate into mesoporous nanofiber membranes; they also consist of nanocrystals [3]. The present study deals with a synthesis and characterization of TiO_2 nanofiber that was prepared by





electrospinning, followed by examination of photoreduction of MO. Furthermore, commercially-available TiO₂ powder of P25 was measured and compared.

Materials and Methods:

The typical synthesis procedure of prepared TiO₂ nanoparticle was adopted from reference [4]. Fibers from the solution of Titanium (IV) isopropoxide (TiP) (Merck) (1.0 ml) and PVAc (Mw=500000, Aldrich) (13.0 wt% in DMF) were electrospun onto a cylindrical target with a diameter of 8 cm (FNM Co, Iran). Morphological properties of the samples were analyzed by SEM (Philips XL- 30ESM. The extent of MO degradation using TiO₂ nanomaterials were monitored using UV-Vis spectrophotometer (Perkin Elmer Lambda2S).

Results and Discussions:

It can be seen from SEM images (Figure 1) that the nanofibers electrospun from PVAc/TiO₂ solutions are randomly distributed in the webs.



Figure 1. SEM images of PVAc/TiO₂ nanofiber (a,b), TiO₂ nanofiber (c,d), and Fiber diameter distribution (e,f).





It was found that the average diameter of the electrospun $PVAc/TiO_2$ nanofiber is decreased as nanofibers are annealed (TiO₂ nanofibers are formed), that is because of elimination of polymer.

Since the electrospun nanofibers have approximately 1-2 orders of magnitude more surface area than found in nanoparticles [5], and the nanofiber itself has a porous structure, the surface absorption of MO in the TiO₂ nanofiber is much more higher compared to the TiO₂ nanoparticles (Figure 2).



Figure 2. Photocatalitic degradation of MO by TiO₂ nanomaterials.

Conclusion:

In summary, this study also explored the nanofibrous structure, surface morphologies, and molecular structure of the electrospun $PVAc/TiO_2$ and TiO_2 nanofibers. The large specific surface area and the good shape retention of TiO_2 nanofiber membrane suggest potential applications of TiO_2 photocatalysis in fields involving environmental purification for polluted water and air, etc.

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The effect of different concentrations of nano-alumina and operating parameters on Ni-Al₂O₃ nano-composite coatings

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Key words: Composite, Morphology, Polarization, Surfactant.

Introduction:

Nickel is one of the most important metals applied by electro-deposition, because the nickel deposits possess a comprehensive variety of properties [1], such as high degree of hardness and good ductility [2]. The deposition characteristics are easily controlled by varying the composition and the operational parameters of the electrolytic bath [3]. Sulphamate baths are normally recommended for producing nickel deposits [1]. Nickel electro-deposits from nickel sulphamate electrolytes have technological advantages in yielding good physical properties such as low internal stress [4] and cathode current efficiency higher than 98% [5]. As the plating industries expand its volume of production, techniques which can speed up the process of electro-deposition and improve the properties of deposits become increasingly vital [6].....

Materials and methods:

Nickel coatings were deposited from a sulphamate bath by direct current (DC) electroplating. All solutions were prepared with analytical-grade chemicals and de-ionized water. Electrolysis was carried out in a 200 ml glass container fixed with a wooden cover containing holes to insert connecting rods to the electrodes. Rectangular steel sheets with dimensions of 3cm*2cm*0.1cm were used as cathode (substrate). A nickel sheet of 99.99% purity with dimensions of 5cm*2cm*1cm was used as anode.





Apparatus:

A DC power supply (PL-5003S, Protek, Korea) was used to control the applied current and Potential. Morphological studies of composite coatings were conducted by using field emission scanning electron microscope (FESEM) (S4160, Hitachi, Japan).....

Result and Discussion:

The influence of different concentrations of nano-alumina particles (5-20 g l^{1-}), current density (0.5-3.0 A dm²⁻) and agitation speed of solution (300-1000 rpm) on the properties of composite coatings was studied. Result obtained showed that increasing nano-alumina up to a certain concentration, improved corrosion potential to the most positive side and corrosion current density to the lowest side. The greatest increase in R_p was obtained for the composite coating which was reinforced with optimum concentration of nano-alumina particles. There is also an optimum values for agitation speed of solution and current density in which the incorporation of nano-alumina particles in the composite coatings will be the most.....

Coclusion:

As nano-alumina concentration increased up to an optimum value in the electrolyte, microhardness of the coatings improved to 587 HV. Corrosion potential shifted toward more positive values with corrosion current density shifted toward lower values by increasing the concentration of nano-alumina particles up to 10 g/l in the electrolyte. There was an optimum value for current density in which nano-alumina particles had the highest degree of incorporation in the coatings and made the grains size smaller.

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Analysis of the effect of chirality on stress intensity factor of epoxy/SWCNT based on multi-scale method

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Keywords: Carbon nanotube, Nanocomposite, Stress intensity factor, Multi-scale.

Introduction:

Carbon nanotube (CNT) is considered as a new generation of material possessing superior mechanical, thermal and electrical properties. Recent investigations [1,2] have shown that CNTs when aligned perpendiculars to cracks are able to slow down the crack growth by bridging up the crack faces. In this research a multi-scale analysis and finite element (FE) method are proposed to study the interaction of nanotubes and matrix at the nano-scale near a crack tip. Opening mode for bridging condition (SWCNT is orthogonal to crack and crack is in middle of representative volume element RVE) with epoxy/SWCNT 0.1% wt is considered. The effect of the chirality of armchair and zig-zag single walled carbon nanotubes (SWCNTs) in a polymer matrix in presence of van der Waals (vdW) interaction as interphase region on the fracture behavior were studied. It was found that the chirality has a significant effect on stress intensity factor of nanocomposites.

Modeling:

Multi-scale simulation, from the nano-scale to the macro-scale or in the reverse order, has the capability to help better understand the toughness mechanism. Multi-scale modeling accomplished with either of two opposite approaches. One way is starting from the (RVE) or unit cell and moving up to higher scales [3,4], i.e., the bottom-up or up-scaling or micromechanics analysis method. The other one starts from the structural scale, moving down




to lower scales [5], i.e., the top-down or downscaling or global-local method. In this research top-down is utilized. The 3D model is developed using the ANSYS commercial FE code.

Results and discussions:

The 3D FE model is proposed to study the effect of chirality of nanotubes on stress intensity factor of RVE (Fig.1). Stress intensity factor (K_I) results for RVE with armchair and zig-zag nanotubes are shown in Table.1. These nanotubes have similar length.



Figure1: (a) Finite element meshes of RVE (iso view) (b) Stress contour of RVE (last step of multi-scale modeling)

Nanotube	Chirality	Radius	Length	$K_{I}(MPa m^{1/2})$
	(5,5)	3.392	99.68	0.488
armchair	(10,10)	6.785	99.68	0.420
	(15,15)	10.177	99.68	0.381
	(20,20)	13.57	99.68	0.342
	(5,0)	1.959	100.181	0.570
zig-zag	(10,0)	3.917	100.181	0.482
	(15,0)	5.876	100.181	0.457
	(20,0)	7.834	100.181	0.384

Table	1:	Stress	intensity	factor f	or arm	chair	and	zig-zag	nanotubes
								0 0	

Conclusion:

Results show that nanotubes have evident influence on crack resistance of nanocomposites. Also chirality has a significant effect on stress intensity factor of RVE. The results represent that in both kind of nanotubes by increasing chirality, the stress intensity factor decrease. Decreasing stress intensity factor due to improving the fracture behavior of nanocomposites.

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Use of nanostructure phragmites australies for nitrate removal

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Key word: Phragmites australis, Nitrate removal, aqueous solution, Nanostructure adsorbent

Introduction:

There are various techniques for nitrate removal from contaminated water. The ion exchange process seems to be the most appropriate for water contaminated by nitrate because of its ease of application, usefulness, selectivity, recovery and relatively low cost (1). The reuse of industrial wastes in the agriculture segment is increasingly encouraged, principally in developing countries. In this study phragmites australis was used as adsorbent for nitrite removal.

Material and Methods :

The phragmites australis was collected in the area of Khuzestan province, Ahvaz. In this work, preparation of anion exchangers based on aminated intermediate is conducted (2).

Adsorption of nitrate ions by phragmites australis was studied by batch experiments. Stock solution of NO₃⁻ was prepared by dissolving KNO₃ in distilled water having 120 mg/L of NO₃. A fixed amount of dry adsorbents (0.3 g) and 30 mL of KNO₃ solution were put in capped volumetric flask and shaken at 120 rpm. After centrifuging of adsorption samples, they was filtered using wattman 42 filter paper to separate the water from the absorbent and the filtrate was analyzed in a UV-Vis spectrophotometer (model Hach, DR5000). In order to study the controlling mechanisms of the adsorption process, the pseudo-first-order, pseudo-second-





order, intra particle diffusion, power and elovich models were used to test the experimental data. In kinetic studies, 30 ml KNO₃ solution and 0.3g of adsorbent was agitated. The mixtures were shaken at 120 rpm. Batch experiments were repeated for different periods between 5 to 210 minutes until reaching the adsorption equilibrium.

Results and discussion:

Particle size of phragmites australis adsorbent was between 51.47 to 406 nanometer. The fittings of the experimental kinetic results to the five models are presented in Table 1.

Table1. Kinetic models for NO_3^- removed from adsorbents

Pseudo first		pseudo second		Elovich model		Power		Intraparticle	
ord	er	order				function		model	
q _{exp}	9.35	q _e	9.9	α	4.02	a	2.92	k	0.348
q_e	6.5	K ₂	0.01	β	0.65	b	0.228	с	4.684
K_1	0.032	R^2	0.993	\mathbb{R}^2	0.901	R ²	0.84	R^2	0.75
R ² 0.984	0.094	RMS	0.295	RMS	0.555	RMS	0.75	RMS	RMS E 0.88
	0.984	Е	0.285	Е	0.555	Е	0.75	Е	
RMSE	2.904			N/					

Among the models examined, the higher RMSE values obtained for the pseudo first-order model (Table1). By considering table 1, intraparticle diffusion equation have intercept 4.684 indicated that plot did not pass through the origin. Suggesting that the intraparticle diffusion was not the sole rate-controlling step of initial adsorption. Comparison adsorption capacity (q_e) showed that for pseudo second order, predicted q_e values (9.9 mg/g) are overestimated as compared to the experimentally observed (9.35mg/g) value. But in pseudo first-order, predicted q_e values (6.5mg/g) are lower than experimentally observed value. The experimental q_e values for pseudo-first-order model did not agree with the calculated ones, obtained from the linear plots (Table 1). The results showed that the calculated and experimental equilibrium uptake value fit well to pseudo-second-order rate model. The same result obtained by other research (3, 4).





Conclusion:

In this paper the suitability of the kinetic models for the adsorption of nitrate on the Phragmites australis was investigated. Adsorption kinetic data were analyzed using the pseudo-first-order, pseudo second order, intraparticle diffusion, power and elovich model. The results shown the process can be described by a pseudo-second-order model. Nanostructure Phragmites australis has adsorption properties due to softer and more pores in its structure, high surface area and high sorption capacities. Since nanostructure phragmites australis are waste material from hand carving, the treatment method seems to be economic.

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Nanoparticles assembly of γ -Al₂O₃ nanorods using γ -AlOOH as precursor

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Key words: γ-Al₂O₃, nanorod, γ-AlOOH.

Introduction:

One phase of alumina, the γ -phase is widely used as catalyst, catalyst support and adsorbent as well as Al₂O₃ is a ceramic metal oxide of great importance as building material, refractory material, electro technology, electronics and biotechnology electrical and heat insulator, attributed to its high strength, corrosion resistance, chemical stability, low thermal conductivity, and good electrical insulation [1,2]. It is conventionally prepared by heating the hydrated trihydroxides, gibbsite and bayerite, to temperature of > 1000 °C [2,3]. In this work, the conventional chemical method for synthesis of alumina is to dehydrate boehmite nanorods which that prepared with hydrothermal method, but the morphology of alumina remains the same.

Materials and methods:

For preparation of γ -Al₂O₃, the γ -AlOOH nanorods [5] was put into a ceramic crucible in a tube furnace and heated to the temperature of 600 °C for 5 h in air with a heating rate of 10 °C/min.

Result and discussion:

X-ray diffraction (XRD), TEM, FESEM and FTIR were used to characterize morphology and structure of the synthesized γ -Al₂O₃ nanorods. The XRD pattern of the calcined sample





indicates that a transformation from boehmite phase to γ -alumina after calcination occurred. All the peaks can be indexed to a cubic unit cell of γ -alumina (JCPDS PDF No.001-1303) and as well as FTIR analysis showed that γ -alumina after calcination occurred [4]. TEM and FESEM images showed that the sample consists of a large number of nanorods with a length of 30–250 nm with the average width of 13 nm.



Fig 1: (A) XRD pattern and (B) FTIR spectrum of the $\gamma\text{-}Al_2O_3 \text{ nanorods}.$



Fig 2: (A) Representative FESEM image and (B) TEM image of γ-Al₂O₃ nanorods.

Conclusion:

In conclusion, alumina nanorods were successfully prepared by using AlOOH nanorods as precursor. The synthesis of uniform single-nanorod γ -alumina is highly helpful to study various properties of these nanorod structures and sample is expected to find potential applications in catalysis and adsorption.

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The rule of basic pH in characterization of AlOOH nanoparticles and nanostructures

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Key words: AlOOH, Basic pH, NaOH, Hydrothermal, nanoparticle, nanostructure.

Introduction:

Boehmite is widely used for industries, such as adsorbents, catalysts, and catalyst supports due to their unique properties and also used for building units and directing template in the preparation of core-shell rods [1]. In recent years, various morphologies of boehmite, such as nanotubes, nanofibers, nanobelts, nanowires and flowerlike 3D nano-architectures have been synthesized through a variety of routes [2]. In this work, hydrothermal route was used to fabricate high-quality pure boehmite nanoparticles and nanostructures in basic pH of 10 and 12 respectively.

Materials and method:

In a typical synthesis experiment, solution NaOH (2M) was added drop by drop to the 40 ml of solution of $Al(NO_3)_3$ (0.4 M) to give lacteous precipitates (pH=10 and 12), then the mixture was transferred into a 100-ml Teflon-lined stainless autoclave. The autoclave was maintained at 200 °C for 24 h, and then was allowed to cool to room temperature. The products were separated from the solution by centrifugation, washed by water tow times and dried at 60 °C for 24 h.

Result and discussion:





The prepared samples were characterized by XRD, FESEM, TEM and FTIR. Fig. 1(A) shows the X-ray diffraction patterns of the samples synthesized in basic pH of 10 and 12. In tow sample all the diffraction peaks can be indexed to the orthorhombic AlOOH (Ref: JCPDS No. 21-1307). More characteristics of AlOOH are also observed in its FTIR spectrum (Figure 1B). The intensive bands at 3290 and 3090 cm¹ belong to the v_{as} (Al)O-H and v_{s} (Al)O-H stretching vibrations. These absorption bands agree precisely with the ones previously reported in the literature [3]. The morphologies of the AlOOH were investigated with TEM and FESEM. Fig. 2A and C shows the sample prepared at pH=10 consist of nanoparticles with the average width of 40 nm. This indicates that the nano-AlOOH is significantly sensitive to the pH value. By the pH of 10 and 12, the 2D nanoparticles (Fig 2A and C) and 3D nanostructures (Fig 2B and D) of AlOOH could be prepared by this facile hydrothermal method.



Fig 1: (A) XRD pattern and (B) infrared spectrum of the nano-AlOOH.



Fig 2: (A and C) FESEM and TEM images in pH=10 and (B and D) in pH=12 of the samples.

Conclusion:





In this study, the AlOOH (boehmite) nanoparticles and nanostructures were synthesized with hydrothermal method by regulating the pH values of the reaction solution. By increasing of pH from 10 to 12 the growth of boehmite nanoparticles could be attributed to the lamellar structure of AlOOH.

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Study of Deposition Time and Concentration Effects on Properties of Nanocrystalline ZnS Thin Films

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Key words: ZnS, Thin films, Deposition time, Semiconductor

Introduction:

There has been considerable interest in the study of semiconductor nanocrystals over last three decades [1]. Wide band gap II-VI semiconductors are expected to be novel materials for optoelectronic devices. Zinc sulphide belongs to II-VI group compound materials with large direct band gap between 3.4 to 3.70 eV depending upon composition [2]. Several techniques such as spray pyrolysis, pulse plating technique, RF sputtering, MOCVD and solution growth deposition technique have been used to deposit ZnS thin films. In solution growth deposition, controlled chemical reactions play a key role for the deposition of the thin films. In the present investigation, we study the effects of deposition time and concentration of precursor solution on the properties of nanocrystalline ZnS thin films prepared by SGD technique [3].

Materials and methods:

The ZnS thin films were deposited onto commercial microscope slide using triethylamine (TEA) solution as a complexing agent for zinc ions. Six of glass slides (substrates) were immersed in a dilute precursor solution containing zinc, TEA and a source of sulfide at 70°C. The chemical solution was not stirred during the film deposition. The coated substrates were removed at the end of the chosen duration of deposition (1 till 6 hours), washed in de-ionized water, dried in air at room temperature, and subjected to further analyses.





The crystal structure and grain size of the prepared films were analyzed by x-ray diffraction (XRD). The elemental composition was determined by EDX technique. The surface morphology was studied by field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM).

Result and discussion:

The XRD measurements indicated that the ZnS thin films had a cubic structure. The values of the band gap energy, E_g , were calculated from the UV-Vis spectra and the average sizes of the the nanocrystallites have been calculated using the Debye-Scherrer equation. Uv-visible measurements showd an average transparency of around 75- 85% in the visible rang. The obtained FE-SEM images of the ZnS thin films prepared at different concentrations of Zn^{2+} ions showed that the ZnS films deposited at molar concentrations of 0.03 and 0.06 have a dense, compact and uniform structure while that of deposited at molar concentration of 0.12 have some big pinholes and cracks. Deposition time effect on films thickness was also studied by FE-SEM. Fig. 1 shows FE-SEM images of cross sectional for ZnS thin films deposited at different deposited at different deposition times.



Fig.1-FE-SEM images of cross sectional for ZnS thin films deposited at: a) 1h, thickness=123nm, and b) 6h, thickness=204nm, Image magnification is 50000.

Conclusion:

In this work , we prepared ZnS thin films by solution growth deposition method in a convenient and simple condition. We observed the concentration changes of the precursor solution and deposition time could greatly affect on quality, thickness, roughness, and





nanocrystalline size of ZnS thin films. The ZnS films prepared in 0.06 molar concentration of Zn were more homogeneous and dense, rather than other concentrations.

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Comparing Photocatalytic activity of In-V Photochemical co-doped TiO₂ sol-gel and Hydrothermal Nanoparticles

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Key words: TiO₂, nanoparticles, photocatalytic activity, photochemical deposition

Introduction:

Titania is one of the best materials as photocatalyst for electrical and optical properties, low cost, high photocatalytic activity, chemical stability, non toxic [1].

Photochemical reactions result from the absorbance of light by the starting reagent conditions for a successful course of the photoreactions are:

1) There is good matching between the emission of the light source and the absorption by the reagent

2) Nothing interferes with the photons before they reach the target molecular

3) Nothing interferes with the electronically excited states and quench them before they react [2,3].

Material and methods:

Different materials were used for preparing mentioned nanoparticles. TTIP [Ti [OCH(CH₃)₄] (Merck, >98%), Glacial Acetic Acid (Merck, >99.8%), Ammonium metavanadate (NH₄VO₃, Merck), Indium chloride (InCl₃, Merck) and dionized water was produced by a Smart-2-Pure type. In this work, first we synthesized the TiO₂ nanoparticles by sol-gel and hydrothermal methods. The photocatalyst was characterized by FT-IR, SEM, TEM, DRS, EDX and XRD analysis. After this, different percents (0.05-2) of In-V co-doped TiO₂ catalyst was prepared by photochemical reduction method by using UV light.





Result and discussion:

In this paper, methyl orange was used for study photocatalytic behavior of pure TiO_2 nanoparticles synthesized by sol-gel and hydrothermal methods that doped with 1:1 ratio In-V to Ti by photochemical reduction process Under visible and UV lamps. Result show In-V binary doped on hydrothermal TiO_2 compared to sol-gel TiO_2 had the best operation in competition between interfacial change transfer ratios to rate of hole-electron recombination. 0.2% In-V codoped on hydrothermal TiO_2 could reduce the recombination rate as electron trapper. Login Indium to V-Tio₂ structure prevent from particle growth and In^{3+} change to In^{2+} as electron trapper and form lower energy level from conduction band (CB).

Conclusion :

The metal ion dopants influence the photo efficiency of TiO₂ by acting as electron or hole trap center within band gap of TiO₂ and alter the e^-/h^+ pair recombination rate through following process. In this paper, different molar percent of In-V codoped on hydrothermal and sol-gel pure TiO₂ by UV photochemical reduction process that In³⁺, V³⁺ deposited on TiO₂ surface as In⁰, V⁰ and photodegradation activity of the MO can improve when 0.2% In-V codoped on hydrothermal TiO₂ and reduce recombination rate as electron trapper. In photochemical doped method, metal ions were into holes in TiO₂ structure with zero oxidation number (Mⁿ⁺ \rightarrow M⁰)

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Chemical synthesis and characterization of poly(3-methylthiophene)/SiO₂ nanocomposites by inverted emulsion technique

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Key words: Nanocomposite, Poly(3-methylthiophene), Surfactant, Electron microscopy.

Introduction:

Poly(3-methylthiophene) (P3MTh) as one of the most important electrically conductive polymers is both organo-soluble and melt processable. It has good chemical and environmental stability with excellent electronic and optical properties suitable for various device applications [1]. Moreover, it has been demonstrated that the deposition of metal and metal oxide nanoparticles in polymer matrixes results in advanced materials, so-called polymer-based nanocomposites [2,3]. In this study, P3MTh/SiO₂ nanocomposites were synthesized by inverted emulsion technique using two anionic emulsifiers including sodium dodecylbenzenesulfonate (SDBS) and sodium poly(styrene sulfonate) (SPSS).

Materials and methods:

All chemicals were purchased from Sigma-Aldrich and used without further purification. Firstly, into a 100-mL round-bottomed flask, toluene (40 mL), SDBS or SPSS (0.500 g) and nanosized SiO₂ (0.050 g) were poured, respectively while stirring at room temperature. In the second step, the solution of 3-methylthiophene monomer (7 mmol, 0.6871 g) in toluene (10 mL) was added dropwise to the vessel. Finally, the solution of FeCl₃ oxidant (7 mmol, 0.6871 g) in deionized water (10 mL) was added. The mixture was then stirred for another 3 h at room temperature to yield a greenish black mixture. Methanol (100 mL) was added to the system to precipitate the products.





Apparatus:

FT-IR spectra of the samples were recorded on a PERKIN ELMER RX I FT-IR spectrometer. UV-vis spectra of the diluted solutions in DMSO were taken with a PERKIN ELMER PTP-1 Peltier System. XRD patterns were performed with film specimens on a Bruker Advance D5 X-ray diffractometer with Ni-filtered Cu/Ka radiation (30 kV, 25 mA). The morphologies were determined with a S-A1600 SEM and a Philips EM 430T TEM. TGA was performed on a Mettler TA 5000 system under N₂ at a heating rate of 20 °C.min⁻¹.

Results and discussion:

In this work, three samples were prepared: (1) P3MTh/SiO₂ nanocomposite with participation of SDBS as micromolecular anionic surfactant (2) P3MTh/SiO₂ nanocomposite with participation of SPSS as macromolecular anionic surfactant (3) pure P3MTh with participation of SDBS. The oxidative polymerization occurs at the interface between the aqueous and the organic phases, since the oxidant FeCl₃ is present in the aqueous solution and 3-methylthiophene in the organic phase. To characterize the nanohybrid obtained, in addition to FT-IR and UV-vis spectroscopies, some other analyses including XRD, SEM, TEM, and TGA were also done. For example, Figure 1 shows the FT-IR spectra (a) and XRD diffractograms (b) of the samples obtained, respectively.



Figure 1. FT-IR spectra (a) and XRD diffractograms (b) of the resulting nanocomposites.





Conclusion:

A facile and efficient route was introduced for the preparation of P3MTh/SiO₂ nanohybrid materials based on a chemical oxidative technique comprising inverted emulsion systems in the presence of two anionic surfactants. It was also concluded that the surfactant type play important role in the course of the polymerization reactions.

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Preparation and characterization of poly(3- methylthiophene)/SiO₂ nanocomposites: Chemical oxidative method in binary organic solvents

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Key words: Nanocomposite, Binary solvents, Poly(3-methylthiophene), Nano-SiO₂.

Introduction:

Poly(3-methylthiophene) (P3MTh),due to the presence of lateral CH₃ group, shows a significant increase in solubility, fusibility, and luminescence compared to polythiophene [1]. In 2010, the idea of utilizing binary miscible organic solvents was proposed for pure polythiophene by S.S. Jean *et al.* [2]. This successful route can be generalized toP3MTh synthesis as well. In thepresent work,this new strategy has been employed to prepare P3MTh/SiO₂nanocomposites using chloroform/acetonitrile binary solvents. At first, a homogenized and stabilized nanofluidis prepared with nano-SiO₂powder and sodium dodecylbenzenesulfonate (SDBS) or sodium poly(styrene sulfonate) (SPSS) stabilizers in chloroform by sonication. Next, 3-methylthiophene and the highly concentrated solution of oxidant in acetonitrileare added to this nanofluid.

Materials and methods:

To prepare CHCl₃-based nanofluids, SDBS (or SPSS) anionic surfactant (0.4326 g) was fully dissolved in CHCl₃ (75 mL). Nano-SiO₂powder (0.1125 g) wasthen added to these mixtures. Next, the vessels were settled into an ultrasonic bath at 40 °C.3-Methylthiophene (1.6 mL) was poured to these nanofluids. A solution of iron (III) chloride (12.1660 g) in CH₃CN (40 mL) was added dropwiseto the previously-prepared nanofluids ofSiO₂in CHCl₃ at 0 °C. The reactions were allowed to proceed for another 24 h under the same condition. A final sonication of the products in deionized water and acetone was also done to unbraid the





contexture of the samples bulks. The two nanocomposites obtained were then dried for 24 h at 60 $^{\circ}$ C.

Apparatus:

FT-IR spectra of the samples were recorded on a PERKIN ELMER RX I FT-IR spectrometer. XRD patterns were performed with film specimens on a Bruker Advance D5 X-ray diffractometer with Ni-filtered Cu/Ka radiation (30 kV, 25 mA). UV-vis spectra of the diluted solutions in DMSO were taken with a PERKIN ELMER PTP-1 Peltier System. TGA was performed on a Mettler TA 5000 system under N_2 at a heating rate of 20 °C.min⁻¹. The morphologies were determined with a S-A1600 SEM and a Philips EM 430T TEM.

Results and discussion:

Structures of the nanocomposites were thoroughly confirmed by FT-IR spectra of the resulting samples (Figure 1a). In addition, from XRD diffractograms both the presence of SiO_2 nanoparticles and their mean sizes were clearly determined (Figure 1b). The nanocomposites obtained were also characterized by their UV-vis absorption spectrum, SEM and TEM images, and TGA thermograms.



Figure 1.FT-IR spectra (a) and XRD diffractograms (b) of the resulting samples.

Conclusion:





Binary miscible solvents to preparepolymer-basednanohybridsusing different kinds of surfactants open a new window toward us in the field of nanotechnology.From the TG analyses it was proved that this route results in P3MTh/SiO₂nanocomposites with higher thermal stability.

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Enhanced photocatalytic and antibacterial performance of nanosized Ag/ZnO

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Keywords: Nano Ag/ZnO, Photocatalyst, antimicrobial, 4-Nitrophenol, E.Coli

Introduction:

The photocatalytic degradation of organic pollutants in water, using semiconductors such asTiO₂ and ZnO, has attracted extensive attention during the last two decades [1]. Previous studies have proved that such semiconductors can degrade organic pollutants and bacteria under UV light irradiation [2]. However, the fast recombination rate of photogenerated electron/hole pair hinders the commercialization of this technique. This has led to great interest in improving the photocatalytic and antibacterial performance of semiconductors by suitable modification. In this work, we developed a facile low-temperature route to deposit metal silver on the surface of spherical-shaped ZnO to form Ag/ZnO nanostructures.

Methods:

For the preparation of Ag/ZnO nano catalysts with different Ag loading, Photo reduction method was used. To test for the photo degradation of 4-NP by the catalysts, 250 mg of each catalyst was suspended into 50 ml aqueous solution containing 20 ppm 4-NP. The antimicrobial activities of the samples were evaluated by the diameter of the E.Coli

Results and discussion:

Figure 1 shows XRD patterns of Ag/ZnO nanoparticles with different Ag loadings. After lower Ag loading (≤ 0.5 wt%) on the ZnO, no characteristic diffraction peak corresponding to Ag or Ag compound impurity phase and no detectable structural change is observed for the





ZnO catalyst, but with higher Ag loading($\geq 1.0 \text{ wt\%}$), It should be pointed out that a residual phase of silver is observed by XRD. Figure 2 shows the TEM images of Ag/ZnO. The mean particle size of them is 20-35 nm





Photodegradation of 10 ppm nitrophenol solution was used to evaluate the performance of Ag/ZnO photocatalyst. The results of the photocatalytic degradation of nitrophenol in aqueous suspensions showed that silver modification greatly improved the photocatalytic efficiency of ZnO nanocrystallites. The enhancement of photocatalytic and antimicrobial performance is due to the fact that the modification of ZnO with an appropriate amount of Ag can increase the separation efficiency of photogenerated electrons and holes in ZnO, and the improvement of photo stability of ZnO is attributed to a considerable decrease of the surface defect sites of ZnO after the Ag loading.

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Degradation of 4-Nitrophenol (4-NP) Using Novel Composites as ZnO Nanoparticles Supported on Zeolites

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Keywords: Nano ZnO, Zeolite, Photocatalyst, 4-Nitrophenol, Degradation

Introduction:

Until now, various methods have been employed to prepare ZnO nanoparticles with extremely small diameters including precipitation of colloids in solution [1], thermal decomposition methods [2], pulsed laser deposition (PLD) [3]. In general it is very difficult to avoid the aggregation of ZnO nanoparticles during the preparation. This work aims to resolve this problem via the growth of ZnO nanoparticles inside the channels of a porous matrix such as zeolite. Zeolites are crystalline nano porous materials possessing interconnected Channels those are accessible to molecules of suitable size.

Methods:

For the preparation of ZnO/HZSM-5, ZnO/Clin nano composites, polymer pyrolysis method was used. To test for the photo degradation of 4-NP by the catalysts, 250 mg of each catalyst was suspended into 50 ml aqueous solution containing 20 ppm 4-NP. Photo catalytic degradation was performed at room temperature (25 °C).

Results and discussion:

In the present paper, hosts of micro porous aluminosilicate such as HZSM-5(MFI type) and Clinoptilolite (HEU type) are used to encapsulate ZnO clusters by using poly acryl amide





pyrolysis method and their photocatalytic activities are tested for degradation of 4-NP for the first time.

The catalytic activity of all specimens was tested by carrying out the 4-NP degradation. The results revealed that zeolites play a key role in the adsorption of 4-NP. HZSM-5 is found to adsorb more 4-NP than HY and Clinoptilolite. The higher activity of supported ZnO is due to improved adsorption of 4-NP and efficient delocalization of photogenerated electrons by the electrostatic field of HZSM-5 support. The time required for complete mineralization of 4-NP under ambient visible light over ZnO/HZSM-5 was 75 min.

Conclusion:

ZnO/zeolite nano composites were successfully synthesized by a poly acrylamide gel method for the first time. The catalytic activity of all specimens was tested by carrying out the 4-NP degradation. The results revealed that zeolites play a key role in the adsorption of 4-NP. HZSM-5 is found to adsorb more 4-NP than HY and Clinoptilolite.

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Synthesis of Vertically Aligned Carbon Nanotubes Using FC-CVD Method

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Key words: Vertically aligned Carbon Nanotubes, Chemical vapor deposition, Floating Catalyst.

Introduction:

During the last two decades, Carbon nanotubes represent a fascinating new material that has attracted much attention and scientific interest subsequently followed to identify their remarkable properties and potential applications. Chemical Vapor Deposition (CVD) method is the thermal decomposition of a gaseous or volatile compound of carbon (carbon source), catalyzed by metallic nanoparticles. Among the available CVD processes, floating catalyst CVD (FC-CVD) has attracted scientific attention because it ensures continuous growth of high purity nanotubes, at a low reaction temperature, low cost and facile fabrication process [1-2].

Materials and methods:

Due to most organic gases are toxic, dangerous and difficult to store or transport, accordingly one aromatic compound –toluene- has been used for CNTs synthesis. It is well known that the choice of support material and the catalyst represent key issues for the CVD growth of nanotubes [3]. Quartz (SiO₂) is a good substrate and ferrocene is a suitable catalyst for nanotube growth.

Apparatus:

The FC-CVD reactor (Fig. 1) consisted of a horizontal quartz tube (100 cm long, 45 mm diameter and 1.8 mm wall thickness) housed in a cylindrical furnace 50 cm long.







Fig. 1 – Schematic diagram of FC-CVD method for growing VA-CNTs

Result and discussion:

Vertically aligned carbon nanotubes (VA-CNTs) have been produced by controlling flow rate, temperature and catalyst nanoparticles using a FC-CVD technique. They were synthesized on quartz substrates at 800°C from toluene as a carbon source. VA-CNT Samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM). The synthesized CNTs have a length of 500 μ m and diameters ranging from 120±40 nm.







Fig. 3 – TEM micrographs, inner and outer diameter of samples are (a) 8 and 85 nm and (b) 10 and 140 nm, respectively.





Conclusion:

In this paper, we report an efficient process to grow well-aligned carbon nanotube (CNT) arrays with a good area distribution density (about 5.6×10^7 CNT/mm²). The CNT filaments form a strength structure and exhibit a good vertical alignment. The remarkable properties of CNTs make them attractive for separation applications, especially for water and wastewater treatment.

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Study of relationship quantitativeenthalpy absorption: nanotube-anionicsurfactant system as a case model

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Keywords: Nanotube, Enthalpy, Anionic surfactant, Structural properties, Neural network.

Introduction:

The undirectional growth of materials to form nanowires or nanotubes has attracted enormous interest in recent years. CNT consist of graphitic sheets, which have been rolled up into a cylindrical shape[1].These materials can produce as single-wall tube and multi-wall. Carbon nanotube as first generation products of nanotechnology in the 1991 has opened new world for scientists.Function of carbon nano-tubes, opened new horizons in the study of biological properties. With inventing new methods for solubility of carbon nanotube in water and biological environments problem of CNT solubility has solved. The carbon nanotube can be function byHydrogenation [2], Cycloadditions[3], Polymer Composites[4], surfactants[5] and... in two ways attracting non-covalent and covalent . thus they would be suitable carriers for transfer drugs material into the body tissues and cells. In this method, function of nanotubewith surfactant by attracting non -covalent and effects of structural parameters on enthalpy adsorption of surfactant on carbon nanotube is studied.According to the results pol and hyd have the greatest effect on the enthalpy.

method and material:

In this work we have used PM6 semi-empirical method implemented. These miempirical method PM6 was designed primarily for the investigation of molecular species of biochemical interest. That is, the objective of parameter optimization was to reproduce the properties of





molecules.In this work we have used PM6 semi-empirical method implemented in MOPAC2009 software package.All calculations performed for estimation structural properties done with Hyperchem7.1 package base on popular molecular mechanic force field implemented in this software.In order to find the most influential structural parameters on absorption enthalpy, Adaptive Neuro Fuzzy Interface System (ANFIS) was used.

Result and discussion:

The structural parameters of surfactant molecules is obtained based on PM6calculation.In order to simulate the absorption process, we construct a model consist of surfactant molecule 1.54Å and 3.08 Å apart from nanotube surface, for absorbed and non absorbedsurfactant molecules.The abovementioned distances were adopted based on van der waals radius of carbon atom.Based on abovementioned algorithm and frequency calculation enthalpy of absorption was calculated and the results were shown in Table 1.

C14H29NaO4S	-10.56	-11.29	-1080.66			
C12H29NO4S	-9.916	4.104	-2711.42			
C12H25KO4S	-1.337	-13.81	-1315.73			
C12H25NaSO4	-5.211	16.85	-1397.19			
C18H35NaO2	-9.201	-13.12	-3334.67			

Tabel1. Estimated enthalpy of absorption of studied anionic surfactants molecules

Conclusion:

Based on frequency calculations, the thermodynamic properties of process were calculated. Hydration energy and polarizability of surfactant have a minimum RMSE that means this quantities have the most influence impact on nano tube. According to the results hydration energy and polarizability have the greatest effect on the Δ H absorbed of nano tube.





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5th Physical Chemistry Confit





Highly selective extraction and preconcentration of ultra-trace level of mercury ion in water and fish samples using Fe₃O₄-magnetite-nanoparticles functionalized by triazene compound prior to its determination by inductively coupled plasma-optical emission spectrometry

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In this paper, new modified magnetite nanoparticles functionalized with Triazene groups were designed and synthesized for extraction/preconcentration of sub-ppb level of mercury ions in water and fish samples prior to its determination with inductively coupled plasma optical emission spectrometry (ICP-OES). In the separation process, aqueous solution of Hg²⁺ ions was mixed with 150 mg of Fe₃O₄ magnetite nanoparticles modified with 1-(p-Acetyl phenyl)-3-(o-ethoxy phenyl) triazene (AET) and then external magnetic field was applied for isolation of magnetite nanoparticles containing mercury ions. Experimental conditions for an effective adsorption including pH, sample volume, eluent concentration and existing of co-existing ions and Under the have been studied established. optimal extraction and preconcentration conditions, the limit of detection (LOD) of 0.04 ng mL⁻¹ and the relative standard deviation (R.S.D) of 2.09% (n = 5) were achieved by ICP-OES. The sorption capacity of functionalized Fe₃O₄ magnetite nanoparticles under optimum conditions has been found to be 10.26 mg of mercury ion per gram at pH 7 with the preconcentration factor of 500 (2 mL of elution for a 1000 mL sample volume). Standard solutions containing Hg²⁺ in the concentration range of $0.2-200 \text{ ng.mL}^{-1}$ were examined by the proposed procedure and it was observed that calibration curve was linear in this range ($R^2 = 0.999$). The special advantages of





proposed method are high enrichment factor, fast separation and low detection limits compared with other methods.

Keywords:Preconcentration; mercury determination,magnetite nanoparticles; Fe₃O₄; inductively coupled plasma-optical emission spectrometry (ICP-OES).

Introduction:

The development of new methods for extraction, preconcentration and determination of emerging contaminants in environmental samples has been always a key area for analytical chemists. For this reason, extensive research has been focused on developing sensitivity, relative simplicity, accurate, speed and cost effective methods for quantification of ions and compounds which have industrial importance and affect human health.Mercury is one of the most toxic ions needing to be controlled precisely. Mercury is a heavy metal that occurs in different chemical and physical forms in the environment. It is a highly toxic and cumulative poison. Mercuric ion can show persistent character in the environment and living organism. Toxic effects include damage to the brain, kidney, and lungs. Total mercuric ion concentration in Marine species and natural water is about 0.1–200 ng mL⁻¹ and the allowed mercurv level set by World Health Organization (WHO) for drinking water is 1 ng mL⁻¹.[1,2]Therefore, we need to develop new methods for determining different mercury species with high sensitivity and good accuracy.Solid-phase extraction (SPE) has become the most common samplepretreatment method for trace enrichment, matrix simplification, and medium exchange in environmental samples because it has several advantages such as high enrichment factor, reusability of adsorbent, safety and is environmentally friendly.[3]This method is very simple and fast separation that needs a little amount of adsorbent for extraction.

Results and discussion:

1. Preparation oftriazene-modified magnetic Fe₃O₄-nanoparticles (AET-APS-FMNPs)

The magnetic nanoparticles (FMNPs) were prepared according to Ref. [4] and shown schematically in Fig. 2. Briefly, FeCl_{3.6}H₂O (11.68 g) and FeCl_{2.4}H₂O (4.30 g) were





dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring at 85 °C. Then, under intensive stirring, 20mL of 30% aqueous ammonia was added to the solution of iron salts. The color of the solution changed immediately from orange to dark after addition of ammonia. The magnetic particles were separated from the resulting solution with a magnet and the supernatant was discarded. The target materials were rinsed twice with deionized water and once with 0.02 mol L^{-1} sodium chloride to remove excess reactants. Then, the magnetite suspension was placed in a 250-mL round-bottom flask and an aqueous solution of TEOS (10% (v/v), 80 mL) was added to this, followed by glycerol (60 mL). The pH of the suspension was adjusted to 4.6 using glacial acetic acid, and the mixture was then stirred and heated at 90 °C for 2h under a nitrogen atmosphere. The excess amount of amino propyl trimethoxy silane (APTS) in 150 ml ethanol was added to FMNPS and the mixture was then stirred and heated at 90 °C for 6h under a nitrogen atmosphere. After that, the prepared product was cooled and then washed with distilled water and ethanol three times, respectively. Finally, the excess amount of triazene (0.2 g, 0.1 mmol) was added to 50 mL of methanol solution containing 2.0 g of APT-FMNPs, and this was then heated for 12 h (Fig. 1) for the preparation of modified magnetic nanoparticles containing triazene group. After that, the resulting nanoparticles were washed with methanol (2×500 mL), deionized water (3×500 mL) and ethanol (2×500 mL) and then dried into powders at room temperature.

2. Sample extraction

The procedure for the magnetic solid phase extraction is asfollows: A portion of 1000 mL of sample solution containing 10mg analyte ions was transferred to a beaker; the pH value wasadjusted to 7 with 1 mol L^{-1} HNO3 or 1 mol L^{-1} sodiumhydroxide. Then, 150 mg of AET-APTS-FMNPs was added, andthe solution was stirred for 10 min to facilitate adsorption of themercury ions onto the nanoparticles. Then, the magneticadsorbent was separated easily and quickly using a magnet andthe supernatant was decanted directly. The magnet was removedand a solution containing 2.0 mol L^{-1} HCl was added as eluentand stirred again for 3 min. Finally, the magnet was used again tosettle the magnetite nanoparticles, and the eluate was transferred into a test tube for subsequent ICP-OES analysis, you can see this process inFig. 1.


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A novel extraction and preconcentration of ultra-trace level of uranium ion using functionalized magnetic-nanoparticles prior to its determination by inductively coupled plasma-optical emission spectrometry

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Abstract:

New modified magnetic nanoparticles functionalized with salicylaldehyde groups were designed and synthesized for extraction/preconcentration of sub-ppb level of uranium ions in water samples prior to its determination with inductively coupled plasma optical emission spectrometry (ICP-OES). In the separation process, aqueous solution of U(VI) ions was mixed with 100 mg of Fe₃O₄ magnetic nanoparticles modified with salicylaldehyde (Sal) and then external magnetic field was applied for isolation of magnetic nanoparticles containing uranium ions. Experimental conditions for an effective adsorption including pH, sample volume, eluent concentration and existing of co-existing ions have been studied and established. Under the optimal extraction and preconcentration conditions, the limit of detection (LOD) of 0.24 ng mL⁻¹ and the relative standard deviation (R.S.D) of 1.5% (n = 8) were achieved by ICP-OES. The analytical curve was linear in the range 1-2500 ng mL⁻¹. The sorption capacity of functionalized Fe₃O₄ magnetite nanoparticles under optimum conditions has been found to be 26.0 mg of uranium ion per gram at pH 8 with the preconcentration factor of 1000 (1mL of elution for a 1000 mL sample volume). The proposed method is characterized with high enrichment factor, easy preparation and regeneration of sorbent, short time of sample pretreatment, fast separation, high extraction yields, wide linear curve and low detection





limits. Finally, the proposed method was successfully used for extraction, preconcentration, and determination of U(VI) in some real samples.

Keywords: Preconcentration; uranium determination,magnetic nanoparticles; inductively coupled plasma-optical emission spectrometry *(ICP-OES)*.

Introduction:

Uranium is an element of great commercial interest because of its use in the production of nuclear energy, in the manufacture of nuclear weapons, in the shielding of industrial radioactive sources and even as anti-tanks ammunition [1]. Frequent contacts with uranium compounds increase the probability of cancer and have serious destructive effects on tissue such as liver and kidney [7]. The WHO, Health Canada, and Australian drinking water guidelines have fixed the maximum U(VI) concentration in drinking waters to be less than 9, 20, and 20µg/L, respectively [8]. So, we need to develop new methods for determining uranium ion with high sensitivity and good accuracy. Uranium ion has been determined by several analytical techniques such as Gas chromatography [9], inductively coupled plasma [10], molecular fluorescence spectrometry [11], α -spectrometry [12], spectrophotometry [13] and neutron activation [14]. Solid phase extraction is a method for pretreatment of uranium ions before of determination by these instrument methods. In SPE, the sorbent is key factor because extraction depends on the partition coefficient of analytes between a solid phase and liquid phase. In this work, we functionalized Fe₃O₄ magnetic nanoparticles with salicylaldehyde groups to prepare a highly selective sorbent for extraction and preconcentration of uranium ion. The proposed method is characterized with high enrichment factor, easy preparation and regeneration of sorbent, short time of sample pretreatment and fast separation, high extraction yields, wide linear curve and low detection limits.





Results and discussion:

1.Preparation of Salicylaldehyde-modified magnetic Fe3O4 nanoparticles (Sal-APS-SCMNP)

The magnetic nanoparticles (SCMNPs) were prepared according to Ref. [38] and shown schematically in Fig. 1. Briefly, FeCl₃.6H₂O (11.68 g) and FeCl₂.4H₂O (4.30 g) were dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring at 85 °C. Then, under intensive stirring, 20 mL of 30% aqueous ammonia was added to the solution of iron salts. The color of the solution changed immediately from orange to dark after addition of ammonia. Then, these magnetic nanoparticles were modified by silans reagent and APTS-SCMNPs were prepared. For the preparation of magnetic nanoparticles containing salicylaldiminato group (Fig. 1), APTS-SCMNPs (2.0 g) were suspended in 100 mL of ethanol and to this mixture was added excess of salicylaldehyde (1.0 mL, 9.58 mmol) and refluxed for 8 h. After that, the resulting modified nanoparticles were washed three times with deionized water, twice with methanol and twice with ethanol, and then dried into powders at room temperature to produce Sal-APTS-SCMNPs.

2. Sample extraction:

The procedure for the magnetic solid phase extraction is as follows: A portion of 1000 ml of sample solution containing 10 μ g analyte ions was transferred to a beaker; the pH value was adjusted to 8 with 1 mol L⁻¹ HNO₃ or 1 mol L⁻¹ sodium hydroxide. Then, 100 mg of Sal-APTS-SCMNPs were added, and the solution was stirred for 15 min to facilitate adsorption of the uranium ions onto the nanoparticles. Then, the magnetic adsorbent was separated easily and quickly using a magnet and the supernatant was decanted directly. The magnet was removed and a solution containing 1.0 mol L⁻¹ HNO₃ was added as eluent and stirred again for 5 min. Finally, the magnet was used again to settle the magnetite nanoparticles, and the eluate was transferred into a test tube for subsequent ICP-OES analysis.



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Synthesis and characterization of mesoporousPVP containing palladium nanoparticles using KIT-6 as templateand it'sapplicationforcross coupling reactions

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Key words:KIT-6, Poly(N-Vinyl-2-pyrrolidone) (PVP), Pdnanoparticles.

Introduction:

The synthesis of mesoporous materials has recently generated great interest due to their importance for a wide range of applications such as the adsorption/immobilization of large molecules, as catalytic supports. Much attention has been paid to the fabrication of mesoporousinorganic materials. On the other hand, only a few works have been focussed on the synthesis of mesoporous materials with an organic framework [1]. The Heck reaction has received growing interest for carbon–carbon bond formation and widespread applications in the organic synthesis of various alkenes. Palladium species have largely been used as catalysts for C–C bond forming reactions in allylic substitutions and Heck coupling of aryl halides. Hence, polymer anchored metal catalysts, which are used extensively as heterogeneous catalysts, and major advantages of using tailor-made polymer supported catalysts are their ease of separation ability to recycle and site specificity in various organic reactions [2].

Materials and methods:

In this work, mesoporous poly (*N*-vinyl-2-pyrrolidone) based on KIT-6 as template, was prepared by in-situ polymerization method. For this purpose, at first PVP/KIT-6 composite was prepared via in situ polymerization of VP in the pores of KIT-6. Then the silica framework is selectively removed by an etching agent (NaOH), which allows a porous





polymer to be retrieved. Finally, this purely organic mesoporous polymer wasused as a support for palladium nanoparticles obtained through the reduction of Pd(OAc)₂.The physicaland chemical properties of the nanocomposite wereinvestigated by XRD, FT-IR, UV–VIS, TG, BET, SEM, and TEM techniques.

Apparatus:

FT-IR spectroscopy using a Perkin Elmer 65 in KBr matrix in the range of(4,000–400cm⁻¹). The BET specific surface areas determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a BEL SORP18 Series. XRD of the catalyst was carried out on a BrukerD8Advance X-ray diffractometer using Ni filteredCu Ka radiation at 40 kV and20mA.

Result and discussion:

The FT-IR spectra of KIT-6, mesoporous PVP and mesoporous PVP containing Pd nanoparticles. FT-IR spectrum of KIT-6 shows the typical vibrations stretching as well as the rocking of Si–O–Si at around 1100, 816, and 458 cm⁻¹. In the spectrum of PVP/KIT-6 the new band at around 1678 cm⁻¹ corresponds to the carbonyl bond of PVP. In mesoporous PVP containing Pd nanoparticles spectrum, the band around 1678 cm⁻¹, which corresponds to carbonyl bond of PVP, is shifted to lower wave numbers (1649 cm⁻¹) (red shift). These observations prove the successful formation of Pd-mesoporous PVP. The powder XRD patterns of mesoporous PVP, The presence of a peak at around 20 = 1.5-2 iscorresponded to mesopore structure and regular pores of PVP which prove the successful formation of mesoporous PVP.

Conclusion:

A novel catalyst Pd nanoparticlemesoporousPVP, was prepared by a simple method.we have developed an efficient catalyst system for cross coupling reactionmaterial-supported palladium as catalyst. This heterogeneous catalyst can practically following advantages: (a) high catalytic activity under mild reaction conditions and (b) replace a homogeneous catalyst in view of the





reusability of the catalyst for several times without any significant loss in the yield of the reaction.

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Polymer/KIT-6 nanocomposite: synthesis, characterization and controlleddrug release

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Keywords: Mesoporous silica, Drug delivery, Poly (N-Vinyl-2-Pyrrolidone), Nanocomposite

Introduction:

Recently, cubic mesoporoussilicas with three-dimensional structure have attracted muchattentionfor potential applications in pharmaceutical. Ryoo et al. reported a new cubicmesoporous silicamaterial called KIT-6, which exhibited a three-dimensional cubic Ia3dsymmetric structure with an interpenetrating bicontinuous network of channels [1]. Thismesoporous silica, KIT-6 possesses large readily tunable pores with thick pore walls, highhydrothermal stability, high specific surface area, and a large pore volume which can act asefficient drug delivery carriers. In addition, the three dimensional polymer network structures with chemical and physical crosslinking are gaining increasing popularity as drug carriers forcontrolled release of drugs due to their biocompatibility and resemblance with natural livingtissues more than any other class of synthetic biomaterials. Drug release from polymerhydrogel carrier, mainly occurs due to polymer swelling in the body fluids as a result ofincrease in segmental mobility of polymer [2,3].

Materials and methods:

Cubic mesoporoussilicasKIT-6 was synthesized in acidic medium under hydrothermal condition. Then, mesoporous poly (*N*-vinyl-2-pyrrolidone) based on KIT-6 as template, was prepared by in-situpolymerization method. For this purpose, PVP/KIT-6 nanocomposite was prepared via in situpolymerization of VP in the pores of KIT-6. The loading of IBU inside the





PVP/KIT-6 sample was carried out for 24h in temperature room under stirring andthe precipitate filtered.Finally,this was conducted by monitoring theibuprofen concentration using UV/Vis spectrometer at a wavelength of 272 nm.

Apparatus:

The samples were analyzed using BET specific surface areas distribution of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a BEL SORP 18 Series. The XRD of the catalyst was carried out on a Bruker D8Advance X-ray diffractometer using Ni filtered Cu Ka radiation at 40 kV and 20 mA. Absorption spectra of samples were collected by using a double beam UV-VIS spectrophotometer model PG Instruments T70.FT-IR spectroscopy using a Perkin Elmer 65 in KBr matrix in the range of(4,000–400cm⁻¹).

Result and discussion:

The low angle XRD pattern of KIT-6 show one intense peak at 2Θ about 0.95 and two weak peaks at 2Θ about 1.65 and 1.9 which can be indexed as (211), (220), and (320) reflections associated with three – dimensional cubic, symmetry (Ia3d). FT-IR spectrum of KIT -6 shows the typical vibrations stretching aswell as the rocking of Si–O–Si at around1080, 815, and 470 cm⁻¹. In the spectrum of PVP/KIT-6 then ewbandat around 1681cm⁻¹ corresponds to the carbonyl bond of PVP.

Conclusion:

This nanocomposite (PVP/KIT-6)was used for adsorption of Ibuprofen as a model drug. Moreover, in vitro drug release from the nanocomposite was carried out in simulated body fluid (SBF). The results showed that this novel nanocomposite can used as a excellent carrier for drug release and adsorption. These results can related to the existence of both polymers and mesoporous materials in the composite, which polymers have proper interaction with





functional group of drug and the pores of mesopores have a proper size for successful adsorption of drug.

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High Solar Photocatalytic Degradation of Azo Dye (MB) by Bismuth Ferrite Synthesized via Ultrasound Method

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Key words: Ultrasound, Sunlight, bismuth ferrite, MB, Photodegradation.

Introduction:

From the viewpoint of the utilization of solar energy, the development of visible light-driven photocatalyst has attracted much attention in order to water splitting and organic contaminants degradation especially in the past 10 years [1-3].

Materials and methods:

In this work, pure bismuth ferrite (BFO) as a visible-light photocatalyst has been synthesized via ultrasonic-assisted method .The structure, Size and morphology of BFO was examined. Then, the photocatalytic degradation of MB was investigated under sun light irradiation.

Apparatus:

The ultrasonic irradiation with equipment operating at 20 kHz (W-450 D), X-ray diffractometer (XRD, Phlips PW1800), UV–vis spectrophotometer (Unico 2800), Fourier transform infrared (FT-IR) spectrometer (Avatar 370), Transmission electron microscopy (TEM) were performed.

Result and discussion:

In this work, we examined the photodegration of MB with Ferrite bismuth synthesized via ultrasonic method under direct sun light irradiation. The BFO have higher





photocatalytic activities in acidic medium, also the sample synthesized via ultrasound method exhibited higher potocatalytic activities than the sample synthesized via conventional method. The effect of various parameters such as type of catalyst, concentration of dye, amount of catalyst and pH on the dye degredation has been studied. The formation of inorganic products (SO₄²⁻ and NO₃⁻) and the evolution of CO₂ revealed complete degredation of aqueous MB during the photocatalytic process by this photocatalyst. The isotherm of adsorption and the kinetic and mechanism of photocatalytic degradation of MB, were investigated and compared using different concentrations of dyes. The stability of catalyst was also examined in this work.

Conclusions:

The photocatalytic decomposition of aqueous solutions of MB was studies under sun light irradiation in the presence of Ferrite bismuth synthesized via ultrasound method accompanied with the formation of end products such as carbon dioxide, sulfate ions and nitrate ions. The reaction kinetics of MB degradation on BFO was investigated, suggesting that these reactions followed approximately first-order kinetics. The photocatalys was stable under visible light irradiation after various cycles.

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Kinetic and thermodynamic study of Cr (III) Adsorption by Nano Organic-Inorganic Adsorbent based on 4H-pyarn-4-one (E3) and TEOS by Sol-Gel Method.

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Key words: Nano adsorbent, Sol-Gel, 4H-pyran-4one, Cr (III)

Introduction:

Various technologies are employed for removing toxic ions from water, witch include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption among this adsorption is the most promising technique.

The adsorption of Cr (III)onto nano-E3 are studied as a function of contact time, pH, Ionic strength, adsorbent mass, and temperature. Kinetic data indicated that adsorption process achieved equilibrium with in 30 min and follows a pseudo-second-order rate equation, the adsorption data fit the Langmuir model and its linearized form well, together with thermodynamic data indicate the spontaneous and endothermic nature of process. We synthesis new podands of 4H-pyran-4-one deivatives that showed in scheme1. Then, these compounds were heterogenized as nano adsorbent by using sol-gel method in acidic catalyst condition in TEOS as a substrate. These nano adsorbent prepared based on 4H-pyran-4one derivatives showed the good performance to uptake of heavy metals, such as Cr (III).









Materials and methods:

All materials were prepared form Sigma-Aldrich and Merck Company, and solution of Cr (III) Nitrate (Analytical grade from sigma co) were prepared in double-distilled water. A batch system was used for removing, the amount of Cr (III) adsorbed(mg g^{-1}), (q_e), were Calculated.

Result and discussion:

The effect of solution pH was studied for Cr (III) removal by Nano- E_2 in range of 1~11, The suitable range of pH for this process is 7<pH<8. Some effects such as effect of nano- E_2 dosage, effect of solution Temperatures were studied.

Accordingly, we evaluated the fitness of the equilibrium data obtained from the experiments at different conditions with the Langmuir, Freundlich, Temkin, Debinin-Radeshkovich Models. The best-fitted model was select based on the determination coefficient (R^2) and the coefficient constants for models are calculated in several solution temperature.

Conclusion:

This study concludes that adsorbent showed effective Cr (III) adsorption from aqueous solution. The ion removal rate of Cr (III) by nano-E3 increased with increase initial metal concentration, and temperature.

The adsorption isotherms of Cr (III) on nano-E3 at 298, 308, 318 K are illustrated. It can be seen that the adsorption is highest at 313K and the lowest at T=293K. The results indicate that high temperature is advantageous for Cr (III) adsorption.

The experimental data of Cr(III) adsorption are regressive fitted with the Langmuir, Freundlich, and D-R isotherm, models and the results are given and the relative values calculated from the three models are listed and the correlation coefficient for Langmuir, Freundlich, and D-R isotherms are calculated.

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Synthesis and usage Nano Organic- Inorganic Adsorbent based on 4Hpyarn-4-one (E₂) and TEOS by Sol-Gel Method for Removal Ni(II)

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Key words: Nano adsorbent, Sol-Gel, aH-pyran-4one, Ni (II)

Introduction:

In this work, new nano heterogenated was synthesized and used as a novel adsorbent for removing Ni(II) from aqueous solution. The adsorption of Ni(II) onto nano-E2 was studied as a function of contact time, pH, Ionic strength, adsorbent mass, and temperature. The results showed that Ni(II) adsorption onto this adsorbent is strongly dependent on pH and adsorbent mass, to a lesser extent, ionic strength. Kinetic data indicated that adsorption process achieved equilibrium with in 30 min and follows a pseudo-second-order rate equation, the adsorption data fit the Langmuir model and its linearized form well, together with thermodynamic data indicate the spontaneous and endothermic nature of process. We synthesis new podands of 4H-pyran-4-one deivatives that showed in scheme1. This new podand was nano heterogenated as a nano adsorbent with TEOS in acidic condition.



Materials and methods:





All materials were prepared form Sigma-Aldrich and Merck Company, and solution of Ni(II) Nitrate (Analytical grade from sigma co) were prepared in double-distilled water. A batch system was used for removing, the amount of Ni(II) adsorbed(mg g^{-1}), (q_e), were Calculated .

Result and discussion:

The effect of solution pH was studied for Ni(II) removal by Nano- E_2 in range of 1~11, The suitable range of pH for this process is 7<pH<8. Some effects such as effect of nano- E_2 dosage, effect of solution Temperatures were studied.

Accordingly, we evaluated the fitness of the equilibrium data obtained from the experiments at different conditions with the Langmuir, Freundlich, Temkin, Debinin-Radeshkovich Models. The best-fitted model was select based on the determination coefficient (R^2) and the coefficient constants for models are calculated in several solution temperature.

Conclusion:

The experimental data showed good agreement with Langmuir, Freundlich, Temkin, and Debinin-Radeshkovich isotherms. The Enthalpy, Entherophy, Gibbs free energy change of adsorption process and each of the isotherm constant at different temperatures are calculated.

Ion	Adsorbent	T(K)	lnK _e	$\Delta G_{(Kj/mol)}$	$S_{(Kj/mol)}$ ် Δ	$\Delta H_{(Kj/mol)}$
		298	3.8079	-9.43	-0.0403	-21.44
Ni ²⁺	E2	308	3.6138	-9.25	-0.0403	-21.67
		318	3.2634	-8.63	-0.0403	-21.44

Langmuir Constants for Ni-E ₂ Adsorption					
T _(K)	Ni-E ₂ Ni-E ₂ Ni-E ₂		Ni-E ₂		
	1/q _{max}	$1/(q_{max}K_l)$	q _{max}	Kı	
298	0.026	0.026	38.941	0.9879	
308	0.019	0.023	52.801	0.8263	
318	0.018	0.021	55.359	0.8398	

FreUndlich Constants for Ni-E ₂ Adsorption						
T _(K)	Ni-E ₂	Ni-E ₂	Ni-E ₂	Ni-E ₂		





	lnK _f	$1/n_{\rm f}$	K _f	$\mathbf{n_{f}}$
298	7.223	1.3071	2258.147	0.765052
308	5.9709	0.9254	391.86	1.080614
318	4.9049	0.6822	134.95	1.465846

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Synthesis and antibacterial evaluation of nano-bioactive-glasses (NBG) by a quick alkali-mediated sol-gel method

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Keywords: Silver; Apatite crystals; Biodegradation rate; Antibacterial effects

Introduction:

Bioactive glasses (BG) are important group of materials with a wide range of application in medicine as bone substitute. These materials are able to bind with bone in a living organism through a layer of hydroxyapatite (HA) formed on their surfaces [1]. Most research on antibacterial effects of silver ions in silica based-bioactive glass systems have been reported [9-16]. However, one should stress that, to the best of our knowledge, physico-chemical interactions of these kinds of bioactive glasses in simulated body fluid (SBF) solution was not studied and interpreted so far. Soaking in solution similar to the human blood plasma they develop an apatite like layer, which is at the origin of the bond formed between bioactive materials and living tissues [21]. The objective of the present study was to produce a sol–gel derived bioactive silicophosphate glass based on SiO₂–CaO–Ag₂O–P₂O₅ system with different molar ratio of silver oxide in the glass composition and compared its physicochemical, bioactivity and antibacterial properties to those of a silver-free bioactive glass using proper analytical techniques.

Materials and methods:

The starting materials for the synthesis of the silver containing bioactive glass and silver-free samples were tetraethylorthosilicate (TEOS: $C_8H_{20}O_4Si$), triethyl phosphate (TEP: $C_6H_{15}O_4P$),





calcium nitrate (Ca(NO₃)₂.4H₂O), silver nitrate Ag(NO₃)₂.4H₂O, ammonia and nitric acid. In a typical procedure, the samples were prepared by sol–gel method with different molar ratios of calcium and silver.

Result and discussion:

Ag₂O was substituted for CaO in the glass formula up to 2 mol%. The samples obtained by sol-gel method were annealed and then characterized by X-ray diffraction (XRD), thermal analysis (TGA), N₂-adsorption measurements, and transmission electron microscopy (TEM). XRD confirmed the amorphous nature of all glasses after stabilization. It was shown by thermal analysis that the stabilization temperature for silver samples was 700 °C. The sample 0.5% mol Ag-BG, showed average pore diameters of 34.47 nm and specific surface areas of 96.6 m^2/g , respectively. TEM micrographs showed that the average particle sizes of all samples were less than 100 nm in diameter. In vitro bioactivity of the samples was evaluated by soaking them in simulated body fluid followed by structural characterization using FTIR and SEM techniques. The results showed that all glasses favored precipitation of calcium phosphate layer when they were soaked in simulated body fluid; however the morphology of apatite crystals changed for 2%mol silver containing sample. In order to determine the optimum concentration of silver ion in bioactive glass, antibacterial effects of this bioactive glass on three strains of bacteria were evaluated. The antibacterial properties of the samples indicated that minimum inhibitory concentration (MIC) was 2 mg/ml for E. coli and P. aeruginosa; and 2.3 mg/ml for S. aureus for 2% silver containing bioactive glass.

Conclusions:

In this study, silver-substituted bioactive glasses have been prepared by sol-gel method. Textural analysis revealed that all glass samples were highly porous and had relatively high surface area. It can be concluded that silver ion releases from bioactive glass into medium and inhibits bacterial growth in a concentration-dependent manner. Finding the optimum concentration of Ag in bioactive glass for best antibacterial property can open a new method to reduce infections after prosthesis implantation, surgery and burn wound.





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Using of γ -alumina porous nanoparticles for loading and releasing of Mefenamic acid

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Keywords: Nanoparticles, y-alumina, Mefenamic acid, Drug delivery

Introduction:

Porous Al₂O₃ has been widely used as a template for preparation of many functional materials for optical, electronic, magnetic, electrochemical applications and drug delivery [4,5]. In this study, porous nano- γ -alumina employed as the carrier for drug delivery of the Mefenamic acid. Alumina nanoparticles were successfully coated by the adsorption of Mefenamic acid in aqueous solutions. Mefenamic acid drug with weight ratio of Alumina/Mefenamic acid, 20/1 (Mefenamic acid-1) and 10/1 (Mefenamic acid-2) were loaded on the nanoparticles surface and porous area. The *in vitro* release of the drugs were investigated in the buffer solution at pH=1.3, 7.2, 9.

Materials and methods:

Mefenamic acid was supplied from Raha Pharmacy Corporation in the Esfahan of the IRAN. γ -alumina nanoparticles (particle size ~ 21 nm, specific surface area (SSA) 138.8 m²/g), was obtained in powder form, dispersions of which were prepared in aqueous solutions under stirring.

Apparatus:





The presence of the drugs at the nanoparticles surface and porous area was checked by Fourier transforms infrared spectrometer (FTIR) and x-ray diffraction (XRD) measurements. The amounts of drugs released were determined by UV-Vis spectrophotometer (PG Instrument LTD, T80).

Result and discussion:

Fig. 1 shows X-ray diffraction of Al₂O₃, Mefenamic acid-1 and Mefenamic acid-2. Loaded drugs on the surface and pore area in the range of 10 to 30 degree are showed several peak.



Fig. 1. X-ray diffraction (XRD) for (a) γ -Al₂O₃ (b) Mefenamic acid-1 and (c) Mefenamic acid-2.

Conclusion:

In this study, porous γ -alumina nanoparticles synthesized with simple, inexpensive method and high surface area was used for drug delivery of Mefenamic acid. The Speed of drug delivery in the early hours is up due to the separation of drug from the nanoparticles surface. The slower release seen in the next hours due to medication separated particles are trapped in the pores.

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Synthesis and characterization of γ-alumina porous nanoparticles from Sodium aluminat liquor with two type surfactants

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Keywords: γ-alumina; Sodium aluminat; Nanoparticles; Surfactant

Introduction:

In recent years, nanomaterials have received considerable attention because of their special structures and functions which are different from traditional materials [1]. The γ -alumina is one kind of extremely important nanosized materials [2]. In this article, we report a novel processing method for synthesize γ -Al₂O₃ nanoparticles by two type surfactants as structure-directing agents. The aim of this study is the synthesis of nanoparticles with very fine crystallite size, low cost, high synthesis rate and also investigates two type surfactants in order to nanoparticles synthesis of γ -alumina with used sodium aluminat liquor.

Materials and methods:

Sodium aluminat liquor, HCl (37%, Merck), NaOH (Merck), Polyvinyl alcohol (Merck) and Polyethylene glycol (2000-4000, Merck) were used as raw materials to prepare nano- γ -alumina. Among the various synthesis methods, we used sol-gel method for synthesis of nanoparticles.

Apparatus:

X-ray diffraction was carried out for phase analysis of samples using ITAL STRUCTURES, APD 2000 model. The morphology and particle size of nanoparticles were characterized by scanning electron microscopy (SEM, Philips-XL30) and field emission scanning electron





microscopy (FE-SEM, S-4800/Hitachi). The BET surface areas and pore volumes were estimated from nitrogen adsorption-desorption data obtained on a constant-volume adsorption apparatus (Quantachrome Instruments, 1994-2006). Also, investigated analysis TGA/DTA and FTIR.

Result and discussion:

XRD results of as-synthesized nanoparticles are shown in Fig. 1a and 1b. The average crystallite sizes of resultant nano- γ -alumina were estimated from the half-height width to be 2.58 nm by using PEG and 3.068 nm by using PVA.





Fig. 1a XRD patterns of as-synthesized nanoparticles γ - alumina by using of polyethylene glycol



Conclusion:

The porous γ -aluminas were successfully synthesized using sodium aluminat liquor as the precursors and with two different surfactants as the structure-directing agents. When the calcinations temperature was at 800 °C, γ -alumina porous nanoparticles by using polyethylene glycol surfactant with the surface area of 138.8 m²/g and and pore volume ~ 0.197 cm³/g were obtained. Examination by SEM illustrated that all the particles with average size 20 nm by using PEG and 46 nm by using PVA.

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