In The Name Of God

Semnan University deems it as an honor and privilege to hold the 26th Iranian Conference of Analytical Chemistry (26th ISAC) on Sunday 25 August to Tuesday 27 August 2019.

The 26th ISAC provides a high impact scientific meeting for the Iranian chemical community with both high profile speakers and opportunities for younger researchers to present their work. The accepted and presented abstracts spanned a large variety of topics in different chemical fields. The abstracts submitted to the 26th ISAC were reviewed at least by two referees, and the final decisions were then made by the scientific committees.

It is essential to appreciate the Semnan University authorities; the Iranian Chemical Society; Steering Committee, Organizing Committee, Scientific and Referee Committees, Student Executive Committees and all university staff who helped us hold this Conference.

Sincerely Yours,

Dr. Alireza Asghari

Chairman of the 26th Conference

به‌نام خدا

پیام دبیر بیست و ششمین کنفرانس شیمی تجزیه ایران

باعنایت به درگاه باری تعالی، مفتخریم میزبان بیست و ششمین گردهمایی جامعه اساتید، پژوهشگران و دانشجویان رشته شیمی تجزیه و متخصصین صنایع مرتبط در دانشگاه سمنان باشیم. این گردهمایی با حمایت انجمن شیمی ایران و دانشگاه سمنان در تاریخ سوم الی پنجم شهریور ماه سال ۱۳۹۸ در دانشگاه سمنان برگزار می‌گردد. هدف از برگزاری این گردهمایی علمی یافتن فرصتی دیگر برای ارائه آخرین دستاوردهای علمی- پژوهشی در رشته شیمی تجزیه و تبادل اطلاعات، تجربیات و برقراری ارتباطات بیشتر بین پژوهشگران، نهادهای دانشگاهی و صنعتی می باشد. در این راستا با در نظر گرفتن سخنرانی‌های کلیدی، توسط اساتید برجسته داخلی و خارجی و برگزاری کارگاه‌های آموزشی مختلف، امید داریم که گامی در جهت رشد و ترقی علمی کشور عزیزمان برداریم.

در این کنفرانس مباحث مختلفی از جمله طیف‌سنجی تجزیه‌ای، الکتروشیمی تجزیه‌ای، کروماتوگرافی و روش‌های جداسازی، کمومتریکس، نانوشیمی، شیمی تجزیه و صنعت، شیمی تجزیه و محیطزیست مورد بررسی و توجه قرار گرفته است.

باتشکر
دکتر علیرضا اصغری
دبیر بیست و ششمین کنفرانس شیمی تجزیه ایران

معرفی کنفرانس

دنیای امروز، محلی برای تبادل اطلاعات، اندیشه‌ها و تجربیات برای خلق ایده‌های نوینی است که موجب پیشرفت علوم و دانش بشری در عرصه‌های مختلف علم و فناوری شده است. برای رسیدن به این هدف، ایجاد بستری مناسب در جهت بروز ظرفیت‌های موجود از اهمیت خاصی برخوردار است. از این‌رو، برگزاری کنفرانس‌های تخصصی، علاوه بر ایجاد زمینه تحقق این مسئله، می‌تواند موقعیت مناسبی را برای ایجاد هم‌فکری و تبادل دیدگاه‌ها فراهم نماید. دبیرخانه بیست و ششمین کنفرانس شیمی تجزیه ایران مفتخر است تا با مد نظر قرار دادن سیاست‌های کلی علم و فناوری ابلاغی از سوی مقام معظم رهبری از جمله: جهاد مستمر علمی با هدف کسب مرجعیت علمی و فناوری در جهان با تاکید بر: ۱- تولید علم و توسعه نوآوری و نظریه‌پردازی ۲- ارتقاء جایگاه جهانی کشور در علم و فناوری و تبدیل ایران به قطب علمی و فناوری جهان اسلام ۳- توسعه علوم‌پایه و تحقیقات بنیادی گامی در جهت انجام رسالت اصلی خویش برای کمک به پیشبرد برنامه‌های علمی جامعه، حمایت از گسترش فعالیت‌های تحقیق و توسعه، ارتباط دانشگاه با صنعت و ایجاد زمینه‌های مناسب برای تبادل اندیشه‌ها بین پژوهشگران جامعه بردارد. دانشکده شیمی دانشگاه سمنان با همکاری انجمن شیمی ایران، بیست و ششمین کنفرانس شیمی تجزیه ایران را در زمینه‌های مختلفی از جمله طیف‌سنجی تجزیه‌ای، الکتروشیمی تجزیه‌ای، کمومتریکس، کروماتوگرافی و روش‌های جداسازی، شیمی تجزیه و محیط‌زیست، نانوشیمی و شیمی تجزیه و صنعت برگزار خواهد کرد. امید داریم، میزبان شایسته‌ای برای شما عزیزان در بیست و ششمین کنفرانس شیمی تجزیه ایران در دانشگاه سمنان باشیم.

با احترام
دکتر علیرضا اصغری
دبیر بیست و ششمین کنفرانس شیمی تجزیه ایران

کمیته علمی کنفرانس:

ردیف	نام و نام خانوادگی	محل خدمت	سمت	تصویر
۱	علیرضا اصغری	دانشگاه سمنان	دبیر سمینار	
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۵	علی اصغر انصافی	دانشگاه صنعتی اصفهان	ریاست کمیته شیمی تجزیه انجمن شیمی ایران	
٦	عباس افخمی	دانشگاه بوعلی سینا همدان	دبیر کمیته شیمی تجزیه انجمن شیمی ایران	

ردیف	نام و نام خانوادگی	محل خدمت	سمت	تصویر
۷	حبیب باقری	دانشگاه صنعتی شریف	عضو کمیته شیمی تجزیه انجمن شیمی ایران	
۸	ناهید پوررضا	دانشگاه شهید چمران اهواز	عضو کمیته شیمی تجزیه انجمن شیمی ایران	
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۱۲	عبدالرئوف صمدی میبدی	دانشگاه مازندران	عضو کمیته شیمی تجزیه انجمن شیمی ایران	

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Sajjadi S.M.	*Semnan University*
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Scientific and Referee Committees

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Gharib A.	*Semnan University*
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Kamandi P.	*Semnan University*
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Saniyan H.	*Semnan University*

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دانشگاه سمنان
دانشکده شیمی

معرفی اعضا هیات علمی و تجهیزات دانشکده شیمی

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دانشگاه سمنان- دانشکده شیمی

گروه شیمی تجزیه

دکتر علیرضا اصغری
رتبه علمی: استاد
دوره کارشناسی و کارشناسی ارشد: دانشگاه تهران
دوره دکترا: دانشگاه صنعتی اصفهان
دوره پسا دکترا: دانشگاه واترلو کانادا
زمینه کاری و تحقیقاتی: سنسورها و بیوسنسورهای الکتروشیمیایی، کاربرد روش های کروماتوگرافی و الکتروفورز مویین در تجزیه نمونه های حقیقی

دکتر مریم رجبی
رتبه علمی: دانشیار
دوره کارشناسی: دانشگاه صنعتی خواجه نصیر
دوره کارشناسی ارشد و دکترا: دانشگاه تهران
زمینه کاری و تحقیقاتی: کاربرد روش های جداسازی شامل GC ، HPLC و CE در آنالیز نمونه های حقیقی، استخراج و میکرواستخراج با فاز جامد، میکرو استخراج فاز مایع، سنتز نانو جاذب های جدید و کاربرد آنها در روش های استخراج

دکتر سیده مریم سجادی
رتبه علمی: استادیار
دوره کارشناسی: دانشگاه یاسوج
دوره کارشناسی ارشد و دکترا: دانشگاه تحصیلات تکمیلی علوم پایه زنجان
زمینه کاری و تحقیقاتی: مطالعه سیستمهای تعادلی و سینتیکی در نانو دارو رسانی با استفاده از روشهای کمومتریکس پیشرفته

گروه شیمی کاربردی

دکتر فریده نبی زاده چیانه
رتبه علمی: استادیار
دوره کارشناسی: دانشگاه تبریز
دوره کارشناسی ارشد و دکترا: دانشگاه بوعلی سینا
زمینه کاری و تحقیقاتی: اصلاح الکترودها با نانو مواد و روش لایه نشانی الکتروفورتیک، تصفیه آب با استفاده از فرآیندهای پیشرفته الکتروشیمیایی، غشا و فرآیندهای ترکیبی

گروه شیمی آلی

دکتر علی عموزاده
رتبه علمی: استاد
دوره کارشناسی: دانشگاه فردوسی مشهد
دوره کارشناسی ارشد: دانشگاه شهید بهشتی
دوره دکترا: دانشگاه مونترال کانادا
زمینه کاری و تحقیقاتی: طراحی و ساخت نانو کاتالیزورها و نانو فتوکاتالیزورهای جدید و استفاده از آنها در واکنشهای آلی، سنتز، کروماتوگرافی

دکتر فیروزه نعمتی
رتبه علمی: دانشیار
دوره کارشناسی، کارشناسی ارشد و دکترا: دانشگاه خوارزمی
زمینه کاری و تحقیقاتی: سنتز و شناسایی نانو کاتالیست ها، طراحی پیش ماده های کربنی جهت ساخت بسترهای مزوپورکربنی حاوی هترو اتم با روش پیرولیز و کاربرد آنها

دکتر اسکندر کلوری
رتبه علمی: دانشیار
دوره کارشناسی: دانشگاه صنعتی شریف
دوره کارشناسی ارشد و دکترا: دانشگاه بوعلی سینا
زمینه کاری و تحقیقاتی: توسعه روش های جدید سنتزی شامل بکارگیری مایعات یونی، مواد فعال سطحی، نانوذرات مغناطیسی

دکتر نادیا کوکبی
رتبه علمی: استادیار
دوره کارشناسی: دانشگاه آزاد اسلامی فیروز آباد
دوره کارشناسی ارشد و دکترا: دانشگاه بوعلی سینا
زمینه کاری و تحقیقاتی: بکارگیری مایعات یونی و نانو کاتالیزگرها شامل نانو ذرات مغناطیسی، نانو ذرات کربنی و معدنی در سنتز ترکیبات آلی

گروه شیمی فیزیک

دکتر مصطفی فضلی
رتبه علمی: دانشیار
دوره کارشناسی، کارشناسی ارشد و دکترا: دانشگاه فردوسی مشهد
زمینه کاری و تحقیقاتی: محاسبات کوانتومی و مدلسازی شیمیایی، پوشش های فلزی و پلیمری، نانو تکنولوژی، شیمی سطح

دکتر احمد باقری
رتبه علمی: دانشیار
دوره کارشناسی: دانشگاه گیلان
دوره کارشناسی ارشد و دکترا: دانشگاه بوعلی سینا
زمینه کاری و تحقیقاتی: شیمی سطح، مواد فعال سطحی، مطالعه سینرژیسم و آنتاگونیسم (هم افزایی مثبت و منفی)

دکتر علی عرب
رتبه علمی: استادیار
دوره کارشناسی: دانشگاه شیراز
دوره کارشناسی ارشد و دکترا: دانشگاه صنعتی شریف
زمینه کاری و تحقیقاتی: الکتروکاتالیست، مطالعات الکتروشیمیایی، خوردگی فلزات و آلیاژها، شیمی محاسباتی

گروه شیمی معدنی

دکتر مهدی بهزاد
رتبه علمی: دانشیار
دوره کارشناسی: دانشگاه زنجان
دوره کارشناسی ارشد و دکترا: دانشگاه صنعتی شریف
زمینه کاری و تحقیقاتی: شیمی کئوردیناسیون بازهای شیف، بررسی ویژگی‌های آنتی باکتریال، ضد تومور و سایر ویژگی‌های زیستی کمپلکس‌های فلزات واسطه بررسی ویژگی‌های کاتالیزوری کمپلکس‌های فلزات واسطه

دکتر مهدی صالحی
رتبه علمی: دانشیار
دوره کارشناسی: دانشگاه رازی
دوره کارشناسی ارشد و دکترا: دانشگاه صنعتی اصفهان
زمینه کاری و تحقیقاتی: سنتز، شناسایی، مطالعه الکتروشیمیایی حلال رنگی، مطالعات تئوری و بررسی بلور نگاری و مطالعه بیوشیمی کمپلکس ها، سنتز و شناسایی نانو ذرات اکسیدی

دکتر عاتکه سادات ترحمی
رتبه علمی: استادیار
دوره کارشناسی: دانشگاه شیراز
دوره کارشناسی ارشد و دکترا: دانشگاه فردوسی مشهد
زمینه کاری و تحقیقاتی: شیمی ترکیبات فسفرآمیدی و ترکیبات کئوردیناسیون آنها، بررسی برهمکنش های بین مولکولی در ساختارهای بلورین به وسیله آنالیز سطح هرشفلد و محاسبات کوانتومی

تعدادی از تجهیزات

نام دستگاه	نام کمپانی	مدل	کشور
ICP-OES	Spectro	Genesis	Germany
Flame Atomic Absorption Spectrophotometer	Agilent	240AA	USA
HPLC	Knauer	Well Chrom	Germany
HPLC	Knauer	Smartline	Germany
GC	Shimadzu	17A	Japan
FT-IR	Shimadzu	8400S	Japan
TGA	Linseis	STA PT1600	Germany
Potentiostat-Galvanostat	Ivium	Vertex	Netherland
Potentiostat-Galvanostat	Origalys	OGF01A	France
Potentiostat-Galvanostat	Origalys	OGF500	France
Polarograph	Metrohm	757 VA	Switzerland
Potentiostat-Galvanostat	Behpajooh	BHP-2066	Iran
UV-Vis Spectrophotometer	Shimadzu	1650PC	Japan
UV-Vis Spectrophotometer	Perkin Elmer	Lambda 365	USA

Lecture

Photoelectrocatalytic Electrodes Materials for Conversion Energy Reactions

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As primary energy demands will double within the next two decades, energy storage and conversion will be among the most significant concerns of the current century. Promising advanced technologies such as fuel cells, water electrolysis, metal–air batteries, and CO_2 to fuel conversion have been recognized as clean energy-converting devices owing to their low cost and high efficiency. The core of these energy conversion technologies is some important electrochemical reactions that have been applied for energy conversions, which include fuel oxidation and oxygen reduction reaction (ORR) in fuel cells, ORR and oxygen evolution reaction (OER) in metal-air batteries, as well as hydrogen evolution reaction (HER) and OER in water splitting. However, the implement of these advanced technologies is still limited due to the requirement of active and durable electrocatalysts for above energy conversion reaction. This presentation mainly focuses on the recent progress of photo-responsive electrodes as electrocatalysts for improving the photoelectrocatalytic activity of energy conversion reactions under light irradiation. It involves the design and the architecting of advanced nanomaterials for light harvesting and enhanced photoelectrocatalytic performances of oxidation and reduction reactions. Different routes to design of semiconducting supports and construct advanced photoelectrocatalytic electrode material systems, will be discussed. Finally, the prospects of the photo-responsive electrodes for energy conversion reactions are also addressed briefly.

Application of nanocomposite-based sorbents in microextraction techniques

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Abstract:NCs are defined as organic– inorganic hybrid materials in which at least one dimension of one component is less than 100 nm. Numerous synthesis routes have been introduced to prepare NCs in recent years. This review provides a general overview regarding the present progress and new applications of NCs toward their synthesis and use in microextraction techniques, including solid-phase microextraction, stir bar sorptive extraction, needle trap extraction, microextraction in packed syringe and thin film microextraction. NCs are multiphase solid materials possessing different properties compared to those of the individual components. Due to the synergic effect of NCs, any specific property of these materials is usually more than the sum of the individual ones. The morphological characteristic of surface area/volume ratio for the reinforcing agents is an important reason for their vast applications in sample preparation procedures. Overall, applying NCs as sorbent in microextraction methods causes increased extraction efficiency due to the multifunctionality resulting from the multiphase structure of NCs and the higher specific surface area. Combination of these parameters allows higher mass transfer of analytes and enhancement of the interaction possibilities between the available sites on the sorbent and the analytes' functional groups. All these phenomena lead to the increased retention of target compounds by NC-based sorbents. Moreover, it is possible to prepare spread NCs with various functionalities by utilizing different kinds of host polymers and nanofillers, which can produce the proper sorbents for all purposes. Most of these features have encouraged some researchers to consider NCs in their research and use them as efficient extracting media. Various methods have been reported for the preparation of nanoparticle-based nanocomposites, including in situ polymerization, melt compounding, solution blending, electrospinning and etc. In the following, the applications of NCs in microextraction methods are comprehensively reviewed according to the type of reinforcing materials. Additionally, based on our literature survey, it was clear that in the research field of developing novel sample preparation methods, the NCs based on sol–gel derived matrix and conductive polymers are extensively prepared and used as extracting media.

Chemical Economy

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Abstract: Chemicals are an integral part of modern daily life. There is hardly any industry where chemical substances are not used and there is no single economic sector where chemicals do not play an important role. Millions of people throughout the world lead richer, more productive and more comfortable lives because of the thousands of chemicals on the market today. Industries producing and using these substances have a significant impact on employment, trade and economic growth worldwide. A variety of global economic and regulatory forces influence changes in chemical production, transport, import, export, use and disposal over time. Global chemical output was valued at US$ 171 milliard in 1970, and it had grown to US$ 4200 milliard in 2010. Although the exact number of chemicals on the market is unknown, it is estimated that there are more than 140,000 chemicals on the EU market, and new chemicals are also introduced into commerce each year.The global chemicals industry has grown rapidly over the past several decades. Within the last decade in particular, this growth has been driven primarily by dramatic growth in developing countries and countries with economies in transition. In the decade 2000 to 2010, the Global Chemical Production Regional Index calculated by the American Chemistry Council (ACC) shows that total production increased 54 percent. Certain countries experienced particularly rapid growth; for example, in China, production nearly tripled over that time period. In 2010, China was the largest chemical producing country, with sales of US$ 754 milliard. The Organization for Economic Cooperation and Development (OECD) countries as a group still account for the bulk of world chemical production, but developing countries and countries with economies in transition are increasingly significant. An analysis by OECD notes that while annual global chemical sales doubled over the period 2000 to 2009, OECD's share decreased from 77 to 63 per cent and the share of the BRIICS countries (Brazil, Russia, India, Indonesia, China and South Africa) increased from 13 to 28 percent. Earlier analyses emphasized a trend in which production of bulk chemicals was shifting to developing and transition economies, while OECD countries continued to lead in the higher-value chemicals such as specialty and life sciences chemicals. However, OECD's most recent analysis notes that some countries with economies in transition are moving increasingly into the markets for specialty and fine chemicals. In particular, OECD notes that companies in China, India, and the Middle East are investing in production of specialty and fine chemicals. OECD's most recent outlook, projecting trends to 2050, predicts that the global chemical sales will grow about 3 percent per year to 2050, with growth rates for the BRIICS countries more than double those of the OECD countries. OECD predicts that chemical production in the rest of the world will grow even faster than BRIICS countries in the period 2010 to 2050, although total volumes produced will be lower. Recent forecasts developed by the American Chemistry Council (ACC) also predict significant growth in chemical production in developing countries in the period to 2021, and more modest growth in developed countries. Consistent with trends seen over the past decade, China is expected to have the highest annual growth rates in chemical production. China's chemical production is expected to exceed 10 percent per year until 2015, and to drop just 10 per cent per year in the years 2016-2021. Rapid growth is expected in India as well, with predicted annual growth above 9 per cent per year in the period 2012 to 2014, and above 8 per cent per year in the period 2015 to 2021. Annual growth rates for Africa and the Middle East are predicted to be just over 6 per cent per year through 2013, and over 5 per cent per year from 2014 to 2021.Duo to the big resource of oil, natural gas, kinds of minerals and basic petrochemicals in Iran, development of the small and medium chemical industries are the best national strategy for converting the country to emerging economics.

Gel Electro-membrane Extraction: Investigation the Effect of Electroendosmosis on Extraction Efficiency in Different Types of Gel Membrane

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Abstract: Recently, gel electro-membrane extraction (G-EME) was introduced for extraction of some basic drugs. Flux of analyte across the gel membrane is based on two driving force; one of them is electro-migration (like EME) and the another one is electroendosmosis (EEO) flow. EEO is a phenomenon that may occur during extraction. Here, anionic groups (e.g., sulfate) in the gel are affixed to the matrix and are thus incapable of motion, but dissociable cations can migrate toward the cathode by means of the electrical field. As a result, EEO (a motion of liquid through the gel) causes an increase and decrease in the volume of cathodic and anodic APs, respectively.

For investigation the effect of EEO on extraction efficiency, agarose with different concentration, types (low, medium and high EEO) and additive (Dextrin, Chitosan, and Xylan) were prepared and used as membrane in G-EME. Cr(III) and Cr(VI) were used as model cationic and anionic species, respectively. During the extraction, positively charged Cr(III) and negatively charged Cr(VI) migrated selectively from an aqueous sample into the cathodic and anodic aqueous acceptor phases (of 400 µL each), respectively.The intensity of EEO and extraction efficiency in G-EME depends on different parameters; such as, the type of agarose, the pH of AP, gel and DP, applied voltage, and also extraction time. In order to obtain the best result, these parameters were investigated. The optimal extraction was obtained at pH of the cathodic AP: 2.0 (HCl); pH of the anodic AP: 3.0 (HCl); pH of the cathodic gel membrane: 5.0; pH of the anodic gel membrane: pH of the DP: 4.0; voltage: 65 V; extraction time: 23 min. The results showed that the highest extraction efficiencies of cathodic and anodic gel membranes were obtained with agarose containing 5% dextrin. By means of this work the mechanism flux of analyte across the gel membrane was found so that there are two main driving force. By electro-migration, analytes are transferred based on their charge. On the other hand, by EEO, the extraction of cationic compounds is accelerated while for anionic compounds, it acts as an inhibitor agent. In addition, the results showed with adding of dextrin in gel membrane, the amount of EEO decreased due to diminish of conductivity of the EME system. Also, via this setup, both cationic and anionic ions could be quantitatively extracted by using solely the gel-based membrane unit.

Bilayer composite of phosphomolybdate doped polypyrrole and nanodiamond at a disposable gold chip as an electrochemical sensor for propylparaben

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Abstract: Parabens are derivatives of synthetic esters of *p*-hydroxybenzoic acid, which due to their biocide activity, have found extensive applications in food products, pharmaceuticals and cosmetics as chemical preservatives. Due to the widespread uses of parabens as preservatives in various industries, development of appropriate analytical methods for determining parabens in different matrices is necessary. The electroanalytical techniques, especially electrochemical sensors, are alternatives for detection of parabens in real samples. Herein, an electrochemical sensor based on a bilayer composite of phosphomolybdate doped polypyrrole (PPy-PMo_{12}) and nanodiamond (ND) at a disposable gold chip (GCHIP) has been introduced for detection of propylparaben (PP). Voltammetry experiments were carried out using an Electroanalyzer system with a conventional home-made glass electrochemical cell and a three-electrode configuration. In order to obtain the optimization condition, the amount of ND, dopant concentration, the scan rate and the pH of buffer solutions were investigated. To evaluate the electrocatalytic activity of the proposed modified electrode, cyclic voltammograms of PP oxidation at the GCHIP, ND/GCHIP, PPy-PMo_{12}/GCHIP and PPy-PMo_{12}/ND/GCHIP modified electrodes were recorded in a solution of Britton-Robinson buffer (pH 7.00) containing 200 μmol L^{-1} of PP. To evaluate the sensing performance of the proposed electrode, LSV technique was employed to construct a calibration curve under the optimum conditions. The linear range 5-200 μmol L^{-1} and limit of detection 2.1 μmol L^{-1} was obtained. In order to evaluate the applicability of the proposed PP sensor for real sample, a commercial shampoo product was subjected to the analysis and satisfactory recoveries were obtained.In this work, a bilayer composite composed of PMo_{12}/PPy organic-inorganic hybrid material electrodeposited on a pre-casted ND film at a disposable GCHIP has been employed for construction of a disposable PP electrochemical sensor. The obtained PPy-PMo_{12}/ND/GCHIP showed favorable electrical conductivity and increased electrocatalytic activity for PP oxidation due to the synergistic effects.

Introduce of simple design, long life time and green rechargeable batteries namely "Li-air batteries" by using ionic liquids

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Abstract: Today, Li-air batteries are currently the most promising new rechargeable batteries because they have much higher energy densities. In general, a lithium-air battery consists of a lithium anode, non-aqueous electrolyte and an air-carbon cathode. Two critical challenges in these batteries are low oxygen solubility in non-aqueous electrolyte and sedimentation of discharge products (i.e Li_2O_2(s) and Li_2O(s)) on oxygen route in air cathode that led to blocked them. Much research's show that use a several catalyst such as CuO, Fe_2O_3, V_2O_5, CeO_2, Pt/Au, Co_3O_4 could be avoided to blocking of oxygen routes and furthermore ionic liquids are satisfying replacing agents to the non-aqueous electrolytes. Some important properties of ionic liquids, such as their high conductivity, non-flammability, non-volatility and wide temperature range of operation, have attracted great interest in view of their application as electrolytes in rechargeable batteries. The battery cell was designed by our team (Fig. 1). The Whatman filter paper was used as separator. The air cathode was prepared by soaking the carbon paper sheet into the slurry mixture of three components containing the catalyst, polytetrafluoroethylene (PTFE) and Kitchenblack carbon (KB) with the weight ratio of 22:12:68 mg, respectively. As shown in Fig. 2, the air cathode with the catalyst of NP-$MnFe_2O_4$ (in the green electrolyte $LiPF_6$/[Omim][PF_6]) shows a discharge capacity of 3391 mAh g^{-1} and battery without the catalyst (in the electrolyte of $LiPF_6$/Dimethyl carbonate) the discharge capacity is 1012 mAh g^{-1}. Fig. 3 indicate that the number of the charge/discharge cycling is increased more than 1000 cycles when the catalyst and $LiPF_6$/[Omim][PF_6], as electrolyte, are used, but it is decreased up to 3 cycles for battery without the catalyst.

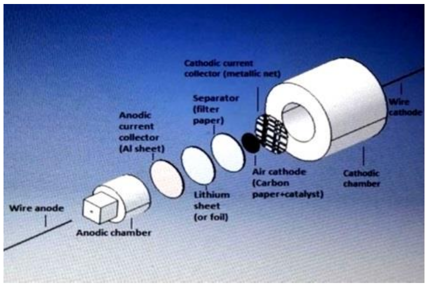

Figure 1

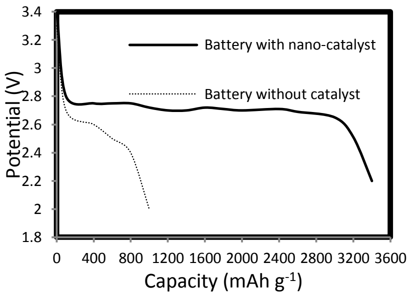

Figure 2

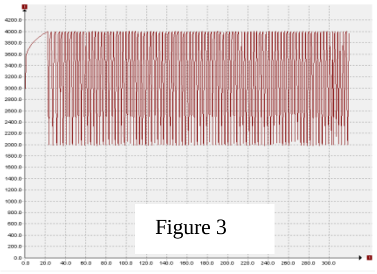

Figure 3

By using the NP-$MnFe_2O_4$ as catalyst and $LiPF_6$/[Omim][PF_6] as green electrolyte, the discharge specific capacity of the Li-air battery was reached to 3391 mAh g^{-1}. The using of the ionic liquid [Omim][PF_6] as a non-aqueous electrolyte increase the safety of the battery because of its high boiling point (more than 350 °C). The designed battery has several advantages such as high cycling charge/discharge capability, high discharge capacity, high safety and longp lifetime.

Application of Some Explosive Materials in Production of Surface-Engineered Activated Carbons from Agricultural Wastes, Using a One- or Two-Stage Activation Process, and studding the Performance of the Prepared Adsorbents for Removal of Pollutants from Aqueous Media

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Abstract: Amongst the technologies used for removal of contaminants from water media, adsorption with activated carbon (AC) is one of the most profitable methods. A large-scale effort has been conducted to use agricultural by-products for preparing cost-effective AC samples, using a one- or two-stage activation process. Due to their explosive characteristics at high temperatures, some ammonium salts like NH_4NO_3 and NH_4Cl can be employed as a novel activating reagent for production of a surface-engineered AC with regular-shaped pores and/or high surface area, using agricultural wastes. Also, a subsequent modification stage by another chemical activating agents can improve the porosity, increase the surface functional groups, and raise the performance for various potential applications. In this work, using NH_4NO_3 and NH_4Cl as activation agents, different agricultural wastes, like pistachio and pomegranate wood wastes and rice husk ash, were exploited for preparation of several AC samples. Also, some ACs were fabricated by inflicting a second activation process by chemical agents like NaOH. The characterization studies were performed with various techniques, and a comprehensive study was performed on the equilibrium, kinetic and thermodynamic aspects of adsorption of some selected pollutants by the new AC samples. The results showed that explosive characteristic of ammonium salts can be employed to produce a char, with a large surface area and/or a highly-ordered pore structure, which can be subjected to a second activation process to prepare a more suitable and modified ACs for removal of different contaminants from aqueous media. In fact, using ammonium salts, good-quality ACs were prepared by applying a one- or two-stage activation process, which were very beneficial for removal of contaminants from water.

Lab on paper analytical device: A postage stamp-size chip made of paper

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Abstract: The requirements for analytical methods that combine high sensitivity, selectivity and accuracy with low cost, portability and user friendliness remains a challenge. Paper-based analytical devices (PADs) are recognized as a powerful analytical platform that can satisfy these requirements. PADs or lab-on-paper chips introduce a novel methodology that use patterned paper as a substrate in a lab-on-a-chip platform. The interest in and use of PADs have grown exponentially over this decade. They offer wide range of applicability such as diagnostics, biological, food safety, environmental analysis and point-of-care (POC) testing. Main advantage include inexpensive, portability, rapid analysis, onsite analysis, disposability, and small sample consumption, ease of fabrication/operation and equipment independence. Paper-based microfluidic analytical devices (μPADs) are becoming valuable tools in analytical area due to their attractive passive movements of analyte (or multiple analytes) without any external forces (like pump or batteries) due to capillary phenomenon. μPADs are made from cellulose or modified cellulose using inexpensive manufacturing. In this discussion after studding of driving mechanisms employed in μPADs, it specially focuses on (1) materials and the fabrication techniques for PADs and μPADs(ranging from photolithography, plasma treatment, inkjet etching, plotting, and commercial eye pencil drawing), (2) detection methods include colorimetric detection with only small and portable devices such as digital cameras and smartphones, electrochemical detection, fluorescence detection, chemiluminescence detection, electrochemiluninescence detection, etc. (3) type of paper based chips for examples spot, two-dimensional (2D) and three-dimensional (3D) (4) how to make choosing proper paper (5)In addition, the novel modification of paper based -chips with micro- and nano-materials possessing is reviewed.

Activity-based Analysis of Potentiometric pH Titrations

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Abstract: The discrepancy between concentrations and activities is a predicament well known to the analytical chemist. Because of the difficulty of determining activity coefficients, the standard technique for quantitative equilibrium studies is to work under a particular ‘constant ionic strength’ by adding an excess of an inert salt. Throughout the numerical analysis of the titration data, activity coefficients for all individual species are approximated by well-known equations based on the work of Debye-Hückel.The mV signal was used directly in the analysis of the potentiometric titration data. For each acid several different titrations were undertaken, they mainly differ in the total concentrations of the acid. The titrations were analysed by the ReactLab pH software. The claim of this contribution is that a single and simple titration at minimal ionic strength delivers good estimates for the thermodynamic equilibrium constants. The standard deviations for activity-based analyses are considerably smaller than those for the classical concentration-based analysis. During any titration the ionic strength will always change and consequently each concentration based, classical analysis is expected to be inferior and this should be reflected in a larger sum of squares.The analysis of potentiometric pH titrations based on activities rather than concentrations serves several purposes. (a) The law of mass action is based on activities and thus the suggested analyses are close to theoretically correct. Classical concentration-based analyses rely on constant ionic strength during the titration which is never completely achieved. (b) The results of the analysis include a set of thermodynamically correct equilibrium constants. These are otherwise only accessible via analysis of extended ionic strength dependences. (c) In classical analyses, inert salts need to be added to the titration solutions; inert salts are never perfectly inert, being of ionic nature they will always interfere with other ions in the solutions. Avoiding inert salts can only be advantageous.

Calibration Augmented Inverse Least Squares (CAILS) Using Tikhonov Regularization, A New Modified ILS Calibration For Unmodeled Interferents

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Abstract: Multivariate calibrations are divided into two directions, Classical (CLS) and Inverse Least-Squares (ILS) [1]. Inverse methods are more popular than CLS because ILS methods allow one to study multicomponent samples where only one or few analytes are of interest, but the concentration, spectra, and chemical identities of other components in calibration samples are unknown. There is a so important restriction for both ILS and CLS that the structure of calibration and prediction samples must be unify, otherwise recalibration is necessary. Estimated model coefficients for ILS methods depends on two main important factors; direction and vector size. Direction is known as the orthogonality of desired analyte spectrum to interfering's spectral space and vector size must be as short as possible to increase the sensitivity of the method [2]. By changing the structure of the prediction samples, there is no longer the orthogonally of regression coefficient on spectral space and, moreover, the length of the vector is not in optimal value.Suggested modified CAILS method corrects the model coefficients in calibration step by augmenting the pure spectrum or spectral shape of unmodeled components to calibration data set. Model coefficient according to Tikhonov Regularization (TR) [3] must fulfilled three condition in calibration step: $\begin{pmatrix} y \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} X \\ \tau I \\ S \end{pmatrix} b$. This process is defined by the minimization of: min ($\|Xb-y\|^2+\tau^2\|b\|^2+\|bS\|^2$). Model coefficient can be estimate by solution: $\hat{b}= (X^TX+\tau^2I+S^TS)^{-1}(X^Ty)$. Where y is the vector of concentration of interest analyte, X is calibration data set, s is pure spectra of unmodeled component(S), τ is ridge parameter and b is model coefficients. Since regression coefficients for desired analyte is Net Analyte Signal (NAS) [4], so including the pure spectra of known interferents in calibration step corrects the direction of model coefficient for analyte of interest.In this contribution a new procedure is proposed based on (TR) which properly solves the problem of presence of un-modeled known interferent(s) that left out the calibration.

Introduce some microextraction methods, enzymatic reactions and solubility measurements

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Abstract: Microextraction methods (dispersive micro-solid phase (D-μ-SPE) and liquid phases (LPME)) as new types of microextraction are attractive for a variety of analytical applications including pre-concentration, clean-up and extraction methods. Up to now the application of D-μ-SPE and LPME for the determination of many analytes is increasing due to the simplicity, fastness and low cost of microextraction methods. With the rise of nanotechnology, a large number of synthetic nano-material is widely used to enhance the extraction efficiency and reduce the extraction time of D-μ-SPE. Most studies focused on the magnetic nano-composites sorbents. The greatest feature of LPME method is excellent clean-up that enables the extraction of analytes from complex matrices such as biological fluids. Deep eutectic solvents (DESs) have attracted interest in analytical and engineering fields. DES formed by complexion of quaternary ammonium salt (usually choline chloride) together with a hydrogen bond donor (HBD). The formation of hydrogen bonding between the halide anion of choline chloride and functional groups of hydrogen donor agent is responsible for the decrease in the freezing point of DESs in relation to the melting points of the individual components. Moreover, they have unique properties such as high purity and environmental friendliness. Most of DESs are liquid at room temperature. These particular features make them as excellent candidates for dissolving a wide variety of materials including salts, proteins, drugs, amino acids, surfactants, sugars, and polysaccharides. The ability of enzymes to catalyze chemical reactions in organic solvents is well established. Esters are compounds with many applications mainly in food, detergents, pharmaceuticals and cosmetic industries. The main advantages of using lipase as catalysts for these kinds of reactions are high yields, mild working conditions, easy recovery, and reusability of the catalyst. In order to identify optimum conditions for performing the ester synthesis, it is useful to know the reaction kinetics and rate constants.The aqueous solubility of organic compounds plays an important role in their industrial, pharmaceutical, separation, purification, and environmental applications. To determine proper solvents and to design an optimized production process, it is necessary to know the solubility of organic compounds in different solvents.

Drug Discovery from Medicinal Plants; From Chemical Analysis to Formulation

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Abstract: Phytochemicals include a broad diversity of bioactive compounds that are a proven source for drug discovery. In this presentation, we introduce conventional and advanced techniques in phytochemicals analyses. Furthermore, a review of some analytical, biological and formulation studies are presented.Various methods of extraction, isolation, identification and biological analyses are introduced. We also present some advanced methods, as “sequential extraction”, “bioassay screening”, “bioassay-guided fractionation”, “bioassay-guided purification”, “TLC-bioautography” and “Q-^{1}HNMR” used in our investigations. Additionally, some herbal formulation studies are discussed. Besides the introduction of conventional and advanced techniques for medicinal plants analyses, some new efficient techniques are recommended for achieving new bioactive natural compounds in the shortest time. We have isolated 17 antidiabetic and antioxidant compounds by applying “sequential extraction”, “bioassay screening”, “bioassay-guided fractionation” and “bioassay-guided purification” methods. We have also detected eight antibacterial compounds using “TLC-bioautography” method. Furthermore, the quantity of 11 active ingredients in a complex mixture (*H. persicum* extract) were measured by “Q-^{1}HNMR” technique. Ultimately, two novel formulations are proposed: 1. A healing cream included 50% purslane extract; 2. An edible and antifungal fruit coating based on thyme essential oil.

The use of carbon quantum dots (CQDs) to develop fluorescence sensors for determination of environmental pollutants and biomolecules

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Abstract: As a kind of fluorescent nanomaterials member of the nanocarbon group, carbon nanodots or carbon quantum dots (CQDs) have attracted scientific research attention because of their unique properties such as high photochemical stability, low photo bleaching, low toxicity, high quantum efficiency, low cost, biocompatibility and solubility in aqueous media that these properties are some advantages of CDs over semiconductor QDs and luminescent organic dyes. In recent years, CQDs were synthesized via different techniques and different primary substance. These methods are mostly classified as top down and bottom up approaches. In this study, some applications of CQDs for determination of environmental pollutants and biomolecules are examined.

Electromembrane Extraction: From the Emergence to the Present and Future Trends

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Abstract: The recent trends in analytical chemistry are focused on down-scaling and development of new sample preparation methods. Application of electrical driving force is the current state-of-the-art, which presents new possibilities for simplifying and shortening the sample preparation process as well as enhancing its selectivity. Thus, here a considerable space is devoted to these methods with an emphasis on the latest efforts put into the electrically-assisted membrane-based sample preparation systems, called as electromembrane extraction (EME). The basis of EME is the migration of charged species in an electric field. The applied voltage in the EME system causes ionizable compounds to be transported from an aqueous sample solution across a supported liquid membrane (SLM) into an acceptor phase. The advantages and disadvantages of this approach as well as the new achievements in these areas especially recent designed SLMs, microfluidic EME and new detection techniques based on smartphone and RGB analysis in combination with EME have been overviewed and discussed. The latest makes it possible to provide a fully portable extraction/quantification approach which facilitates reaching to the goal of in-situ analysis and might be helpful for further progress in analytical chemistry.

Separation and preconcentration of trace species: Nanomaterials for solid phase microextraction and new solvents for microextraction

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Abstract: Separation-preconcentration for trace species is the one of the main part of the sample pretreatment step for them. Solvent extraction, solid phase extraction, coprecipitation etc. are widely used separation-preconcentration techniques. In the last decade, the miniaturization of these techniques for the green chemistry purposes is very popular. Nowadays microextraction and solid phase microextraction studies for traces organic and inorganic species from environmental samples with different strategies are the main part of separation-preconcentration techniques by scientists from Turkey, Iran, and China etc. with new nanomaterials and new generation solvents.

In this presentation, the main strategies for the microextraction of organic and inorganic species at trace levels with new generation solvents including ferrofluids, switchable solvents, deep eutectic solvents, supramolecular solvents etc. and solid phase microextraction with new nanomaterials have been discussed with some examples from our research group at Erciyes University- Kayseri, Turkey.

Magnetic nanofluid based liquid phase microextraction coupled with ETAAS for separation/preconcentration of nickel from water samples

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Abstract: One of the most considerable environmental pollution in recent years is heavy metals pollution which leads to the pollution of food, soil, and water sources. Nickle enhances the iron absorption of the body and also prevents anemia and osteoporosis. Carcinogenesis, severe allergy, respiratory problems are some health effects of nickel [1]. The mixture of magnetic carbon nanotubes (MCNTs) and deep eutectic solvent (DES) called as “magnetic nanofluid” was used as a new generation of the extraction phase [2]. Magnetic nanofluid based liquid-phase microextraction was applied for separation/preconcentration of nickel.To a sample solution containing 10 mL of 100 ng L^{-1} nickel, 20 µL of DES-MNF was added. The mixture was ultrasonicated. Then, the DES-MNF was separated from the solution using an external magnet. The upper phase was taken away. In the back extraction step, 40 µL nitric acid (1 mol L^{-1}) was added to the metal ions-enriched DES-MNF and sonicated for 10 s. the DES-MNF was easily separated by the magnet and 10 µL of the supernatant solution containing metal ions was injected to ETAAS to determine nickel amounts. In this study the green efficient method of magnetic nanofluid based liquid phase microextraction was applied for separation/preconcentration of nickel and determination ETAAS. The extraction solvent is novel magnetic nanofluid consists of DES based MCNTs which can easily be separated from the media with no need to centrifugation. The influential parameters including the amount of magnetic nanofluid, type and volume of back extraction solvent, ionic strength, and sample volume were studied. The detection limit of 4.5 ng L^{-1}, preconcentration factor of 500, and RSD % of 3.1% were acquired. The potential of the method was considered in water samples which showed high capability of the proposed method for application in the complex matrixes.In this research study, deep eutectic solvent based magnetic nanofluid based liquid phase microextraction was introduced for extraction of nickel from water samples. Short extraction time, no need to centrifugation, application of green solvent, facile extraction procedure, high enrichment factor, low detection limit are the advantages of the proposed method.

Application of layered double hydroxides in optical sensors

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Abstract: In the past decades, optical chemical sensors have attracted great attention by researchers because of their high selectivity and sensitivity. They are considered as powerful detection and analysis tools that are mainly based on absorbance, fluorescence and chemiluminescence (CL) principles. Research on fluorescent chemical sensors has received increasing interest due to their inherent simplicity, high sensitivity, and an easy measurement. Fluorescent chemosensors consist of receptor and fluorophore. The ideal fluorophore in chemosensors has high quantum yields of fluorescence, high extinction coefficients, long excitation and emission wavelengths, a long lifetime, and photostability. Therefore, the choice of fluorophore is the most important factor in the design of new fluorescent chemosensors. On the other hand, owing to their extensive linear dynamic range, simplicity, low-cost instrumentation, fast response and low background signal leading to high sensitivity, many research interests have been focused on CL-based sensors. However, application of some optical chemical sensors is limited because the intensity of their signals is not strong sufficient for ultra-trace analytical applications. For this purpose, nanomaterials have been employed. They can enhance luminescence intensity through a catalytic process, energy transfer, redox reactions or Plasmon resonance based on the metal nanoparticles. The introduction of nanomaterials has provided a broad perspective on the application of optical chemical sensors. Layered double hydroxides (LDHs), an important member of host-guest nanomaterials, have brucite-like and positively charged layers with compensating anions in the interlayer. LDHs has become a popular hierarchical material for amplifying fluorescence and CL in recent years, mainly because of its ease of preparation and modification, large specific surface area, and high catalytic activity. Hence, in recent years, the use of LDHs as host materials has become of increasing interest because of creating inorganic-organic host-guest hybrid nanostructures for fabrication of various optical sensors. LDH matrix provides a special structure for intercalated fluorophores such as immobilization of fluorophore in a stable environment improving fluorescence efficiency and optical stability of the fluorophore. Some reported LDH-based amplified CL systems are based on surfactant-LDH composite, quantum dot-LDH hybrids, and organic chromophore-LDH hybrids. In addition, LDHs have been utilized as photocatalysts or photocatalyst supports in the field of energy and environment due to their various unique properties. Given the fact that the LDHs have two different metals and the ratio between them can be controlled, so they can be considered as a good product as doped semiconductor. By varying the metal ions in the brucite-like layers, LDHs show a broad spectrum of photocatalysis.

Isotope Ratio Mass Spectrometry Combined with Chemometrics as New Fingerprinting Method for Saffron Quality Control

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Abstract: Chemical Fingerprint is an analytical signal related to the composition of food which can mainly use for characterization and authentication of food. Isotope ratio mass spectrometry (IRMS) of food bio-elements has been reported as an alternative tool for food quality control. Among different food, saffron as a spice produced from the red stigmas of Crocus sativus L., has attracted great attention in recent years due to its coloring, flavoring and biological properties. However, determining saffron quality is challenging because of the effects of geographical origins and processing methods of its quality. The objective of this work was to propose elemental analysis (EA)-IRMS and gas chromatography (GC)-IRMS fingerprinting combined with chemometrics for authentication of saffron provided from main regions of Iran. Sixty-two saffron samples were provided from Khorasan province. For EA-IRMS, the samples were powdered and then analyzed for measuring bulk carbon and nitrogen isotope ratios. In other words, saffron metabolites were extracted using ultrasonic-assisted extraction-dispersive liquid-liquid microextraction (UAE-DLLME) before GC-IRMS. The optimum extraction factors were obtained using response surface methodology (RSM). Principal component analysis (PCA) as an unsupervised classification method and partial least squares-discriminant analysis (PLS-DA) as a supervised classification method were used for data exploration and interpretation.First of all, EA-IRMS data of C and N for 62 samples were analyzed using PCA. The scores plot showed a good discrimination of samples which was related to N delta values according to PCA loadings plot. These results were related to the bulk analysis of samples, to have a detailed picture of the contribution of individual metabolites on these discrimination, GC-IRMS analysis was mandatory. For GC-IRMS data, first, baseline was corrected using asymmetric least squares (AsLS) and elution time shifts were corrected using interval correlation optimized shifting (icoShift) and correlation optimized warping (COW). Then, delta values for ten major peaks were calculated and data matrix (62×10) was submitted to PCA. The PCA results were used as class labels for PLS-DA which could correctly assign samples to two groups. The figures of merit were reasonable and always higher than 0.90. It is concluded that EA- and GC-IRMS coupled with chemometrics can open a new window for authentication of complex food samples such as saffron.

An overview on designing chemical sensors, biosensors, and nanosensors: Challenges and Opportunities ahead

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Abstract: Rapid, simple and inexpensive determination methods are one of the demand of today's scientific, clinical and industrial societies. Although there are many advanced instruments which can work accurately and precisely, sensors/biosensors can be response to such a need because of inexpensiveness and portability and having simple operatory. They are generally composed of three parts: a sensing element, a transducer, and a signal processor (or detector). They have been designed for numerous industrial, environmental, agricultural, biological, pharmaceutical and clinical applications. From the invention time to now, numerous sensory systems have been designed and developed for fast monitoring of many species (from ions to bio-macromolecules). Some of them can be even commercialized and possess a large marketing size. Nowadays, by progress in sciences and technologies, and by expanding the interdisciplinary collaborations, the number of sensors which find a chance to be commercialized and enter the market are growing fast. However, there are many challenges behind the designing chemical sensors/biosensors or even nanosensors which affect their operations and performances. The main challenges in these systems are finding a suitable analyte/biomarkers, decreasing the limit of detection for an analyte, increasing the sensitivity and accuracy of analyses, increasing life-time and miniaturization ability which is very important for placing them on lab-on-chip. Besides such difficulties in designing each part, by utilization of sensory systems in today industrial life of the humans, there are some opportunities which makes the life better. In this lecture, some challenges and some opportunities will be discussed focusing on our experience on sensors/biosensors and nanosensors.

Simultaneous separation of silver (I) and lead (II) ions through two supported liquid membranes composed of selective crown ethers in supra molecular solvents

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Abstract: This research, for the first time, explores an innovative application of SLMs in the simultaneous selective transport of Ag^+ and Pb^{2+} ions and also the suitability of supra molecular solvents (SUPRAs) constructed of vesicles of decanoic acid as a proper solvent instead of organic solvents. In this work, two carriers Dibenzyl diaza 18 crown 6 (DBzDaza18C6) and Dicyclohexyl 18 crown 6 (DC18C6) were easily dissolved in SUPRA and imbedded in pores of two thin polypropylene films. SUPRA was prepared from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutyl ammonium ion (Bu_4N^+). All transport experiments were carried out at ambient temperature and a two-membrane-three-compartments glass cell was used. The middle compartment with a volume of 500ml contained the source solution and the receiving solutions for silver (I) and lead (II) ions were located in the first and third compartments, respectively, with a volume of 100 ml. Two membranes with an area of 12.6 cm^2 could be fixed in between the three cell compartments. The source solution contained 1.85×10^{-4} mol L^{-1} picric acid, 2 ppm Ag^+ and 2 ppm Pb^{2+} ions, was placed in the middle compartment, one side of which comprised the DBzDA18C6 (8×10^{-3} mol L^{-1})-loaded SLM and the other side the DC18C6 (8×10^{-3} mol L^{-1})-loaded SLM. The first and third compartments contained the receiving solutions (100 ml each) 0.6 mol L^{-1} sodium thiosulfate at pH 6.4 for stripping of Ag^+ ion and 0.25 mol L^{-1} sodium pyrophosphate at pH 7 for stripping of Pb^{2+} ion, respectively. Each compartment was equipped with a Teflon coated magnetic stirrer for stirring the aqueous solutions and an inlet for filling and draining the source and receiving solutions. Under optimal conditions, silver and lead ions were transported into their receiving phases after 75 and 15 min, respectively, and a simultaneously quantitative separation of the cations was achieved in a relatively short time (i.e. 97.5% Ag^+ and 96.5% Pb^{2+}). A novel application of supported liquid membranes (SLMs) to the selective and simultaneous separation of Ag^+ and Pb^{2+} ions from a dilute source by employing a two-membrane-three-compartment cell and two selective crown ethers dissolved in SUPRA solvent is introduced.

Synthesis and characterization of novel heterostructures and their application for selective and sensitive monitoring biological compoundsand/or subsequent visible light photocatalysts or adsorbents for wastewater treatment: Mechanism investigation and multivariate optimization

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Abstract: Water pollution resulted from the organic dyes in industries has been a pointed issue worldwide. The release of the dyes into the environment is considerable sources of environment hazards including non-aesthetic pollution as well as eutrophication, and also believed endanger human health owing to the dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater. The dyes are toxic and harmful for human and animals that lead to production of cancer-causing and mutagenesis hazards. Consequently, these difficulties make emergency to design and develop of high importance, safe and clean economical technique to treat and removal of dyes from environment and aqueous media. Different technique such as coagulation, flocculation, adsorption, precipitation, electrochemical techniques, membrane filtration, ozonation and bio sorption have been widely used for dyes removal. Novel heterostructure including molecular imprinted polymers, ion imprinted polymers, heterojunction composites was successfully designed with no require to any additives or post preparation treatments and subsequently were characterized by XRD, EDX, UV–Vis-DRS, SEM, PL and EIS techniques. Our findings indicate promising applications for the bismuth oxychloride photocatalysts in the presence of blue and/or sunlight to improve quality of water and wastewater treatment and help their expanding for the degradation of diverse pollutants under visible-light irradiation. Application of MIP lead to enhance in selectivity and improvement in characteristic performances.

Label free DNA biosensor for drug analysis

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Abstract: In the recent year's new advantages in analytical sensors developed using sensitive and specific DNA biosensors. DNA biosensors, based on nucleic acid recognition methods, are being developed towards the assay of fast, easy and economical testing of anticancer drugs. In between, the label free DNA biosensors, was suggested using interaction of drugs with adenine and guanine bases in DNA structure by intercalation strategy. The reduction in adenine and guanine bases in DNA structure after intercalation by drugs are the main strategy in label free DNA biosensors. The reduction in current can be used as a sign for determination of drug concentration. In this presentation, we described different modified electrode as electrochemical biosensor for determination of epirubicin, didanosine, 6-mercaptopurine and etc.The presence study described the Experimental and docking theoretical investigation for determination of drugs compounds using label free DNA biosensors. The optimization factors and other relative parameters were described in this presentation and results showed the pH, interaction times, concentration of DNA are very important factors in this type of bio-sensors.

L-norm based penalty methods in Chemometrics

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Abstract: There are different problems for resolution of complex LC/GC-MS data, such as the existence of embedded chromatographic peaks, continuum background and overlapping in mass channels for different components. These problems usually cause rotational ambiguity in recovered profiles and bring uncertainties in the final solutions found using the multivariate curve resolution (MCR) methods. Since mass spectra are sparse in nature, the sparsity constraint has been proposed recently as a constraint in MCR methods for analyzing LC/GC-MS data. There are different ways for implementation of the sparsity constraint, and the majority of methods rely on imposing a penalty term based on the L0-, L1- and L2-norms of recovered mass spectra. Ridge regression and least absolute shrinkage and selection operator (Lasso) can be used for implementation of L2- and L1-norm penalties in MCR, respectively. However, the main question is which Lx-norm penalty method is more worthwhile for implementation of the sparsity constraint in MCR methods. In order to address this question, two and three component LC/GC-MS data were simulated and used for the case study in this work.The areas of feasible solutions (AFS) were calculated using the grid search strategy and fminsearch algorithm. Moreover, the magnitude of the L0, L1- and L2-norms of all mass spectra in AFSs were calculated and visualized as contour plots. The results revealed that the gradient of optimization surface for minimization of L1-norm is much more than those seen for minimization of L2-norm. Therefore, minimization of L1-norm would be a more reliable and practical way for confining AFS and reducing rotational ambiguity for these simulated LC/GC-MS data. Calculating Lx-norms in AFS for $0\leq x\leq 2$ revealed that the gradient of optimization surface increased from x=2 to x values near zero. However, for x=0, the optimization surface was similar to a plateau, which increased the risk of sticking in local minima. The results in this work, recommend the use of L1-norm penalty methods like Lasso for implementation of the sparsity constraint in the MCR-ALS algorithm for finding more sparse solutions and reducing the extent of rotational ambiguity.

Recent advances in quantum dots based electrochemical biosensors

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Abstract: Recently, semiconductor nanocrystals or quantum dots (QDs) have attracted considerable attentions due to their unique optical, electronic and catalytic properties. QDs have been regarded as promising and attractive building blocks for the development of efficient biosensors with high sensitivity, good selectively, rapidity and simplicity. Although there are many reports on the application of QDs in the analytical chemistry, there are many challenges in the development of selective and sensitive chemical sensors. Among the recently developed quantum dots, carbon dots and graphene quantum dots (GQDs) are the latest research frontiers which have attracted great interest in the development of electrochemical biosensors. In this presentation, a review of recently reported papers in the field of quantum dots especially GQDs based electrochemical biosensors will be presented. Also, a review of projects which have been done in my research team will presented.

Development of an origami paper-based microfluidic device for separation and simultaneous quantification of color additives in food samples

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Abstract: Numerous analytical methods applied to determine mixtures of colorants in different matrices for monitoring the quality and safety of food products. In many of these methods pre-treatment steps are required. Liquid-liquid extraction (LLE), solid-phase extraction (SPE), membrane filtration, cloud point extraction and other extraction. Nowadays, studies focused mostly on the developing microfluidic paper-based devices (µPAD) technology due to several advantages as low-cost material that can be readily modified and patterned, power-free fluid transport via capillary action, and adaptability with a wide range of detection methods. Amongst, digital imaging devices are a simple, sensitive, and reliable alternative for the expensive analytical instruments for food colorant analysis. In this work, after creating hydrophobic barriers on paper, 0.5 µl aliquot of the mixture was injected into the µPAD. Next, it was folded to origin an origami 3D µPAD. Then, the µPAD was fixed between two rectangular glass plates connected by bolts and nuts. A pore embedded in the center of the glass plates, therefrom the mobile phase was applied by micropipette. After completing the separation process each µPAD was scanned, ImageJ computer program was applied and the mean pixel value of each channel (R, G and B) were stored in Excel for subsequent calculations. The potentially effective parameters such as µPAD size, pH, solvent, and color space were studied. Following the optimization steps, analytical signals based on the color value were plotted for standard samples.The proposed analytical method using the origami paper-based microfluidic device coupled with digital image analysis proved to be effective for the rapid separation and simultaneous quantification of the synthetic azo dyes. Linear ranges 0.01 g. L^{-1} - 20 g. L^{-1} (R2= 0.988) for E102 and a logarithmic relation was observed between 0.05 g. L^{-1} - 10 g. L^{-1} for E132 and limits of detection (3σ/slope) was between 0.07 and 0.09 g. L^{-1} respectively. This method was successfully applied in the separation and quantification of these dyes in jelly, candy, and three kinds of drinks samples with acceptable recoveries. Finally, the developed method presents advantages such as quickness, simplicity, environmentally friendly, economical, and ease of operation compared with other methods.

Verification of Nerve Agents Exposure by Identification of Free Metabolites and Protein Adduct Biomarkers in Human Urine and Plasma Samples Followed by GC & LC-MS/MS in the 4th Official OPCW Biomedical Proficiency Test

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Abstract: The purpose of this study was to analyse human plasma and urine samples for protein adducts and free metabolites with different analytical methods for the presences or absence of nerve agent exposure. Organophosphorus Nerve Agents (OPNAs) including tabun, sarin, soman, cyclosarin, and VX target the enzyme Butyrylcholinesterase (BuChE) and albumin to cause acute toxicity [1-2]. In this Biomedical Proficiency Test, plasma samples (4×5 mL vial with codes P451-P454) and urine samples (3×5 mL vial with codes U455-U457) receipted (23 February, 2019) from (OPCW) Laboratory (Rijiswijk, The Netherlands) analyzed for verification of human exposure to nerve agents. The spiking protocol was kept unknown for participating laboratories. The identification of each test chemical must be based on at least two different analytical methods giving consistent results base on identification criteria. BuChE activity was measured spectrophotometrically using an Ellman assay as a preliminary test to diagnose exposure to OPNAs. Fluoride regeneration method and clean-up with HLB solid phase extraction applied to release the agents again. BuChE from plasma purified with Sepharose Q fast flow gel (anion exchange)-procainamide affinity gel chromatography and digested with pepsin, clean-up with C18 solid phase extraction identified the modified nonapeptide adducts by LC-MS/MS. Totally protein precipitation, digestion with enzyme of Pronase E, clean-up with 10KD MWCO identified the tyrosine adducts using LC-MS/MS. Clean up with LC-Si cartridge, derivatization with Pentafluorobenzyl bromide followed by GC-MS/MS analysis was applied to identify the free metabolites of nerve agents in urine samples. All reported chemicals were in accordance with preliminary report of the fourth Official OPCW Biomedical Proficiency Test. Cyclosarin was identified in plasma samples with code P451 and P454 with real concentration of 8 and 5 ng/mL respectively according to OPCW reports. Sarin with concentration of 20 ng/mL was identified in plasma sample with code P452. Isopropyl methylphosphonic acid (20 ng/mL) and Cyclohexyl methylphosphonic acid (5 ng/mL) were identified in urine samples with code U455 and U457 respectively. Reference chemicals (own synthesis) were used for the comparison to the data obtained with the test samples. The samples with code P453 and U456 were blank samples. The Defense chemical research laboratory (DCRL) identified all the spiked chemicals in the concentration range of 5-20 µg L^{-1} in plasma and urine samples correctly with sufficient analytical data.

Magnetic Nanomaterials in Analytical Chemistry

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Abstract: In recent years, magnetic nanomaterials, such as iron oxide nanoparticles, have attracted great attention in different fields including Analytical Chemistry. Due to their magnetic properties, low-cost, and excellent biocompatibility, iron oxide nanoparticles have a wide application as adsorbents in food analysis, bioanalysis, environmental monitoring, forensic chemistry, and magnetic digital microfluidics as well as colorimetric sensors, resonance light scattering sensors, surface-enhanced Raman spectroscopy sensors, electrochemical sensors, and biosensors. Various chemical methods have been developed for the synthesis of iron oxide nanoparticles such as sol-gel, microemulsion, thermal decomposition, and coprecipitation, hydrothermal/solvothermal, sonochemical, and electrochemical methods. Furthermore, they can be easily functionalized using polymer coatings including MIP and IIP layers, nanocomposites, nanoparticles immobilizations, and anchoring functional moieties. In Analytical Chemistry, magnetic nanomaterials can be utilized in methods such as magnetic solid-phase extraction, magnetic headspace-adsorptive extraction, magnetic in-tube extraction, cloud point-magnetic dispersive-SPE, electrochemical methods, and Resonance light scattering.

Ultrasound Assisted Extraction of Valuable Natural Compounds with Preparative Approach

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Abstract: Ultrasound-assisted extraction (USAE) is a process to obtain high valuable compounds and could increase the value of some food by-products when used as sources of natural compounds. The USAE is a more effective extraction process with low energy consumption. Also USAE is carried out at moderate temperatures, which makes it suitable for extraction of heat-sensitive compounds. The most effective parameters on extraction efficiency in USAE are applied ultrasonic power, the frequency, the extraction temperature, the reactor characteristics, and the solvent–sample interaction [1]. Stevia rebaudiana Bertoni (Asteraceae) is a perennial shrub originating in Paraguay and Brazil where it is still known as “stevia” or “honey leaf. The leaves of this plant have been used for centuries as natural sweetners [2]. Leaves of Stevia rebaudiana Bertoni have been used for the last 20 years in countries of South America and Southeast Asia as a low-calorie sugar substitute. Steviol Glycosides extracted from stevia rebaudiana that contain Stevioside, Rebaudiosides A, B, C, D, E, F and Dulcoside. On the other hand, In the recent years the trans-resveratrol (trans-3,5,$4'$-trihydroxystilbene), a polyphenol with significant properties such as antioxidant, anti-cancer, anti-diabetic, cardio protective, and even anti-aging have attracted grate attention [3]. In this work, application of USAE for extraction of steviol glycosides from stevia leaves was optimized. At the next step application USAE was described for extraction of trans resveratrol from dried red grape skin.

Single particle analysis by inductively coupled plasma mass spectrometry (sp-ICP-MS) as a novel and fast tool for nanoparticle characterization in Environmental Matrices

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Abstract: Nanomaterials transport of contaminants in the environment is a matter of concern because colloids can travel long distances along surface waters and fractured aquifers. The fate of contaminants in the environment is controlled by complex interactions and transport mechanisms including colloidal, chemical and, hydrodynamic processes. The critical parameters that affect the toxicity of nanoparticles are the particle size which might be related to the larger surface-to-volume ratio, and the surface charge. Water, soil and peppermint samples collected from Mazandaran and Alborz providence. Samples were stored in refrigerator temperature. Samples were prepared in 1 mM SDS and introduced into ICP-MS in TRA mode. Aqueous suspensions of standard spherical Ag and Au nanoparticles with diameters of 30, 60 and 100 nm and mass concentration of 1.0 mgL^{-1} stabilized with citrate. An Agilent 7700x ICP-MS was used for nanoparticles characteristics. The instrument should be prepared and sat up for analysis. The sp-ICP-MS technique has been validated for the determination of standard NPs and tested in an inter-laboratory study for the determination of nanoparticles in standard aqueous suspensions. Calculation of particle size, mass concentration and size distribution from the spICP-MS data was performed using a spreadsheet was developed by our group. In sp-ICP-MS, the transport efficiency should be firstly obtained to estimate the nanoparticles content in the particles of the samples. Transport efficiency was evaluated by comparing the signal of dissolved standard of Au of 100 ngmL^{-1} with the signal of a suspension of Au of 60.0 nm at a concentration of 50 ng mL^{-1}. Under the optimized conditions, natural and engineered nanoparticles were detected in all samples. Limits of detection and quantification of total Ag, Au, TiO_2 and ZnO determined by ICP-MS were 0.01, 0.01, 0.03 and 0.05 ng mL^{-1}, respectively. The recoveries were ranged from 91% - 93% in real samples. The repeatability for the determination of the particle size of a 60 nm Ag based nanoparticles in water samples were 1.4% and 2.3%.

1-Analytical Electrochemistry

Author	Page	Author	Page	Author	Page
Mir-Mahdi Abolghasemi-1	1	Mahdieh Zolfaghari	23	Erfan Ghafari	45
Mir-Mahdi Abolghasemi-2	2	Hamidreza Rahmanian	24	Javad Gholami	46
Ali Ehsani-1	3	Zeinab Rahmati	25	Ghasem Fouladi Vanda	47
Ali Ehsani-2	4	Ali Sadat Nabi	26	Zohre Fahimi Rudposht	48
Shirin Ehsanifard	5	Bahman Sargolzaei	27	Azar Gharib	49
Narges Ashraf	6	Samira Saidi-1	28	Khadijeh Ghanbari-1	50
Hamid Reza Akbari Hasanjani	7	Samira Saidi-2	29	Khadijeh Ghanbari-2	51
Ameneh Amani	8	Esmail Sohouli-1	30	Kamalodin Kor	52
Amirhassan Amiri	9	Esmail Sohouli-2	31	Solmaz Kia	53
Abbas Hassanoghli	10	Masoud Sivari-1	32	Arman Mohammadi	54
Razieh bavandpour	11	Masoud Sivari-2	33	Hamideh Mohammadi	55
Mahmood Payehghadr	12	Saeed Shahrokhian	34	Seyedeh Fatemeh Mokhtari	56
Ali Farahani	13	Somayeh Sharifi-1	35	Atena Mazinani	57
Zahra Tofighi	14	Somayeh Sharifi-2	36	Zahra Monsef	58
Saleh Javaherian-1	15	Abbas Sabahi	37	Roya Mirzajani	59
Saleh Javaherian-2	16	Maryam Abedi-1	38	Fatemeh Nazari	60
Mehdi Hosseini	17	Maryam Abedi-2	39	Mehran Nozari-asbemarz	61
Hamidreza Haghgoo Qezelje	18	Samaneh Abbasi	40	Zahra Noori	62
Sajad Heidari Fathabad	19	Mehdi Abdolmaleki	41	Maryam Vafadar	63
Zahra Khodabandelou	20	Mansure Alizadeh	42	Farzaneh Yari	64
Sadegh Khazalpour	21	Vahid Alizadehfard	43	Nesa Yousefloei	65
Azar Dehnavi	22	Fatemeh Amouzad	44		

Electrochemical Sensor GPE/Cu NPs/4-Phenoxyaniline to Determination the Pyriproxyfen

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Background: The use of pesticides in commercial agriculture has led to an increase in farm productivity. The disadvantage of pesticide use is that residues may remain on agricultural commodities. Many of these compounds are known carcinogens and/or toxins, and therefore, it is desirable to reduce these residues [1]. Pyroproxyfen is a pyridine-based pesticide that is effective in eliminating various types of arthropods [2]. In this work, the graphite pencil chose as the material of the electrode because the graphite pencil electrode(GPE) has a larger active electrode surface area and is therefore able to detect low concentrations and/or volumes of the analyte. Graphite pencil electrodes have several advantages over other carbon-based or commercial metal electrodes, including widespread availability, very low cost, and ease of modification [3].

Methods: First, the surface of the electrode of the pencil was covered with teflon strip. Then the tip of the electrode was polished with soft polishers and then washed with acetone, ethanol and water under ultrasonic conditions. The electrode was first coated with Cu NPs and then coated with 4-phenoxyaniline and an electrochemical sensor of the GPE/Cu NPs/4-phenoxyaniline was prepared.

Results: By the modified graphite pencil electrode/Cu NPs/4-phenoxyaniline a cathode peak have appeared at 0.32V. The modified electrode using square-wave voltammetric(SWV) method showed a linear behavior on concentrations of 100 to 800 nM than pyriproxyfen.In addition, the scanning electron microscope(SEM) images was used to investigate the surface of the electrode and to confirm the successful deposition.The modified electrode also displayed excellent electro-catalytic properties (α =0.56, LogK_s =3.45s^{-1}, and Γ =4.56×10^{-5}mol cm^{-2}) for the oxidation of pyriproxyfen at the optimized pH=3 and the working potential of 0.32V (*vs.* Ag/AgCl).

Conclusion: A modified GPE/Cu NPs/4-phenoxaniline as an electrochemical sensor was used to determination the pyriproxyfen. Owing to the good selectivity and high sensitivity of the proposed sensor, it was successfully used for the determination of the pyriproxyfen content in real samples with satisfactory results and free from side interferences.

Keywords: Graphite pencil electrode; Pyriproxyfen; Voltammetric; 4-phenoxyaniline.

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Electrochemical Sensor GPE/Cu NPs/Alizarin to Determination the Clodinafop propargyl (Topik)

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Background: The use of pesticides in commercial agriculture has led to an increase in farm productivity. The disadvantage of pesticide use is that residues may remain on agricultural commodities. Many of these compounds are known carcinogens and/or toxins, and therefore, it is desirable to reduce these residues [1]. Topik is a foliar-absorbed aryloxyphenoxypropionate herbicide, which is translocated to the meristem [2]. These herbicides have increasingly become a key component of weed management programs in the arable lands of Iran. hence, they could be qualified as high-risk herbicides [3]. Graphite pencil electrodes(GPEs) have several advantages over other carbon-based or commercial metal electrodes, including widespread availability, very low cost, and ease of modification. The GPE, when combined with a more highly sensitive and accurate voltammetric technique, becomes an attractive electrode for trace analysis [4].

Methods: First, the tip of the electrode was polished with soft polishers and then washed with acetone, ethanol and water under ultrasonic conditions. The electrode was first coated with Cu NPs and then coated with alizarin and an electrochemical sensor of the GPE/Cu NPs/Alizarin was prepared.

Results: By the modified GPE/Cu NPs/Alizarin an anode peak have appeared at -0.1V. The modified electrode using square-wave voltammetric(SWV) method showed a linear behavior on concentrations of 1 to 11 µM than topik. In addition, the scanning electron microscope(SEM) images was used to investigate the surface of the electrode and to confirm the successful deposition.The modified electrode also displayed excellent electro-catalytic properties (α =0.78, LogK_s =3.23s^{-1}, and Γ =1.70×10^{-4}mol cm^{-2}) for the reduction of topik at the optimized pH=10 and the working potential of -0.1V (*vs.* Ag/AgCl).

Conclusion: A modified GPE/Cu NPs/Alizarin as an electrochemical sensor was used to determination the topik. Owing to the good selectivity and high sensitivity of the proposed sensor, it was successfully used for the determination of the topik content in real samples with satisfactory results and free from side interferences.

Keywords: Alizarin; Clodinafop propargyl; Graphite pencil electrode; Topik.

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Electrochemical and DFT study on corrosion inhibition of aluminum by natural biopolymers

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Background: Corrosion is a worldwide problem to be addressed by educational and industrial divisions because it unfavorably affecting the economy of developed as well as developing countries. The damage of corrosion is most pronounced during industrial cleaning processes such as acid descaling and acid pickling of metallic ores to remove the corrosion products collected on the metallic surfaces. Organic compounds, especially those containing polar functions with oxygen, nitrogen and/or sulfur in a conjugated system, have been frequently reported to inhibit the corrosion of metals in aggressive environments[1,2]. In recent decade investigations, ionic liquids (ILs) and natural polymer have been pro-posed as green inhibitors to control corrosion of different metallic substrates exposed to corrosive media, particularly acid solutions. Utilizing natural polymer is one of the goals of green chemistry.

Methods: In the present work, different natural polymer such as chitosan inhibiting action on the corrosion of stainless aluminum in HCl was investigated by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

Results: The results of the investigation show that the newly mentioned polymer show excellent inhibition efficiencies against the corrosion of Al in acidic solution. The adsorption of polymer onto the Al surface followed the Langmuir adsorption model. Electronic properties such as highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and frontier molecular orbital coefficients for inhibitors have been calculated.

Conclusion: inhibition efficiency values augmented with the used inhibitor extent and reaching the maximum 95% at 500 ppm based on Tafel plot measurements. Tafel plots study disclosed the used inhibitors behaves as a mixed type corrosion inhibitor cum a prevailingly cathodic type. The EIS study revealed that the application of the natural polymer inhibitor significantly augmented the R_{CT} extent and decreased the double layer capacitance value into molar hydrochloric acid, suggesting that corrosion inhibition of the biopolymer occurs through adsorption. Quantum chemical analysis results confirmed the electrochemical measurements about the effectiveness of the inhibitor.

Keywords: biopolymer, corrosion, impedance, adsorption. tafel

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Nanocomposite of new functionalized graphene oxide/electroactive conductive polymer as most efficient electrode materials in electrochemical pseudocapacitors

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Background: Owing to a unique combination of features such as superb electrical conductivity, corrosion resistance in aqueous electrolytes, highly modifiable nanostructures, long cycle life and the large theoretical specific-surface area, the use of binary and ternary nanocomposites as a supercapacitor electrode material has become the focus of a significant amount of current scientific researches in the field of energy storage devices [1, 2].

Methods: In this study, amino acid functionalized graphene oxide (FGO) was synthesized by chemical route. The prepared functionalized graphene oxide was characterized by different analytical techniques such as FT-IR, Raman spectroscopy, thermogravimetry coupled with mass spectrometry (TG-MS), X-Ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS). In terms of electrochemical methods, galvanostatic charge–discharge experiments, cyclic voltammetry (CV) and electrochemical impedance spectroscopy are carried out in order to investigate the performance of the system.

Results: In this work, for improving electrochemical properties of the poly ortho aminophenol (POAP), we fabricated FGO/ POAP films by electro-polymerization of POAP in the presence of synthesized FGO and with porous structure, to serve as the active electrode for electrochemical supercapacitor. The electrochemical measurement results indicate that nanocomposite electrodes have higher specific capacitances as they have higher redox activity than POAP and FGO electrodes. The highest specific capacitance obtained for POAP/FGO nanocomposite electrode was obtained 480 Fg-1.

Conclusion: This work introduces the new most efficient materials for electrochemical redox capacitors with benefits including ease synthesis, high active surface area and stability in an aqueous electrolyte.

Keywords: nanocomposite, supercapacitor, electroactive, charge/discharge.

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Electrochemical determination of pirimicarb using poly-L-methionine-gold nanoparticles/chitosan-multi-walled carbon nanotube/pencil graphite electrode

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Background: Pirimicarb, is an extensively used carbamate insecticide. Due to its increasing use as an alternative to more toxic organochlorinated and organophosphorinated pesticides, there is growing interest in the analytical methods for its determination at low concentration levels in water, soil, plant, and fruit samples. Several analytical techniques have been proposed to determine pirimicarb, especially gas [1,2] and liquid [3,4] chromatography.

Methods: Initially, the MWCNTs/chitosan coated electrode was prepared by casting of MWCNTs/chitosan solution on the pencil graphite electrode surface. After that, the electropolymerization of L-methionine (MET) was performed in presence of $HAuCl_4$ on the MWCNTs-chitosan/PGE using cyclic voltammetry in an aqueous solution of L-methionine and $HAuCl_4$ in phosphate buffer solution. For this purpose, six successive cycles were applied in a potential range of −0.5 to 2 V vs Ag/Agcl at a scan rate of 50 mV/s. In this way PMET-AuNPs/MWCNT-Chitosan/PGE was fabricated.

Results: Pirimicarb was detected in the linear dynamic range of 1.8 µM to 187 µM, and the detection limit was determined as 0.75 µM using differential pulse stripping voltammetry (DPSV) under optimized conditions. The PMET-AuNPs/chitosan-MWCNT/PGE demonstrated good reproducibility, repeatability and selectivity for the determination of pirimicarb.

Conclusion: In this work, PMET-AuNPs/chitosan-MWCNT/PGE was simply fabricated by electropolymerization of MET and electrochemical entrapment of AuNPs on the chitosan-MWCNT/PGE. This sensor showed excellent performance toward pirimicarb determination such as suitable detection limit, wide linear dynamic range and good selectivity. Real samples studies were carried out in the environmental samples.

Keywords: Pirimicarb, Differential pulse stripping voltammetry, Poly (L-Methionine), Gold nanoparticles, Chitosan, MWCNT

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Bilayer composite of phosphomolybdate doped polypyrrole and nanodiamond at a disposable gold chip as an electrochemical sensor for propylparaben

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Background: Parabens are derivatives of synthetic esters of *p*-hydroxybenzoic acid, which due to their biocide activity, have found extensive applications in food products, pharmaceuticals and cosmetics as chemical preservatives [1]. Due to the widespread uses of parabens as preservatives in various industries, development of appropriate analytical methods for determining parabens in different matrices is necessary. The electroanalytical techniques, especially electrochemical sensors [2-4], are alternatives for detection of parabens in real samples. Herein, an electrochemical sensor based on a bilayer composite of phosphomolybdate doped polypyrrole (PPy-PMo_{12}) and nanodiamond (ND) at a disposable gold chip (GCHIP) has been introduced for detection of propylparaben (PP).

Methods: Voltammetry experiments were carried out using an Electroanalyzer system with a conventional home-made glass electrochemical cell and a three-electrode configuration.

Results: In order to obtain the optimization condition, the amount of ND, dopant concentration, the scan rate and the pH of buffer solutions were investigated. To evaluate the electrocatalytic activity of the proposed modified electrode, cyclic voltammograms of PP oxidation at the GCHIP, ND/GCHIP, PPy-PMo_{12}/GCHIP and PPy-PMo_{12}/ND/GCHIP modified electrodes were recorded in a solution of Britton-Robinson buffer (pH 7.00) containing 200 μmol L^{-1} of PP. To evaluate the sensing performance of the proposed electrode, LSV technique was employed to construct a calibration curve under the optimum conditions. The linear range 5-200 μmol L^{-1} and limit of detection 2.1 μmol L^{-1} was obtained. In order to evaluate the applicability of the proposed PP sensor for real sample, a commercial shampoo product was subjected to the analysis and satisfactory recoveries were obtained.

Conclusion: In this work, a bilayer composite composed of PMo_{12}/PPy organic-inorganic hybrid material electrodeposited on a pre-casted ND film at a disposable GCHIP has been employed for construction of a disposable PP electrochemical sensor. The obtained PPy-PMo_{12}/ND/GCHIP showed favorable electrical conductivity and increased electrocatalytic activity for PP oxidation due to the synergistic effects.

Keywords: Propylparaben, Molybdatophosphoric acid, Polypyrrole, Nanodiamond, Disposable gold chip, Electrochemical sensor

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A new pencil graphite modified for electrochemical determination of carboxin

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Background: Carboxin is one of the several systematic fungicides that it is used in agriculture for controlling various pathogenic fungi. Various methods have been reported for the carboxin detection. Most analytical methods for determining fungicides are based on spectroscopy and chromatographic techniques such as UV-Vis [1], gas chromatography (GC) and high-performance liquid chromatography. Although several types of biosensors have been developed in the analysis of environmental samples [2,3], but to our knowledge only one electrochemical sensor has been reported for the determination of the carboxin [4].

Methods: The electrode modification of poly-L-methionine-silver nanoparticles on pencil graphite electrode was performed by using cyclic voltammetric (CV) technique in the potential range of -0.6 V to 2 V with a scan rate of 200 $mV.s^{-1}$ during 6 cycles in the presence of L-methionine (LMT) and $AgNO_3$, and then DNA was electrodeposited on the modified electrode.

Results: Adsorptive differential pulse voltammetry indicates that the peak current increases linearly with respect to the increment in the carboxin concentration. Carboxin was determined in the linear dynamic range of 8.0 pM to 1.0 µM, and the detection limit was determined as 5.0 pM by using AdDPV under optimized conditions. The modified electrode demonstrated good selectivity toward carboxin against other pesticides and also metal ions.

Conclusion: In the present work, a new modified electrode was introduced for the determination of the carboxin. The modified electrode was favorably applied in the environmental samples for the voltammetric determination of the carboxin with a low limit of detection and suitable linear range.

Keywords: Carboxin; Adsorptive differential pulse voltammetry; L-methionin; Silver nanoparticls

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Electrochemical Oxidation of 2,5-Dihydroxybenzoic Acid in the Presence of 2-thiobarbituric acid and 1,3-diethyl-2-thiobarbituric acid

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Background: Synthesis of molecules with desirable functional groups in the absence of catalysts and drastic conditions continues to be of great interest. In organic synthesis, electrochemical electron-transfer-driven reactions have been widely used for various transformations [1]. Our previous studies show that the electrochemically generated *p*-quinone is a reactive intermediate and as a Michael acceptor, participates in different types of reactions [2]. On the other hand barbituric acid derivatives are well known to possess antibacterial, sedatives, herbicides, fungicides and antiviral agents [3]. However, until now, no report has been published about the electrooxidation of 2,5-Dihydroxybenzoic acid **(1)** in the presence of 2-thiobarbituric acid derivatives.

Methods: electrochemical studies was performed in water/acetonitrile (80/20) solution containing 0.2 M acetate buffer (pH=5.5). Controlled-potential coulometry and electrolysis were performed in water/acetonitrile (80/20) solution (60 mL) containing 0.2 M acetate buffer (pH=5.5), 0.2 mmol of **1** and 0.2 mmol of **3a, 3b** at 0.45 V *versus* SCE.

Results: In this work electrochemical oxidation of 2,5-Dihydroxybenzoic Acid (**1**) has been studied in the presence of 2-thiobarbituric acid (**3a**) and 1,3-diethyl-2-thiobarbituric acid (**3b**) as nucleophiles (Fig. 1). Some electrochemical techniques such as: cyclic voltammetry using diagnostic criteria derived by Nicholson and Shain for various electrode mechanisms and controlled-potential coulometry(Fig. 2) were used. Our results indicate the participation of electrochemically generated *p*-quinone in Michael-type addition reaction with 2-thiobarbituric acids (**3a, 3b**) to form new barbituric acid derivatives.

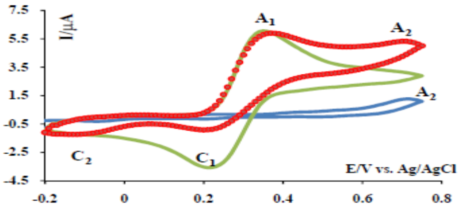

Fig. 1

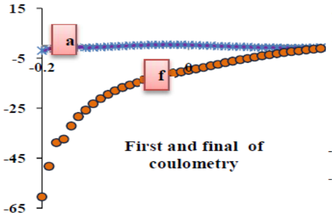

Fig. 2

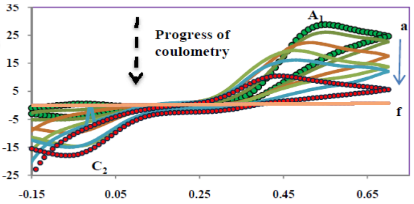

Fig. 2

Conclusion: Diagnostic criteria of cyclic voltammetry, the consumption of four electrons per molecule of 2,5-dihydroxybenzoic acid (**1**), and the spectroscopic data of the isolated products, indicated that the reaction mechanism of electrooxidation of **1** in the presence of **3a,b** is ECE mechanism. Nature stability of *p*-quinones in comparison with *o*-quinones in one hand and stability of final products arising from intramolecular hydrogen bonding, on the other hand, are responsible for remaining the final products in quinone form.

Keywords: cyclic voltammetry; 2,5-dihydroxybenzoic acid; 2-thiobarbituric acid; 1,3-diethyl-2-thiobarbituric acid.

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Anodic Stripping Voltammetric Detection of Arsenic (III) at a dendrimer/nano gold-modified glassy carbon electrode

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Background: Arsenic is one of the most serious natural pollutants in soil and water in most countries around the world. The World Health Organization (WHO)'s arsenic guideline value is about 10 ppb [1]. According to WHO reports, contamination of groundwater by arsenic at least in 20 countries is more than licensed levels [2]**.** Many analytical methods have been developed for arsenic detection [3]. The most of these techniques are time-consuming and only suitable for laboratory conditions. Among different detecting performances, electrochemical techniques can be used for routine detections in field monitoring of a large number of samples [4].

Methods: Herein, detection of arsenic is reported by synergic effect of a synthesized dendrimer and gold nanoparticles (AuNPs) on the surface of a glassy carbon electrode. The modified electrode showed excellent performance in detection of As (III) in some real water samples by square wave anodic stripping voltammetry.

Results: Under the optimized conditions, the modified electrode obtained direct detection of As (III) within the desirable limit range of WHO, with a detection limit of 0.03 ppb.

Conclusion: We have presented a simple, reproducible and fast method of detecting As(III) in water by modification of glassy carbon electrode by dendrimer and gold nanoparticle using square wave anodic stripping voltammetry. The modified electrode had a detection limit lower than the permissible limit for arsenic in water demonstrating its analytical significance.

Keywords: Arsenic; Gold nanoparticles; Anodic stripping voltammetry; Dendrimer.

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Pencil graphite electrode modified with nitrogen-doped graphene, molecular imprinted polymer/ Sol-Gel as a novel electrochemical sensor for the determination of fexofenadine

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Background: Fexofenadine (FXF) is a histamine H1-receptor antagonist which is widely used as anti-allergic agent [1]. The determination of FXF has been described using HPLC [2] and fluorimetry [3] techniques. Electrochemical sensors are one of the most important measurement tools which can be modified with various modifiers in order to increase the selectivity and sensitivity of determination. Using of modifiers such as functionalized carbon nanoparticles due to high electrical stability and electrocatalytic properties [4], and also molecular imprinted polymers due to increase selectivity has been considered in recent decades [5,6]. In this work, an electrochemical sensor was developed for the determination of FXF using a modified pencil graphite electrode (PGE).

Methods: Modification of the PGE was performed by the nitrogen-doped graphene (NDG) which was deposited by an electrosynthetic method as the first modifier layer on the PGE. Then, prepared molecular imprinted polymer was immobilized on the first layer by Sol-Gel. Acrylamide (AAm) and *ethylene glycol*dimethylacrylate (EGDMA) and tetraethyl orthosilicate (TEOS) were used as monomer, cross linker and Sol-Gel, respectively. The modified electrode was used for the determination of FXF by differential pulse voltammetry (DPV) technique at the obtained optimum conditions.

Results: Several parameters were optimized in the preparation of the modified electrode and also determination process such as the molar ratio of analyte to monomer and crosslinker, the amount of NDG and MIP on the electrode surface, pH of the test solution and the type and concentration of electrolyte. In optimum experimental conditions, DPV was used for the determination of FXF which exhibited a linear calibration graph of I_p versus FXF concentration in the range of $33.0\text{-}3.5\times10^3$ nM. The detection limit of the procedure was calculated equal to 3.7 nM.

Conclusion: A pencil graphite electrode was modified using N-doped graphene incorporated with MIP-Sol-Gel film for selective low trace determination of FXF. The sensor can be successfully applied for the determination of FXF in pharmaceutical and biological samples.

Keywords: Pencil graphite electrode; Nitrogen doped graphene; Molecular imprinted polymer; Sol-Gel; Fexofenadine

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Electrochemical sensor for determination sulfisoxazole using a carbon paste electrode modified with a ZnO–Pd nanoparticles and 1-hexyl-3-methyl imidazolium bis (tri fluoro methyl sulfonyl) imid

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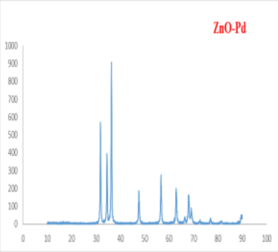
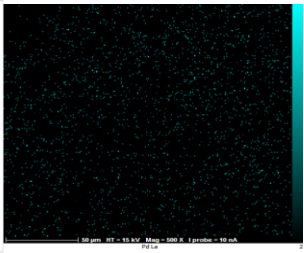
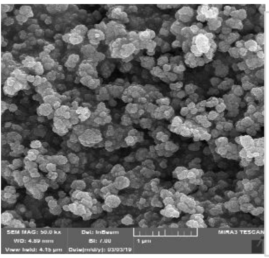
Background: Sulfisoxazole is a sulfonamide antibiotic used to prevent or treat many different types of infections. The Overdose of drug can be harmful to the human body [1]. Electrochemical technique due to easy operation and fast response are a strong tool in the analysis of biological samples. ZnO-Pd nanoparticles due to higher the electrical conductivity and surface area properties compared with ZnO nanoparticles have been employed successfully as the modifier [2].

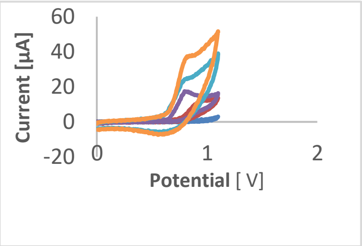
Methods: ZnO-Pd/IL/CPE was fabricated by mixing of 0.05g of ZnO-Pd 0.95 g of graphite powder and suitable amount nujol oil (80% w/w) and IL (20% w/w) as binders. The above mixture was mixed for 1h for obtaining a good paste. The obtained ZnO-Pd/IL/CPE paste was added to the end of a glass tube and a copper wire insert in paste for electrical connection devices.

Results: The ZnO-Pd nanoparticle was synthesized by co-precipitation method, and characterized by FE-SEM, EDAX, MAP, and XRD techniques. In continuous, we study application of the ZnO-Pd nanoparticle for the preparation of carbon paste electrode modified with IL as a suitable and high conductive binder. The electrode provides a good linear range (0.03–1200 µM), it has a good limit of detection (0.008 µM). The modified sensor has been successfully applied to determine sulfisoxazole in real samples.









Conclusion: In this work, the ZnO-Pd/ILs/CPE was used to investigate the electrochemical behaviors of sulfisoxazole. The ZnO-Pd/ILs/CPE showed great improvement to the electrode process of sulfisoxazole compares to the CPE.

Keywords: ZnO-Pd nanoparticles; sulfisoxazole; Modified electrode

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Carbon paste electrode modified by molecular imprinted polymer as a voltammetric sensor for ultra trace determination of Theophylline in aqueous samples.

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Theophylline (1,3-dimethylxanthine) as a xanthine derivative has been commonly used as an additional treatment drug in the asthmatic acute phase in children and asthma and bronchospasm in adults[1,2], thus trace determination of this drug in biological samples is important [3-4].

In this project. a carbon paste electrode (CPE) modified with designed molecularly imprinted polymers (MIP) was developed for determination of Theophylline in aqueous and biological samples. The MIP has been synthesized using methacrylic acid (MAA) as functional monomer, ethyleneglycol dimethacrylate (EGDMA) as crosslinker and theophylline as template, in polymerization solvent.The electrochemical behavior of the modified CPE was investigated employing cyclic voltammetry (CV) and differential puls voltammetry (DPV).The experiments were conducted with a certain electrode composition of 30% paraffin oil, 70% high purity graphite powder, 12% MIP as well as the usage of 0.1 M phosphate buffer as supporting electrolyte.The effect of pH, scan rate, percentage of modifier and buffer as supporting electrolyte on the electrode process were investigated.

Experiments were performed with an optimum MIP12% electrode in phosphate buffer pH = 6, which was used as electrolyte. scan rate of 10- 250mV / s was performed. Optimal electrode linear response in the concentration range of 2×10^{-6} to 3×10^{-5} fore Theophylline with a detection limit for Theophylline 0.036×10^{-6}, respectively. Accuracy was measured for 6 times in two concentrations Theophylline 8×10^{-6} and 16×10^{-6} the standard deviation for Theophylline was 1.23 , 1.52 , respectively.

it was found that this method was unobtrusive and finally, the method for determining the drug Theophylline in the urine sample and plasma and Syrup was used.

Keywords: Theophylline, Modified carbon paste electrode, MIP, DPV.

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Designing a Miniature Potentiostat and Microfluidic Device for Rapid Determination of Glucose

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Background: Point-Of-Care (POC) testing provides highly sensitive and practical means for accurate detection of a variety of biomarkers, such as glucose, in biological samples. The key parts of electrochemical POC diagnostics are microsized and portable devices and electrodes [1,2].

Methods: a miniature potentiostat in tandem with highly oriented CNT arrays was developed as an electrochemical assay for real-time and sensitive detection of glucose. A microcontroller-based potentiostat including Arduino Due and LMP9100-EVM was developed to perform electrochemical measurements such as cyclic voltammetry (CV) and amperometry (Fig. 1A). Vertically oriented carbon nanotubes were grown by chemical vapor deposition (CVD) method on a silicon substrate (Fig. 1B). VACNT arrays, in combination with the potentiostat and the syringe pump, was utilized as a point-of-care (POC) device for rapid detection of glucose.

Results: The structure and morphology of samples were characterized by field emission scanning electron microscopy (FESEM) (Fig. 1C) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry (CV) was used to evaluate the electrochemical behavior of the prepared electrode. The fabricated biosensor has a low limit of detection, 1.3 µM. Its sensitivity toward glucose detection was 642µA $mM^{-1}cm^{-2}$ at the linear range of 10-60 µM and 278 µA. $mM^{-1}cm^{-2}$ at the linear range of 60-423µM (Fig. 1D). The presence of other biological compounds such as uric acid (UA) and ascorbic acid (AA) did not interfere with the detection of glucose.

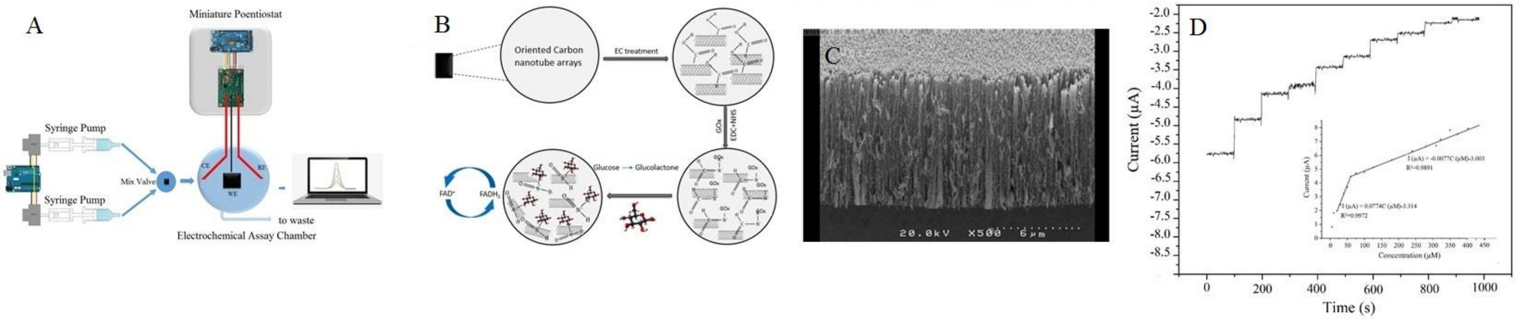

Fig.1 A) The POC system. B) Schematic plan of immobilization. C) SEM image of VACNT. D) Amperometric response of the electrode.

Conclusion: By integrating a micro-size biosensor, a low-cost potentiostat, and a miniature syringe pump in tandem with a microfluidic chamber, a POC assembly was achieved which can be applied for determining glucose in biological samples.

Keywords: Point-of-care; VACNTs; Microfluidic chamber; Portable detector; Lab on a chip.

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Voltammetric Determination of Mesalazine by using Carbon Paste Electrode Modified with Poly-dopamine Nanoparticles

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Background: Mesalazine or 5-aminosalsilyc acid is one of the most important drugs used for bowel disease and it can be useful for gastrointestinal agent. It was determined previously using voltammetric techniques [1]. Also, recently, nanoparticles are attracted because of their conductivity and widely range of their variety compositions. Poly-dopamine nanoparticles (PDA NPs) are biopolymers with extraordinary properties [2]. Actually, self-polymerization of dopamine made it a good case for bio-sensing researches. Carbon paste electrodes because of their low noise, anodic and cathodic potential ranges, rapid surface renewal and low cast is a excellent occasion for modifying [3].

Methods: PDA NPs were synthesized by a modified procedure based on previous report. Typically, 180 mg dopamine hydrochloride was dissolved in 90 mL of deionized water. Under vigorous stirring, 0.8 mL of freshly prepared NaOH solution (1 mol/L) was added to a dopamine hydrochloride solution and stirred under 50°C for 5 h. After that, PDA NPs were collected by centrifugation at 20000 rpm for 20 min, and washed thrice with deionized water. Carbon paste electrode modified with poly-dopamine nanoparticles by casting method.

Results: PDA NPs were characterized using SEM, XPS and FTIR techniques. The cyclic voltammograms shows a well-known peak for mesalazine compare to unmodified electrode. The effect of some parameters such as the amount of modifier, pH and scan rate was studied. The results showed a diffusion controlled mechanism. Finally, differential pulse voltammetry was applied for quantitative determinations in 1M phosphate buffer with pH 2 at scan rate 0.1 V/s. Dynamic linear range was 10^{-8} mM to 10^{-3}mM and limit of detection was calculated $3.7*10^{-10}$mM.

Conclusion: In this approach, the carbon paste electrode modified easily with PDA NPs that it is a low cast and easy way for modification. Also, determination of mesalazine performed at low concentrations with long resistance. Additionally, human serums utilized for protection of our method and it exhibits acceptable respond.

Keywords: Modified carbon paste; Poly-dopamine Nanoparticle; Mesalazine

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Voltammetric determination of Methyldopa using a copper (II) Schiff base complex nanoparticles modified glassy carbon electrode

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Background: Hypertension is a disease whose insidious progression presents many threats to human health, which in turn led to the development of a wide therapeutic arsenal to minimize patient morbidity. Methyldopa [α-methyl-β-(3,4-dihydroxyphenylalanine)]is noteworthy amongst these drugs, as it is a phenolic derivative broadly prescribed to manage mild to moderate hypertension by relaxing blood vessels. Nonetheless, the implications that this drug has on therapeutics imply the importance of its determination in pharmaceutical samples. As blood vessels relax, Methyldopa relieves high blood Pressure. Several techniques have been reported in the literature for the determination of Methyldopa, but electrochemical methods have attracted great interests because of their simplicity, rapidness and high sensitivity in determination of Methyldopa and various other analytes, without any tedious pre-treatments [1-3].

Methods: The GCE was polished using Al_2O_3 before each electrochemical experiment. Following this mechanical treatment, the GCE was placed in phosphate buffer solution and differential pulse voltammograms were recorded until a steady state baseline voltammogram was obtained. The next step is to preparation of copper (II) Schiff base complex nanoparticles ([Cu_2L] nanoparticles), by mixing nanoparticles with organic solvent takes place for 20 minutes for homogenization under Ultrasonic will appear after surface modification done by using voltammetry the parameter different will be examined [4-5].

Results: The electrochemical behavior of methyldopa was studied in different pH values (2.0 pH 11.0). pH 7 was selected as the optimal pH. The methyldopa linear limit and the detection limit 0.5-100 and0.28 µmol/L were respectively.

Conclusion: According to the results of this study, the experimental design is an advantageous strategy for ensuring the optimization of the effective experimental variables. The [Cu_2 L] nanoparticles/GCE sensor developed in this study is a cheap, reliable, and useful strategy to detect methyldopa in pharmaceutical samples, since it presents excellent electrochemical behavior, and was able to detect methyldopa with a good linear range at pH = 7 between 0.5–100 µmol L^{-1} (Limit of Detection 0.28 µmol/L).

Keywords: Methyldopa; Modified electrodes; copper (II) Schiff base complex nanoparticles; glassy carbon electrode.

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Voltammetric determination of Omeprazole using a copper (II) Schiff base complex nanoparticles modified glassy carbon electrode

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Background: Omeprazole (OMZ) is considered as a substituted benzimidazole drug consumed worldwide and acted as gastric acid pump inhibitor OMZ, an antiulcer drug, is widely used to cure the gastric, Zollinger-Ellison syndrome, and duodenal ulcers, and various gastrointestinal disorders such as gastroesophageal reflux disease, erosive esophagitis, pathologic hypersecretory conditions, etc. It can efficiently control and inhibit the production, and secretion of gastric acid by its covalent binding to the proton pump (H^+/K^+ ATPase) on the gastric parietal cells surfaces and thus preventing the last step in the hydrogen ions secretion into the gastric lumen. The quality control assessment of this drug in pharmaceutical formulations and biological samples is required due to its widespread and worldwide commercialization [1].

Methods: In the first step, a bare GCE sequentially with 0.3 mm Al_2O_3 water slurry was polished using a polishing cloth and was then rinsed with doubly distilled water and sonicated in a 1:1 distilled water solution, acetone, for 10 min. For preparing the copper (II) Schiff base complex nanoparticles [Cu_2 L] suspension, 0.0025 mg [Cu_2 L] nanoparticles was dispersed in 0.230 μL ethanol under ultrasonic for 20 min and then to form a [Cu_2L] nanoparticles thin layer at the GCE surface and create a [Cu_2 L] nanoparticles /GCE. For real sample preparation, one capsule of OMZ (20.0 mg) to was transferred into a 50 mL volumetric flask and were dissolved in PBS of pH 7.0. Finally, the signal of the samples was measured by the DPV technique [2].

Results: The electrochemical oxidation of OMZ was studied using differential pulse voltammetry (DPV) in aqueous buffer supporting electrolytes over a pH range from 3 to 12. The pH 7.0 was chosen as the optimum pH for electrocatalysis OMZ oxidation. The DPV currents of OMZ at [Cu_2 L] increased linearly with the OMZ concentration in the range from 0.5 to 100 μM with a detection limit of 0.3 μM.

Conclusion: Modification of the GCE with [Cu_2 L] nanoparticles led to an enhancement in the oxidation peak current and sensitivity, increase in the sharpness of the peak, and decrease of the over the potential of OMZ oxidation at the electrode surface. Among the advantages of the prepared sensor as compared to previous reports, can be mentioned the very low detection limit, wide linear dynamic range, high sensitivity, very good repeatability, and simple procedure for the surface modification and determination of OMZ. Finally, the modified electrode can be applied for the determination of OMZ in pharmaceutical samples and biological fluids.

Keywords: Omeprazole; Electrochemical sensor; Oxidation; Copper (ii) schiff base complex nanoparticles.

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Introduce of simple design, long life time and green rechargeable batteries namely "Li-air batteries" by using ionic liquids

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Background: Today, Li-air batteries are currently the most promising new rechargeable batteries because they have much higher energy densities [1]. In general, a lithium-air battery consists of a lithium anode, non-aqueous electrolyte and an air-carbon cathode. Two critical challenges in these batteries are low oxygen solubility in non-aqueous electrolyte and sedimentation of discharge products (i.e Li_2O_2(s) and Li_2O(s)) on oxygen route in air cathode that led to blocked them [2]. Much research's show that use a several catalyst such as CuO, Fe_2O_3, V_2O_5, CeO_2, Pt/Au, Co_3O_4 could be avoided to blocking of oxygen routes and furthermore ionic liquids are satisfying replacing agents to the non-aqueous electrolytes. Some important properties of ionic liquids, such as their high conductivity, non-flammability, non-volatility and wide temperature range of operation, have attracted great interest in view of their application as electrolytes in rechargeable batteries [3].

Methods: The battery cell was designed by our team (Fig. 1). The Whatman filter paper was used as separator. The air cathode was prepared by soaking the carbon paper sheet into the slurry mixture of three components containing the catalyst, polytetrafluoroethylene (PTFE) and Kitchenblack carbon (KB) with the weight ratio of 22:12:68 mg, respectively.

Results: As shown in Fig. 2, the air cathode with the catalyst of NP-$MnFe_2O_4$ (in the green electrolyte $LiPF_6$/[Omim][PF_6]) shows a discharge capacity of 3391 mAh g^{-1} and battery without the catalyst (in the electrolyte of $LiPF_6$/Dimethyl carbonate) the discharge capacity is 1012 mAh g^{-1}. Fig. 3 indicate that the number of the charge/discharge cycling is increased more than 1000 cycles when the catalyst and $LiPF_6$/[Omim][PF_6], as electrolyte, are used, but it is decreased up to 3 cycles for battery without the catalyst.

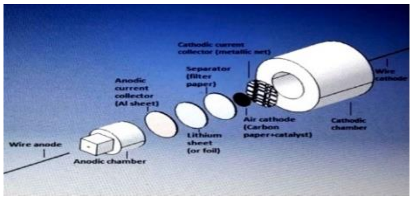

Figure 1

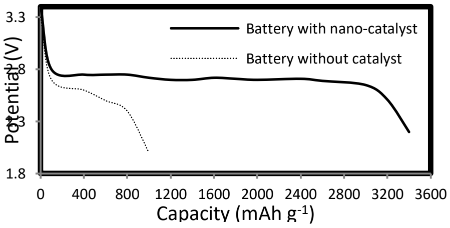

Figure 2

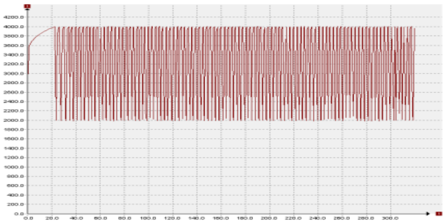

Figure 3

Conclusion: By using the NP-$MnFe_2O_4$ as catalyst and $LiPF_6$/[Omim][PF_6] as green electrolyte, the discharge specific capacity of the Li-air battery was reached to 3391 mAh g^{-1}. The using of the ionic liquid [Omim][PF_6] as a non-aqueous electrolyte increase the safety of the battery because of its high boiling point (more than 350 °C). The designed battery has several advantages such as high cycling charge/discharge capability, high discharge capacity, high safety and longp lifetime.

Keywords: Li-air battery, Ionic liquids, Simple design, Long life, Green battery

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Solution complexation reaction studies of thiocarbohydrazide ligand by some metal ions in acetonitrile solution

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Background: During the past two decades, considerable attention has been paid to the chemistry of the metal complexes with nitrogen and sulfur donor atoms ligands. The study of complexation reaction of N & S donor ligands in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as potentiometric sensor, bulk and supported liquid membrane transport, solid phase and cloud point extraction and biochemistry fields [1]. Thus, the studies of complexation reaction of these ligands with metal ions, not only result effective information about complexation, but also lead to a better understanding of the selectivity of these ligands toward different metal cations. It is important for an analytical chemist to know what kind of complexes with what stability may be expected [2].

Methods: The complex-formation reactions between of Ag^+, Hg^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{3+} and Pb^{2+} iones with thiocarbohydrazide has been studied by conductometric methods in acetonitrile at 25 °C temperature. Formation constants of the 1:1 and 1:2 (metal ion to ligand) complexes were evaluated from computer fitting (the KINFIT program) of the absorbance mole ratio data, and molar conductance-mole ratio data at 25 °C temperature.

Results: The molar conductance of the nitrate salts of Ag^+, Hg^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{3+} and Pb^{2+} in acetonitrile solvent was monitored as a function of the thiocarbohydrazide ligand to metal ion mole ratio at 25 °C temperature. The results showed that ML complexes are formed in solution. The resulting formation constants (K_f) of the thiocarbohydrazide ligand complexes at 25 °C are 3.96, 3.91, 4.35, 4.96, 3.86, 3.79 and 2.55 for Ag^+, Hg^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{3+} and Pb^{2+}, respectively. The formation constants of the metal complexes obtained is as follows: $Cu^{2+} > Ni^{2+} > Ag^+ > Hg^{2+} > Cd^{2+} > Fe^{3+} > Pb^{2+}$.

Conclusion: The conductometric technique offer the advantages for such investigations of sensitive and accurate measurement as well as inexpensive cost with a simple experimental arrangement .The ligand can be used for solid phase extraction and determination of trace amounts of these metallic ions in aqueous samples.

Keywords: Complexation; Conductometry; Formation constant; Thiocarbohydrazide.

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Synthesis Samarium Molybdate of Nitrogen and Phosphorus co-doped to Reduce Graphene Oxide as a High Performance Supercapacitors

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Background: Nanocomposites produced with samarium (Ⅲ) molybdate/N, P co-doped reduced graphene oxide combination may be very useful in the field of supercapacitors due to the active interaction between these two components [1, 2].

Methods: In this study, we used sonochemical method, which is quite simple and cheap, to produce Sm_2MO_6/N, P co-doped reduced graphene oxide nanocomposite, which draws attention with its high-quality electrochemical performance. Surface and structural properties of Sm_2MO_6 nanoparticles, N, P co-doped reduced graphene oxide and Sm_2MO_6/N, P co-doped reduced graphene oxide nanocomposite structures were characterized by scanning electron microscopy, Brunauer-Emmett Teller X-ray diffraction and X-ray diffraction analysis. Supercapacitive performance of as-prepared samples were characterized by, galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy.

Results: The Sm_2MO_6/N, P co-doped reduced graphene oxide electrode exhibits a specific capacitance of 689 F g_{-1} (at 2 mV s_{-1}) and could maintain 99.9% capacity after 4000 chargedischarge cycles. Additionally, the symmetric supercapacitors based on nanocomposite electrode demonstrate a high energy density (23.2 W h kg_{-1} at 250 W kg_{-1}), outstanding power density (8000 W kg_{-1} at 14.4 W h kg_{-1}). Generally, this nanocomposite was synthesized for the first time and its supercapacitive properties were investigated. The nanocomposite electrode exhibited good supercapacitor response, remarkable rate performance and excellent cycling stability in both 0.5 M Na_2SO_4 electrolyte.

Conclusion: The enhancement of supercapacitive performance in the case of SmMO/NPRGO electrode was considerable. The notable enhancement can be attributed to improving conductivity of RGO and simulations redox activity of doped N and P and SmMO nanoparticles. As a result, co-doping of N and P into RGO through hydrothermal method is a suitable strategy for enhancing supercapacitive performance of commercial RGO.

Keywords: Supercapacitors, Samarium Molybdate, Nanostructures, N, P co-doped graphene, Nanocomposite.

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Electrocatalytic Oxidation of Thiourea by Bromide

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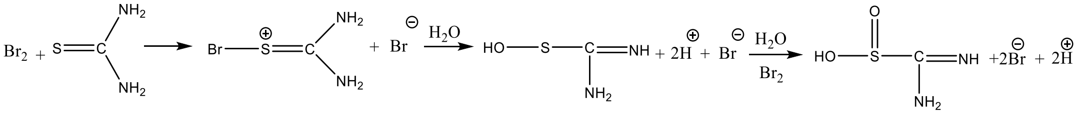
Background: Thiourea is one of the industrial potential compounds. These compounds are hazardous, while the corresponding oxidized products, ureas, are non-toxic and useful to natural habitats. Thiourea and its derivatives are susceptible to oxidation by a large number of oxidants giving rise to various products including urea, sulfide, oxide of sulfur, and nitrogen [1].

Methods: A three electrode system was used; it consisted of the glassy carbon electrode (GCE) as the working electrode, SCE as the reference electrode and a Pt wire as the auxiliary electrode. The synthesis was carried out in an undivided cell equipped with the carbon and stainless steel as anode and cathode electrodes at the (H_2O ; pH 4) mixture.

Results: The electrochemical behavior and electrocatalytic performance of NaBr were studied initially in the oxidation of thiourea (Tu). Fig 1 The CVs show an anodic peak (A1) related to the oxidation of Br^- to Br and a corresponding cathodic peak (C1) for the reduction of electrogenerated Br at the electrode surface. In the presence of Tu, the height of the A1 anodic peak increases, the C1 cathodic peak disappears, and the formal potential of the CV shifts to more negative values. These observed changes in the presence of Tu agree well with the characteristic of a quasi electrocatalytic mechanism (EC'). Based on the experimental results and the previous reports [2,3], a possible pathway was proposed as following:



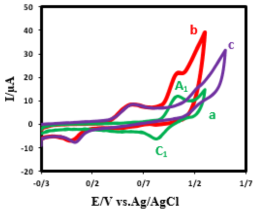


Fig.1 CVs of 1mM of NaBr (a) in the absence (b) in the presence of 1mM Tu (c) and 1 mM NaBr in pH 4.0 and Scan rate 100mV/s.

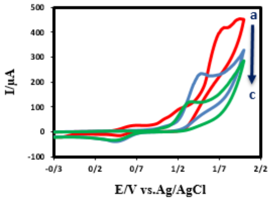


Fig.2 CVs of 1 mmol Tu in the presence of 1mmol NaBr in buffer pH 4.0 at various times of constant current electrolysis: (a-c) 0, 5400, 7200 s.

Conclusion: The obtained results indicated quasi EC' mechanism for this system. Also, we have developed a mild and green electrochemical procedure for the synthesis of thiourea dioxide by electrocatalytic oxidation of the Thiourea by sodium bromide in room temperature and aqueous solution.

Keywords: Thiourea, electrocatalytic, Oxidation, Sodium Bromide, Thiourea dioxide, Cyclic Voltammetry

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Electrochemical synthesis of new dye via oxidation of 4-nitroso-*N,N*-dimethylaniline in aqueous buffered solution: an investigation of exhaust process for synthesized dye

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Background: Electrochemical methods are widely applied to obtain both thermodynamic and kinetic information about reactions of organic and inorganic species over a wide time frame. This method provides a versatile means for the selective reduction and oxidation of organic compounds. Unique selectivity due to in situ formation of an active species at the interface, inversion in polarity by transfer of an electron and variability, in product formation by the control of the electric potential are some of the advantages of electrosynthesis [1-2].

Methods: In this study, electrochemical synthesis of new dye was carried out by the electrochemical oxidation of 4-nitroso-*N*,*N*-dimethylaniline in aqueous ethanol at pH 2.0, divided cell and gave the pure product. We investigated and studied this product by using cyclic voltammetry and controlled-potential coulometry. These methods are the one-pot and environmentally friendly electrochemical approach for the synthesis of new dye compound via the Michael type addition reaction of anodically generated p-quinonediimine with 4-nitroso-*N*,*N*-dimethylaniline [3], at a carbon electrode, without toxic reagents.

Results: In the next, we used the so-called exhaust process for the dyeing of wool, nylon, polyester, cotton and acrylic. The results showed that synthesized dye (violet dye) exhibits a higher affinity for acrylic, nylon and wool fabrics, but it was ineffective against other fabrics.

Conclusion: The present methods for the synthesis of Violet dye have several advantages. Both processes are practically convenient to carry out and can be performed at atmospheric pressure and room temperature. Neither catalyst nor organic/inorganic oxidizing agents are necessary and the reaction can be performed under sustainable and green conditions.

Keywords: Electrochemical synthesis; 4-nitroso-*N*,*N*-dimethylaniline; Dye synthesis; Coulometry.

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Sensitive electrochemical determination of propranolol using modified multiwall carbon nanotubes/TiO_2 Nanoparticles/pencil graphite electrode

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Background: Propranolol (PRO), 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanol, is a greatly used β-adrenergic drug which has been prescribed for the management of different irregular cardiovascular such as hypertension. Several techniques have been reported for the analytical determination of PRO such as spectrophotometry [1-3] and chromatography [4,5]. However, due to the therapeutic effects of PRO, it is still motivated to develop more selective and sensitive analytical techniques for low level determination of this drug in various media.

Methods: In this study, a modified pencil graphite electrode (PGE) was applied as an excellent electrochemical sensor for low level determination of propranolol. The PGE was modified with multiwall carbon nanotubes (MWCNTs) and TiO_2 nanoparticles as a coating layer on its surface. After modification of electrode, differential pulse voltammetric (DPV) technique was used for the investigation of the electrochemical behavior of sensor and determination of PRO.

Results: Electrochemical impedance spectroscopy (EIS) technique was used for the electron transfer modification of the PGE. The obtained results in 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl represented that R_{ct} for the MWCNTs-TiO_2/PGE is much smaller than bare PGE and also MWCNTs/PGE indicating the modification of TiO_2 on the surface of the MWCNTs increased the rate of the electron transfer. Considering morphology of the modifier accomplished by SEM, XRD showed that the homogeneous surface of MWCNTs was covered with rough nanotubes.

Conclusion: A simple and rapid electroanalytical method was described for the determination of PRO in 0.1 mol L^{-1} H_2SO_4. Under this condition, propranolol can be determined by DPV in the linear range of 8.5×10^{-8} M to 6.5×10^{-6} M with a detection limit of 3.1×10^{-8} mol L^{-1}.

Keywords: Pharmaceutical determination; propranolol; carbon nanotubes; pencil graphite electrode.

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Electro-oxidation of ethanol on the nanostructured bimetallic NiPd electrocatalysts in alkaline solution

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Background: The excellent synergistic effect of Pd and Ni compositions generates some novel catalytic properties for bimetallic NiPd electrocatalysts compared to monometallic Pd or Ni catalysts. The electro-oxidation of ethanol is a vital reaction in direct alcohol fuel cells technology. In this purpose, both reaction kinetics and selectivity should be improved.

Methods: A platinum plate and a glass frit Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The electrodeposited Ni-Pd samples were employed as working electrode. The electrodeposition was done using double potential step chronoamperometry.

Results: Five NiPd samples with different compositions were prepared and their reactivity were compared with a Pd sample. For example, Fig 1a compares the cyclic voltammograms of NiPd-3 and Pd samples in 1 M NaOH solution containing 0.05 M ethanol. It indicates that the NiPd-3 sample is more reactive than Pd for electro-oxidation of ethanol. In addition, we calculated the ratio of forward to backward peak current density in order to evaluate the catalytic tolerance against the poisoning effects of adsorbed intermediates generated during incomplete oxidation of ethanol. The higher ratio of the peaks indicates that the electrocatalyst NiPd-3 oxidizes ethanol more effectively and generate less poisoning intermediates.

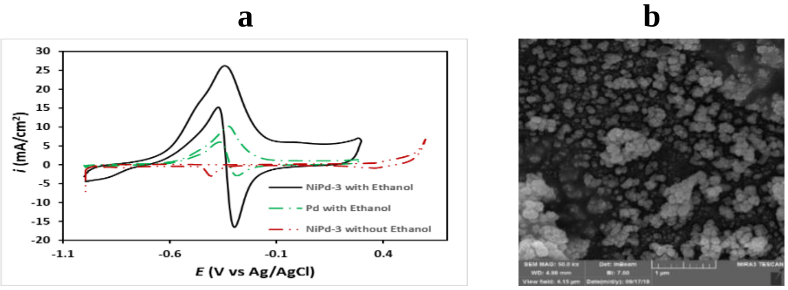

Fig 1. (a) The cyclic voltammograms of NiPd-3 and Pd samples in 1M NaOH +0.05 M ethanol solution and (b) SEM image of NiPd-3 sample.

Conclusion: Among the electrodeposited samples, the NiPd-3 sample (7.1% of Ni) is the more reactive electrocatalyst for oxidation of ethanol. In addition, the NiPd-3 oxidizes ethanol generates less poisoning intermediates, more effectively.

Keywords: Ethanol oxidation**,** NiPd electrocatalysts, electrodeposition, nanostructures

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Fabrication of an Ion Selective Sensor Based on 1,2-bis(2-hydroxybenzamido)-4,5-dimethylbenzene for Determination of dysprosium ion (Dy^{3+})

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Background: The potentiometric membrane sensors have shown to be very effective tools for the analysis of a wide variety of metal ions. They are very simple, fast, inexpensive andcapable of a reliable response provision in broad concentration ranges [1]. Due to the vital importance of Dysprosium (III), we introduce a novel selective and sensitive Dysprosium ion selective PVC membrane electrode for potentiometric monitoring of trace amount of Dy^{3+} by using 1,2-bis(2-hydroxybenzamido)-4,5-dimethylbenzene (HBD) as an excellent sensing material for determination of this ion.

Methods: Membrane solutions were prepared by thoroughly dissolving 3 mg of HBD, 30 mg of powdered PVC, 65 mg of NB and 2.0 mg of NaTPB in 3 mL of fresh THF. The tube was then filled with an internal solution (1.0×10^{-3} mol L^{-1} $DyCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} Dy^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode. Activities were calculated according to the Debye–Huckel procedure [2].

Results: In optimized conditions, the proposed sensor exhibits a wide linear response with a Nernstian slope of 20.3 ± 0.2 mV/decade over the concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} (Fig 1), and a detection limit of 8.5×10^{-7} mol L^{-1} of Dy^{3+} ions. The sensor response is independent of pH in the range of 3.2 – 8.8 (Fig 2). the response time is about 7s in the whole concentration range (Fig 3).

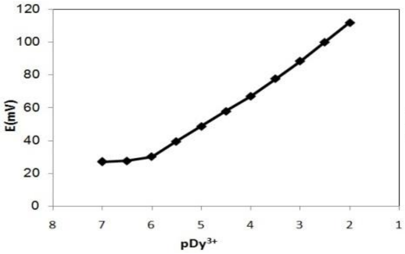

Fig 1: Calibration curve

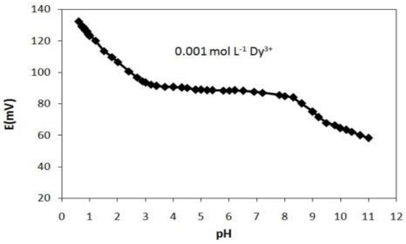

Fig 2: pH effect

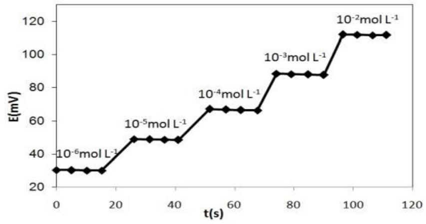

Fig 3: Response time

Conclusion: This sensor can be used over a period of 1 month without significant drift in potentials. To investigate the membrane sensor selectivity, its potential response was determined in the most common cations including alkali, alkaline earth, transition and heavy metal ions.

Keywords: Ion-Selective Electrode; PVC Membrane; Sensor; Potentiometry; Dysprosium.

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Development of electrochemical sensor for sensitive determination of metanil yellow

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Background: They are extensively used in a number of industries, such as food, cosmetics, with the textile industry as the largest consumer [1, 2]. The extensive discharge of such dyes through wastewater effluents have had considerable environmental concerns [3]. Therefore, the accurate, sensitive and fast detection of these dyes has gained considerable attention. The method of MY determination described in the present work proved its superiority in terms of time requirement, labor need, material consumption, and simplicity.

Methods: This work presents an electrochemical method based on modified GC electrode by using MWCNT-Chit nanocomposite for determination of MY by DPV technique. The physical morphology of the surface of modified electrode was investigated by scanning electron microscopy (SEM). The presence of CNTs-Chit nonocomposite due the high surface area, good conductivity as well as excellent catalytic property can accelerate the rate of electron transfer between MY and electrode.

Results: The prepared MWCNTs-Chit/GC electrode showed a linear response to MY concentration in the range of 1.0 µM to 2.5 mM with a sensitivity and a limit of detection (S/N=3) of 40 nAµM-1 cm-2 and 0.1 µM, respectively. The proposed sensor was successfully applied for the determination of MY in real samples with satisfactory results.

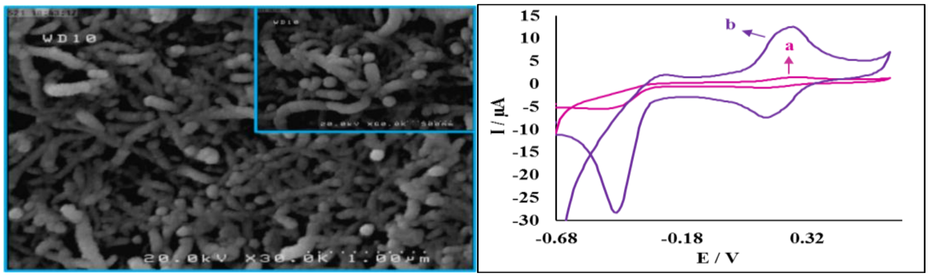

Fig. SEM image of MWCNT-Chit/GCE and CVs of GCE (a) and MWCNT-Chit/GCE (b) recorded in 0.1 M PBS (pH = 7.0) containing 0.2 mM MY at scan rate of 100 mV s^{-1}.

Conclusion: The modified electrode exhibited excellent catalytic activity toward MY oxidation. Under optimized conditions the fabricated sensor showed low detection limit, acceptable reproducibility, high selectivity and long term stability toward the MY monitoring. The sensor was further utilized to determine of MY in real sample with satisfactory results.

Keywords: Electrochemical sensor, metanil yellow, nanocomposite, multiwalled carbon nanotube.

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Electrochemical Study of Riboflavin (Vitamin B2) in Aqueous Solution in the Presence of Metal Cations on Glassy Carbon Electrode

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Background: Riboflavin (vitamin B2) is a water-soluble biochemical molecule widely existing in food and pharmaceutical products. These pharmaceutical products range in complexity from single vitamin to multivitamin formulations [1]. The electrochemical behavior of VB2 had been examined in detail [2,3]. It is generally accepted that VB2 undergoes a reversible reduction process. In this work, we decide to study electrochemical behavior of vitamin B2 in aqueous solution on glassy carbon electrode. We achieve that VB2 undergoes a reversible reduction process involving one electron and one proton in aqueous solution. In the next step, we study electrochemical reduction of VB2 in the presence of different metal cations and calculate the formation constant of complexes using half-wave potential ($E_{1/2}$). In addition, the adsorption and orientation of this molecule in aqueous solution on glassy carbon electrode were studied.

Methods: All electrochemical experiment were carried out using cyclic voltammetry. The electrochemical cell equipped with the working (GC), reference (Ag/AgCl), and auxiliary (Pt) electrodes. Differential pulse voltammetry measurements were additionally performed to determine the number of transferred electrons in the reduction process of riboflavin and Gaussian 09w was used for structure optimization of VB2.

Results: The pourbaix diagram for reduction of riboflavin includes two lines with different equation and slope around pH value 10.2 is shown in Fig. 1. Cyclic voltammogram of riboflavin in the absence and in the presence of cobalt (II) were shown in Fig. 2. As can be seen, in the presence of cobalt ions (curve b) the half-wave potential ($E_{1/2}$) shifts to the less negative potentials because of complex formation between riboflavin and cobalt ion. In this work also, the optimized structure of riboflavin at B3LYP/6-311G level of theory for the estimation of riboflavin's orientation is shown in Fig. 3.

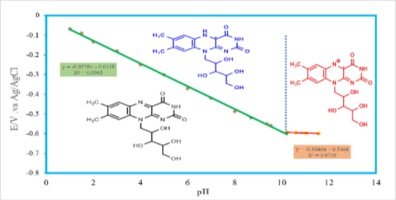

Fig. 1. The potential-pH diagram of riboflavin

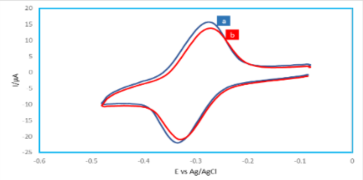

Fig. 2. Cyclic voltammograms of 0.1 mM of VB2 a) in the absence b) in the presence of 1mM cobalt cation

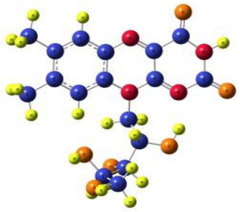

Fig. 3. The optimized structures of riboflavin at B3LYP/6-311G level of theory

Conclusion: The results of this study indicate that the reduction potential of riboflavin as shown in Fig.1, is dependent on the solution pH. Furthermore, riboflavin’s complexes formation with different metal cations has been examined using cyclic voltammetry, this data showed that complex formation with half wave potential displacement.

Keywords: Riboflavin; Electrochemical Study; Complex Formation; Cyclic Voltammetry; Molecular Orientation

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The inhibition effect of CTAB surfactant on the corrosion of mild steel in 3.5% NaCl solution

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Background: Most of the corrosion inhibitors including heterocyclic compounds that have bonded a phosphorus, sulfur, oxygen or nitrogen heteroatom are toxic and environmentally hazardous. Considering these problems, different types of surfactants have been considered as effective corrosion inhibitors of metals [1-3]. In this study, the corrosion of mild steel has been investigated in the presence of CTAB surfactant in 3.5% NaCl solution.

Methods: Electrochemical experiments were carried out in a conventional three electrode cell with a platinum counter electrode and an Ag/AgCl reference electrode using an Ivium Stat Potentiostat/Galvanostat, model Vertex (Netherland). Impedance measurements were performed at open circuit potential with the AC voltage amplitude of 10 mV in the frequency range of 100 kHz to 10 mHz.

Results: Tafel Polarization curves and Nyquist diagrams of mild steel in 3.5% NaCl solution at 298 K and in the presence of different CTAB concentrations were presented in Fig 1. The parameters related to the corrosion behavior of mild steel such as corrosion potential, corrosion current density, charge transfer resistance, and inhibition efficiency (IE%) were calculated according to this figure.

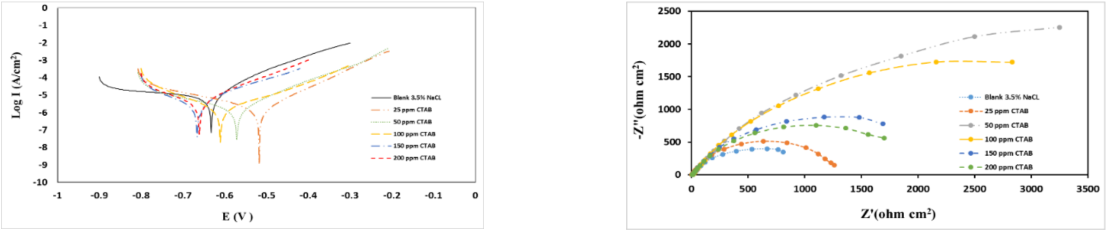
(a) (b)

Fig 1. (a) Tafel Polarization curves and (b) Nyquist diagrams of mild steel in 3.5% NaCl solution at 298 K and in the presence of different CTAB concentrations.

Conclusion: Our results revealed that the corrosion of mild steel in 3.5% NaCl solution can be inhibited using the CTAB surfactant due to the formation of protective film on the surface of mild steel. Potentiodynamic polarization studies indicated that the studied inhibitor is mixed type inhibitor. The maximum inhibition efficiency (up to 90%) was observed for 50 ppm concentration of CTAB.

Keywords: Corrosion, Inhibition, CTAB surfactant, Mild steel

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Preparation of Sensor for Determination of Enalapril by Differential Pulse Voltammetry Based on Poly (*P*- Phenylene) Nanoparticles Doped with Perchloric Acid on GC electrode

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Background: Based on WHO reports, high blood pressure is estimated to cause 12.8% of the total deaths worldwide every year. Enalapril is one of the effective drugs to treat hypertension [1]. A lot of electroanalytical methods have been developed for the determination of different drugs [2]. Between these methods, electrochemical methods with high sensitivity and selectivity, simplicity in sample preparation and low-cost instrumentations, have widely used in the analysis of biologically active compounds [3].

Methods: This work reports on a novel and sensitive sensor employing Poly (*P*-Phenylene) nanoparticles doped with perchloric acid(dPPP)/ Glassy Carbon Electrode(GCE) for determination of enalapril by Differential Pulse Voltammetry (DPV). Cyclic voltammogram of modified electrode (dPPP/GCE) in the presence of enalapril showed a sensitive anodic peak in 0.13 V at pH 5.0, in Britton-Robinson buffer solution (BRBS).

Results: On the surface of the modified electrode, the accurate investigation and optimization of the effective factors e.g. potential and time of pulse, type and pH of electrolyte solustion on the response of enalapril were done. After optimization the dynamic linear range were from 0.5 to 400 μM and detection limit of 0.013 μM. This sensor was used for determination of dexamethasone in human blood plasma and urine sample with the recoveries of 98% and 101%.

Conclusion: The structure of the synthesized Poly (*P*- Phenylene) Nanoparticles was irregular. Also the effective surface area of this modified sensor was increased 180% compared with the bare GCE, so enalapril in real samples were determined with this sensor perfectly.

Keywords: Electrochemical Sensor; Poly (*P*- Phenylene) Nanoparticles; Glassy Carbon Electrode; Differential Pulse Voltammetry; Enalapril.

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Computational Study and Multivariate Optimization of Dexamethasone Using a Novel Electrochemical Sensor Based on Nano composite of Poly (*P*-Phenylene) Doped with Perchloric Acid/RGO/GCE

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Background: Dexamethasone (DXA) is a potent synthetic member of the glucocorticoid class of steroid hormones. It acts as an anti-inflammatory and immunosuppressant agent [1] for the treatment of conditions such as inflammation, allergy, and autoimmune conditions [2]. So, the therapeutic importance of dexamethasone required the development of sensitive and rapid methods for industrial quality control and clinical monitoring.

Methods: At first, Poly (*P*-Phenylene) nano particles that doped with perchloric acid and GO were synthesized. Then the nano composite that consist of these matarials was prepared and was used as sensor modification. Also A Plackett–Burman experimental design was used to evaluate the influence of several variables on the analytical response (current).

Results: This design was used to select the most important factors among many candidates such as (concentration of GO and polymer, reaction time, autoclave temperature, sonication time, pulse time, potential time, pH of electrolyte, ethylene glycol volume) in order to make the study smaller. Then, the significant selected parameters (concentration of Poly (*P*-Phenylene) nano particles and GO in the synthesis of modification also the pH of electrolyte and pulse potential in the electrochemical determination of Dexamethasone) were optimized using a central composite design, simultaneously. A response surface model was developed using the regression analysis. Also adequacy of each model was checked using the analysis of variance (ANOVA). After that, the optimum amount of these factors (concentration of Poly (*P*-Phenylene) nanoparticles= 5.00 mg/ml, concentration of GO=1.91 mg/ml, pH of electrolyte= 3.00 and pulse potential= 0.007 V/s) were used for determination of dexamethasone by this sensor.

Conclusion: With the use of Plackett–Burman experimental design the most important factors in the electrochemical determination of Dexamethasone by the modification sensor was selected. After optimization the dynamic linear range were from 0.015 to 125 μM and detection limit of 0.002 μM. This sensor was used for determination of dexamethasone in human blood plasma and urine sample with the recoveries of 99% and 102%.

Keywords: Electrochemical Sensor; Computational Study; Nano composite; Poly (*P*- Phenylene) Nanoparticles; RGO; Dexamethasone.

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Preparation of Acetaminophen Electrochemical Sensor Based on Carbon Nanaonion and Gold Nanoparticles Nanocomposite

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Background: Acetaminophen (AC) is an antipyretic, non-steroidal and anti-inflammatory drug. This drug as an analgesic compound is commonly used in cases of mild to moderate. There are no side effects in the therapeutic doses, but overdose of this drug can lead to damage in liver and kidneys and may even lead to death [1]. Carbon nano-onions (CNOs) is one of the newer carbon nanostructures (CNs). Sumio Iijima discovered CNOs in 1980 while looking at a sample of carbon black using a transmission electron microscope. Although their discovery dates in parallel with carbon nanotubes (CNTs), interest of them has grown since 2007 [2].

Methods: 1 mg of synthesized CNO was mixed with 10 mL DMF in a test tube and placed it in an ultrasonic bath for 1 hour. 2 µl of this mixture was placed on the electrode located in the oven at 50 ° C to prepare the CNO / GCE after evaporation of the solvent. To deposit the gold nanoparticles on the CNO/GCE for 30 minutes, the electrode was placed in the synthesized gold nanoparticles solution. The electrode was then removed from the gold nanoparticles solution and placed in the open air for 1 hour, thus CNO / AuNPs / GCE was prepared.

Results: The provided electrochemical sensor showed good electrocatalytic activity and an appropriate sensitivity for oxidizing-reducing of acetaminophen. These results have been achieved by special properties such as increasing the surface area of carbon nano onion in addition to the electrocatalytic properties of gold, which showed the synergistic effect of the two compounds with each other. The concentration ranges of 0.025-0.1 µM and 0.5-50 µM for the determination of acetaminophen by using differential pulse voltammetry method was obtained with a 9 nM limit of detection. Carbon nano-onion modified electrode and gold nanoparticles have repeatability and good selectivity for acetaminophen determination.

Conclusion: In this work, an economical, easy, and fast electrochemical sensor was prepared to measure acetaminophen using carbon nanocomposite and gold nanoparticles.

Keywords: Acetaminophen, Carbon nano-onions, electrochemical sensor

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Graphene/Fe3O$_4$-CdWO$_4$ Nanocomposite, Supercapacitive properties Evaluation

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Background: Energy demand in modern society is increasing day by day; in addition, environmental issues are of the greatest challenges of present century, so the use of clean and renewable energy sources are essential. Supercapacitors are one of the energy storage devices that can save a lot of energy [1]. Recently, it has been proposed that graphene and metal oxide nanocomposite should be a competitive material for supercapacitor application [2].

Methods: The glassy carbon electrode was used as the current collector, working electrode was fabricated by dispersing 4 mg of (Graphene, Fe_3O_4-$CdWO_4$) (85%) and 0.7 mg of carbon black (15%) in 0.4 mL of Nafion (0.25 wt%) to obtain a uniform suspension.

Results: We investigated the supercapacitive behaviors of the as-prepared Graphene, Fe_3O_4-$CdWO_4$ electrode by means of a three-electrode system in 1.0 M KCl. We did these measurements under ambient conditions in the optimized potential range of 0.0 V to 0.6 V (vs. Ag/AgCl) at various scan rates.

Conclusion: The study the capacitance behavior of the prepared Graphene, Fe_3O_4-$CdWO_4$ electrode showed that this electrode has a very good capacitive behavior. The evaluations on Graphene, Fe_3O_4-$CdWO_4$ -based electrodes revealed the material to have a specific capacitance (SC) of 412 F g^{-1} at a scan rate of 2 mV s^{-1}, an energy density (ED) of 18.7 W h kg^{-1}, and a high rate capability. Continues cyclic voltammetry evaluations using Graphene, Fe_3O_4-$CdWO_4$ based electrodes proved the electrodes to be capable of maintaining almost 97.2% of its initial SC after 4000 cycles.

Keywords: Supercapacitors, Graphene, Fe_3O_4-$CdWO_4$, Glassy Carbon Electrode

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Electropolymerization of aniline in the presence of azo dyes

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Background: Conducting polymers (CPs) are polymers that inherently conduct electricity. At present it is possible to create conducting polymers with a diverse range of chemical, electrical and mechanical properties [1, 2]. and biosensors. Polyanilines are prepared by chemical or electrochemical oxidative polymerisation of the respective aniline monomers in acidic solution. The dopant incorporated in the polyaniline chain has a profound effect on the propertieties of the resultant polduct. In this paper incorporation of azo dyes such as Hydroxynaphthol blue (HNB) as dopants for PAni was investigated.

Methods: PAni film was deposited on the GC-HNB using potentiodynamic polymerization of aniline by applying a potential sweep between -0.5 V and 1.1 V (vs. Ag/AgCl) for 20 cycles at a scan rate of 50 mV/s using a three-electrode electrochemical cell. For comparison studies, the same procedure was applied for conventional electrosynthesis of PAni on a bare GC but using 0.1 M aniline monomer.

Results: Fig 1 shows the CVs during electrochemical polymerization of 0.01 M aniline in the presence of dye. The polymer film was characterized by cyclic voltammetry and Uv/vis spectroscopy. The film represented the characteristic electrochemical and optical properties of conducting polyanilne.

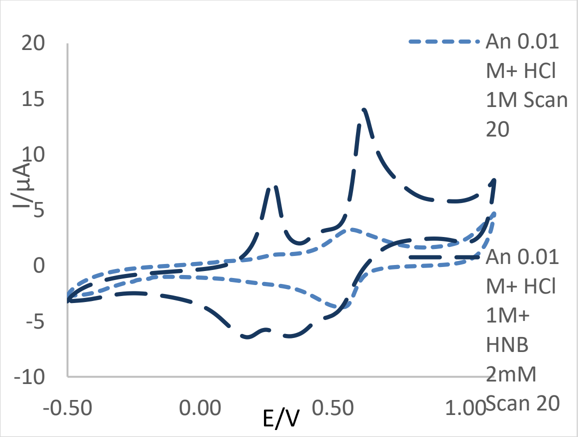

Fig 1 shows the CVs during electrochemical polymerization of 0.01 M aniline in the presence of dye.

Conclusion: Polyaniline film was deposited on GC electrode in the presence of azo dyes as dopants. Due to modifying properties of azo dye on the conducting and electroactive PAni layer, these modified electrodes can be used for electro-catalytic determination of drugs and biological compounds.

Keywords: conducting polymer, polyaniline, azo dye, dopant.

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Electroc-catalytic determination of dopamine at 1,5-Diphenylcarbazone modified electrode

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Background: Dopamine (DA), 4-(2-aminoethyl) benzene-1,2-diol, plays an important role in the function of the central nervous, cardiovascular, renal and hormonal systems. Insufficient DA concentration due to the loss of DA-producing cells may lead to a disease called Parkinson's disease[1,2]. In this study, we describe the electro-analytical applicability and performance of 1,5-Diphenylcarbazone (DPCO) as a modifier in the determination of DA.

Methods: Glassy carbon electrode (GCE) was simply modified with a uniform film of DPCO using cyclic voltammetry, and determination of DA was carried out on the modified electrode using differential pulse (DP) voltammetry.

Results: Figure A represents CVs during modification of GCE. DP voltammograms of DA at a bare GCE and DPCO-GCE are shown in Fig 1(B) for comparison. As shows in Fig 1(A), the sensitivity of DA measurement is significantly enhanced at the modified electrode. The effect of several parameters on the electrochemical determination of DA including pH, concentration of DPCO, scan rate, pulse amplitude and ionic strength were studied and the optimal conditions were obtained**.** The sensor response was reproducible (RSD ≤5%). Under the optimum conditions, the detection limits were 0.04 (µM).

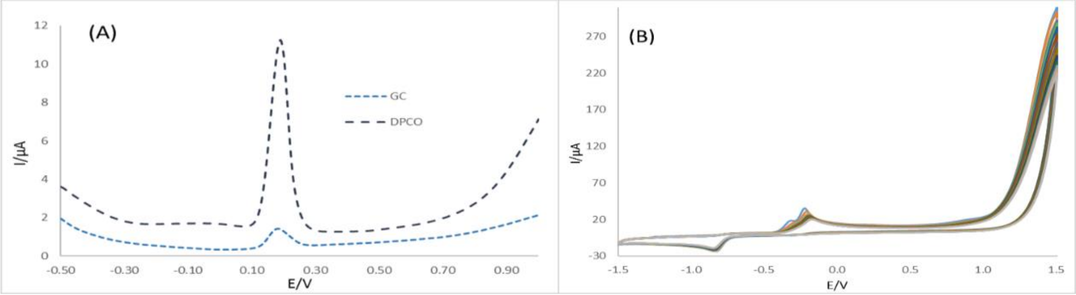

Fig 1. (a) DPs of DA at a bare GCE and DPCO-GCE, (b) CVs of DPCO at a GCE in NaOH solution.

Conclusion: An electro-chemical method was developed for sensitive determination of DA using DPCO-GCE. The proposed method could be applied to the determination of DA in real pharmaceutical and biological samples.

Keywords: 1,5-Diphenylcarbazone,electorchemistry, dopamine,GC,

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Fabrication of non-enzymatic electrochemical glucose sensors based on Cobalt based Metal-Organic Frameworks

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Background: Metal-Organic Frameworks (MOFs) are a class of crystalline compounds consisting of metal or a cluster of metal ions coordinated to organic ligands to form one, two, or three-dimensional structures, which were first introduced by Yaghi et.al[1]. These materials have been used in a wide range of applications like sensing, supercapacitors, gas adsorption/storage, chemical separation, chemical catalysis, drug delivery, electrocatalysis, electrochromic devices, etc. Presence of a broad range of applications are due to their unique features such as large internal surface areas, high porosity, crystalline ordered structure, high thermal stability, and chemical tenability. In order to take advantage of the interesting features of MOFs in practical, these crystalline materials must be accurately deposited on the device surface as thin films or coatings[2]. Herein, several strategies have been developed for the deposition of MOF thin films such as self-assembled monolayer, microwave-induced, solvothermal, gel layer synthesis, electrochemical deposition, layer by layer deposition, dip coating from colloidal solutions and in situ growth methods. Among different strategies for the deposition of MOFs on the substrate surface, in situ growth is considered as a straightforward and powerful method, because it utilizes a relatively simple synthetic procedure, with only a few reaction steps, via facile conversion strategy and without using any binder or an organic layer[3].

Methods: Herein, we reported a fast and facile three-step in situ strategy for direct controllable growth of the Co-based MOFs thin films on the GCE, through the rapid conversion of the $Co(OH)_2$ nano-flakes on rGO/GCE, to crystalline MOFs. The as-prepared MOFs were used to construct a non-enzymatic sensing platform for determining the glucose in alkaline solution via amperometry technique.

Results: Using the amperometric method, the designed electrode demonstrated two wide linear dynamic range of 1 µM - 0.33 mM and 0.33 mM - 1.38 mM with high sensitivity of 1792 µA mM^{-1} cm^{-2} and 1002 µA mM^{-1} cm^{-2}, respectively, good repeatability and reproducibility, high selectivity against interference species and good poisoning resistance against chloride ions and a low detection limit of 0.33 µM (S/N=3). The application of the proposed sensor for the determination of glucose in the human blood serum samples was investigated and results showed excellent recoveries, which confirmed that the fabricated sensor can act as a reliable and sensitive platform for biological and clinical samples analysis.

Conclusion: The present study provides a practical strategy for the fabrication of crystalline Co-MOFs as a promising material for designing non-enzymatic sensors, and this strategy can be used to design other types of these compounds in the future.

Keywords: Co- MOF; Modified Electrode; Non-enzymatic glucose sensor; Amperometry

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Voltammetric Determination of Acetaminophen Using Fe_3O_4/MWCNTs Nanocomposite Modified Carbon Paste Electrode

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Background: Acetaminophen is a safe and effective analgesic and antipyretic agent, although its anti-inflammatory effect is weak is frequently used to relieve severe pain in patients. Therefore, many analytical methods have been developed to determine of acetaminophen concentrations. On the other hand, the development of a simple, precise and accurate procedure for the determination of this drug in pharmaceutical products is still very useful [1, 2]. In this work, Fe_3O_4 nanoparticles/multi-walled carbon nanotubes composite modified carbon paste electrode (Fe_3O_4/MWCNTs-CPE) was developed for the electrocatalytic determination of acetaminophen in aqueous solution.

Methods: The Fe_3O_4/MWCNTs nanocomposite was prepared by co-precipitation method. Then, the Fe_3O_4/MWCNTs-CPE was fabricated thorough hand mixing this nanocomposite, graphite powder and paraffin as the pasting liquid, in a mortar and pestle for 15 min until a uniformly wetted paste was obtained. This mixture was packed into the end of a glass tube with a 3 mm inner diameter. The electrical connection was implemented by a copper wire lead fitted into the glass tube.

Results: The electrochemical behavior of acetaminophen was investigated on the Fe_3O_4/MWCNTs-CPE. Also, the differential pulse voltammetric determinations showed that under the optimal experimental pH, the obtained anodic peak currents were linearly proportional to acetaminophen concentration.

Conclusion: The modifiers and CTAB significantly facilitated the electron transfer rate between acetaminophen and the electrode, and the oxidation property of acetaminophen was improved on the modified electrode. Thus, the proposed electrode was successfully utilized for the determination of acetaminophen.

Keywords: Fe_3O_4/MWCNTs nanocapmosite; Carbon paste electrode; Acetaminophen; Differential pulse voltammetry

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Electrochemical Detection of Noscapine Based on the Enhancement Effect of Hexadecyltrimethylammonium Bromide at Modified Carbon Paste Electrode

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Background: Noscapine is an opioid agonist without significant analgesic properties. This agent is primarily used for its antitussive (cough-suppressing) effects. It has also been shown to have anticancer activity. The antitussive agent noscapine has been shown to inhibit the proliferation of cancer cells by disruption of tubulin dynamic. In illicit heroin samples, noscapine can be present in a wide concentration range [1]. Electrochemical sensors are considered reliable, selective and sensitive compared to alternative analytical tools, and also entail benefits such as simplicity, prompt response time and are also cost-efficient [2]. Multiwalled carbon nanotubes (MWCNTs) continue to receive remarkable attention in electrochemistry. The differential pulse voltammetry (DPV) results indicated that using surfactant especially hexadecyltrimethylammonium bromide (CTAB) in the presence of MWCNTs and TiO_2 nanoparticles remarkably enhances electrocatalytic activity toward the oxidation of noscapine, which is leading to considerable improvement of anodic peak current for noscapine, and allows the development of a highly sensitive voltammetric sensor for its determination.

Methods: The TiO_2/MWCNTs-CPE was prepared by mixing TiO_2, MWCNTs, and graphite powder with nujol as the pasting liquid and thorough hand mixing in a mortar and pestle for 15 min until a uniformly wetted paste was obtained. One portion of this modified carbon paste was then packed into the end of a glass tube with a 3 mm inner diameter. The electrical connection was implemented by a copper wire lead fitted into the glass tube.

Results: The oxidation peak current on the modified electrode in the presence of CTAB was appeared in the less potential values versus the bare CPE and in the absence of CTAB. The DPV results showed that under the optimal experimental pH, the obtained anodic peak currents were linearly proportional to concentration.

Conclusion: The modifiers significantly facilitated the electron transfer rate between noscapine and the electrode and the oxidation property of noscapine was improved on the modified electrode. Therefore, the propose electrode is a suitable sensor for detection of noscapine.

Keywords: Carbon paste electrode; Noscapine; Differential pulse voltammetry; Surfactant; TiO_2 nanoparticles; MWCNTs

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Lable-free electrochemical nano-genosensor for detection of prostate cancer miRNA-21 biomarker in serum samples based on AuNPs decorated in PANI and N-doped graphene

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Background: Prostate cancer is known as the most common non-skin cancer worldwide also diagnosed male malignancy and the second leading cause of male cancer-related death in the world[1]. MicroRNAs (miRNAs) appear as a novel reliable candidate in biomarkers for early diagnosis of prostate cancer [2].

Methods: A highly sensitive and label-free nano-genosensor was fabricated for the detection of miRNA-21, known as a prostate cancer biomarker, based on nitrogen-doped functionalized graphene (NFG), and gold nanoparticles (AuNP) which decorated to polyaniline (PANI) that resulted in a remarkable effect on signal amplification. For this reason, a certain amount of NFG was cast coated on the FTO electrode and after drying, the AuNPs and PANI simultaneously were electrodeposited on the NFG surface by CV technique in 0.5 M H_2SO_4. After that, the nano-composite was functionalized by 1-Ethyl-3-(3 dimethyl aminopropyl) carbodiimide hydrochloride and N-hydroxysuccinimide prepared in DI water. Then aminated complementary probe of miRNA-21 immobilized on the nano-composite for detection of miRNA-21. Furthermore, to block the unreacted surface with probes, prepared nano-composite was immersed in 11-mercapto-1-undecanol to fill the empty spaces between the complementary oligonucleotide probes.

Results: After biosensor preparation and characterization, its performance for electrochemical detection of miRNA-21 target in the presence of a redox probe under optimal conditions was examined. The results showed that applying this highly sensitive nano-genosensor enabled detection in a wide dynamic range of 0.01 fM - 1 μM with a sensitivity of 2.3 μA.cm^{-2} and a low detection limit of 0.01 fM.

Conclusion: The proposed electrochemical nano-genosensor has a wide linear range with a very low detection limit and was successfully used for early detection of prostate cancer by direct detection of the miRNA-21 in real clinical samples without any need to sample preparation.

Keywords: Electrochemical nano-genosensor; Graphene; Gold nanoparticle; Polyaniline; Prostate cancer

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Ion association and solvation behavior of tetraalkylammonium bromides in binary mixtures of sulfolane + dimethylsulfoxide probed by a conductometric study

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Background: The conductometry is the analytical method used both in research laboratories as well as in industry. The electric conductivity is one of the most important properties of electrolyte solution. In recent years, extensive studies on electrical conductances in various mixed organic solvents have been performed to examine the nature and magnitude of ion–ion and ion–solvent interactions [1]. tetraalkylammonium salts are characterized by their low surface charge density and they show little or no solvation in solution as such they are frequently selected as desired electrolytes in conductance studies. In continuation of our investigation on electrical conductance, the present work deals with the conductance measurements of some tetraalkylammonium bromides, R_4NBr (R = n-butyl to n-heptyl) in binary mixtures of DMSO and sulfolane at 298.15 K.

Methods: Precise measurements on electrical conductances of tetraalkylammonium bromides, R_4NBr (R = n-butyl to n-heptyl), in different mass% (0–100) of DMSO + sulfolane at 298.15 K have been performed. Limiting molar conductances (Λ_0), association constants (K_A) and co-sphere diameter (R) for ion-pair formation in the mixed solvent mixtures have been evaluated using the Fuoss conductance-concentration equation [2]. Limiting ionic molar conductances $\lambda_0^{\pm}$ have been calculated by the reference electrolyte method along with a numerical evaluation of ion pair and triple ion formation constants ($K_P = K_A$ and K_T). The results have been interpreted in terms of ion–solvent interactions and structural changes in the mixed solvents.

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c.$$

Results: The calculated limiting molar conductance (Λ_0) and ion-pair formation constant K_P are given in the table below:

	n-Bu_4NBr	n-Pen_4NBr	n-Hex_4NBr	n-Hep_4NBr
Λ_0	130.4	125.8	122.1	118.6
K_P	3.91×10^5	1.89×10^5	1.72×10^5	1.54×10^5

Conclusion: According to calculations, the limiting molar conductivity values (Λ_0) of tetra-n-butylammonium bromide are always found to be higher than those of its higher homologues. This means that the mobility of the (n-Bu_4N+) is greater than that of the (n-Pen_4N+), (n-Hex_4N+), (n-$Hept_4N$+) (anion being common) in all of the mixed solvent media.

Keywords: conductometry; Fuoss equation; ion-pair; association constants.

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Application of the Ion-Selective Electrode in the Modeling of Thermodynamic Properties of the Ternary NH_4Br + KBr + H_2O Mixed Electrolyte Systems

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Background: With the recent development and appearance of new sensors and selective membranes, ion-selective electrodes (ISEs) have become an attractive alternative method to the more usual vapor pressure or solvent activity methods for the investigation of thermodynamic properties of electrolyte systems. In this research, it seemed interesting to explore the ability of the ion-selective electrode in the modeling of thermodynamic properties of mixed electrolyte systems [1].

Methods: In this work, the ternary electrolyte system (NH_4Br + KBr +H_2O), and related galvanic cells containing the solvent polymeric (PVC) NH_4^+ ISE and Ag/AgBr and also K^+ ISE and Ag/AgBr electrodes, were utilized to calculate the mean molal activity coefficients for NH_4Br and KBr, respectively, in these electrolyte systems. it is well-known that in a mixed electrolyte system the response of ISEs could be more or less affected by the presence of an interfering ion, as expressed by the potentiometric selectivity coefficient (K_{ij}) of the ISE. For each of these studied ternary electrolyte systems, different series of mixed electrolyte systems, at similar ionic strengths, by a defined molal ratio ($r = m_1/m_2$), were used at 298.15 K for the activity coefficient modeling. To calculate the thermodynamic parameters, The semiempirical Pitzer ion interaction theory was successfully applied to investigate the various high-concentrated pure and mixed electrolyte systems [2].

$$\ln \gamma_{\pm} = |z_+z_-|f^{\gamma} + m\left(\frac{2\upsilon_+\upsilon_-}{\upsilon}\right)B^{\gamma} + m^2\left(\frac{2(\upsilon_+\upsilon_-)^{3/2}}{\upsilon}\right)C^{\gamma}$$

Results: Using experimental data, values of K_{12}^{pot} and mean activity coefficient values in mixed salt solutions were calculated.

r	$k_{NH4,K}$ (a_K/a_{NH4})	r	$k_{K,NH4}$ (a_{NH4}/a_K)
100	2.6×10^{-4} to 5.3×10^{-4}	250	9.2×10^{-4} to 1.5×10^{-3}
1000	2.6×10^{-5} to 5.2×10^{-5}	500	6.7×10^{-4} to 4.2×10^{-4}
2500	1.1×10^{-5} to 2.1×10^{-5}	4000	8.8×10^{-5} to 5.9×10^{-5}
5000	5.2×10^{-6} to 1.1×10^{-5}	10000	3.4×10^{-5} to 2.1×10^{-5}

Conclusion: The potentiometric selectivity coefficient of the ISE membrane (K_{12}^{pot}) effect on the potentiometric measurement was analyzed. It may be concluded that the interfering role of ions on the ISE measurements could be counterbalanced by using the choice of a high molal fraction of mixed electrolyte systems. Effectively, as shown in the reported data, reliable mean activity coefficient values up to four decimal significant numbers correspond to the mixed electrolyte systems with molal ratio $r \geq 1000$ for NH_4Br + KBr system and $r \geq 4000$ for KBr + NH_4Br system.

Keywords: Ion-Selective Electrode; activity coefficients; potentiometric measurements; mixed Electrolyte.

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Fabrication of binary nickel-cobalt oxides/carbon sphere cell as a high performance supercapacitors

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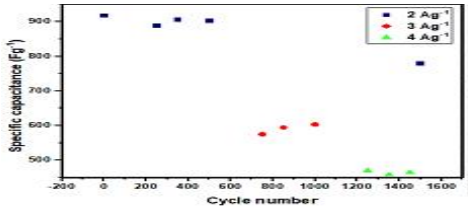
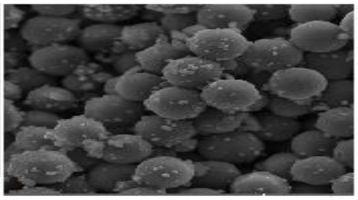
Background: Various energy storage technologies have been designed to meet the growing demands of development of portable electronic devices and electrical vehicles [1]. Supercapacitors are of great interests as energy storage devices, because of their high power density, fast charge discharge rates and long cycle life [2]. Porous carbon materials by owning large surface area, good chemical stability and high electronic conductivity, attract much attentions for application as electrode materials in supercapacitors. Since Porous carbon materials suffer from low specific capacitance and consequently low energy density, a lot of efforts have been made to embedded porous carbon materials with transition metal oxides, which possess high specific capacitance and high energy density. Using this strategy, hybrid electrode material with high specific capacitance and good cycling life were achieved [3]. Among different types of carbon porous materials, carbon sphere by owning good electric conductivity and low production cost, have great potential for application in supercapacitors. Herein, the fabrication of a new electrode material consisting of porous carbon spheres imbedded with Ni-Co oxides is reported.

Methods: Carbon spheres have been prepared from glucose solution by a hydrothermal method followed by carbonization. Ni-Co oxides are directly grown on carbon spheres by the hydrothermal method and characterized by SEM, EDS, elemental mapping, XRD, voltammetric and galvanostatic and electrochemical impedance spectroscopy techniques.

Results: The obtained results demonstrated that the fabricated electrode displays excellent electrochemical properties with a high specific capacitance of 1300 F g^{-1} at 1 A g^{-1}, and good long term cycling life (85% retention after 1500 cycles)





Conclusion: In summary, we have successfully synthesized Ni-Co oxide-carbon sphere core/shell structure on Ni foam with enhanced supercapacitor performance via a tow step hydrothermal method.

Keywords: Carbon spheres; Transition metal oxides; Nickel/Cobalt oxides, Hybrid Supercapacitors; hydrothermal method.

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Electrodeposition of Ni-W/SiO_2 Nanocomposite Coatings and Investigation of their Corrosion Resistance in 3.5 wt.% NaCl Solution

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Background: The protection of industrial materials from corrosion process is of paramount importance [1, 2]. Significant interest in the development of nanocrystalline Ni-W alloy as surface coatings is receiving considerable attention, since its potential applications are in multiple [3, 4]. The present work aims to prepare electrodeposited Ni-W/SiO_2 nanocomposite coatings, using different SiO_2 plating baths and to evaluate their corrosion behavior by open circuit potential (E_{OCP}), electrochemical impedance spectroscopy (EIS) and polarization studies.

Methods: The surface morphology and composition of the composite coatings were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) measurements. The corrosion characteristics of Ni-W/SiO_2 composite coatings were investigated by electrochemical measurements, including open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization in a 3.5 wt.% NaCl solution.

Results: The study reveals significant shift in corrosion potential towards the noble direction, decrease in corrosion current density, and increase in charge transfer resistance with the incorporation of SiO_2 particles in the Ni-W matrix. The significant improvement in corrosion resistance observed for Ni-W/SiO_2 composite coatings compared to pure Ni-W could have resulted from the microstructural differences.

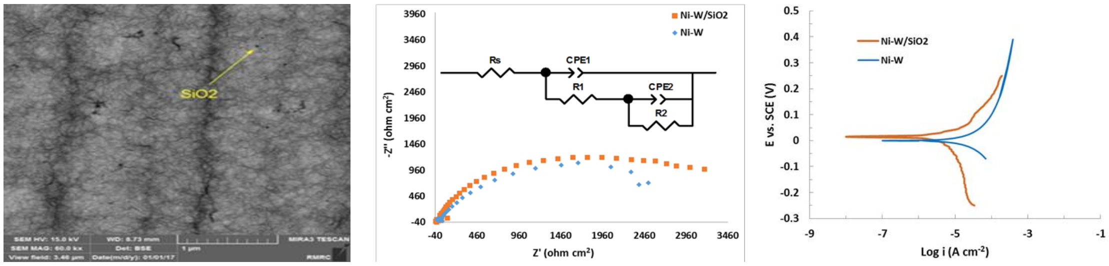

Fig. SEM image, EIS and polarization curves of pure Ni-W and Ni-W/SiO_2 nanocomposite coatings.

Conclusion: The Ni-W/SiO_2 composite coatings were properly prepared by electrodeposition from tartrate bath. The SEM results showed that the incorporation of SiO_2 particles in the Ni-W matrix decreases the surface roughness, alters the chemical composition and increases the corrosion resistance.

Keywords: Ni-W/SiO_2; Nanocomposite; Corrosion; Polarization measurements

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Electrocatalytic determination of Amikacin using glassy carbon modified with gold nanostructures

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Background: Gold nanoparticles (AuNPs) due to their properties such as continuity in synthesis and unique optical properties, are the perfect scaffold for the fabrication of novel biological and chemical sensors [1]. Also, use these nanoparticles on surface electrodes as modifier, increases the efficiency of the electrodes by high mass transfer, catalysis, high surface area. Amikacin is an antibiotic used for a number of bacterial infections [2]. Amikacin (AMK) is most often used for treating severe infection with multidrug resistant, aerobic gram-negative bacteria.it is used either by injection into a vein or muscle [3]. In this study, a voltammetric sensor for the determination of Amikacin with gold nanostructures is proposed.

Methods: AuNPs were synthesized on the GCE surface by electrochemical method. The glassy carbon was immersed in 1 mM HAuCl4. Deposition time a 200 s and deposition potential was -0.4 V.

Results: The electrochemical behavior of 0.1 mM AMK in 0.1 M phosphate buffer solution at pH 7.0 at the surface of AuNPs/GCE was studied by using cyclic voltammetry and an oxidation peak appeared at 0.893 V with peak current of 48.4 µA. The effect of some parameters such as time and potential deposition, pH and scan rate was studied. The differential pulse voltammetry technique was applied for quantitative determination of the AMK. Under the optimum conditions, calibration curves of AMK was obtained. The reduction peak current was linearly proportional to the concentration of AMK. The sensor performance is promising in real samples. Dynamic linear range was $1.0 \times 10^{-8} – 1.0 \times 10^{-3}$ M. The presented electrode was used for determination of AMK in real samples such as human serum and Ampules.

Conclusion: A novel electrochemical sensor for determination of AMK was presented in this study. High sensitivity, good repeatability and rapid response among the advantages of this sensors.

Keywords: Gold nanoparticles; Amikacin; Deposition; Voltammetric sensor.

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Study of electrooxidation of formic acid on the glassy carbon electrode modified by conductive polymers, graphene and palladium nanostructures in the acidic media

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Background: Direct formic acid fuel cells (DFAFCs) have attracted significant consideration because formic acid has many advantages such as easy storage, low operating temperature, non-toxic, higher power density and smaller crossover flux through a Nafion® membrane [1]. Recently, supporting materials such as carbon nanotubes, grapheme and polymers are used to enhancement the catalyst's efficiency and diminish the cost of metal catalyst. Graphene is a good choice as support material because of it's fascinating properties [2]. Also, conducting polymers (CPs) such as polypyrrole (PPy) and polyaniline (PANI) have been used for different applications such as metal catalyst supporting materials because of their unique properties [3]. On the other hand, there has been extensive research on various sizes and shapes of Pd nanostructures. In particular, three-dimensional (3D) nanoflowers has received great attention due to its unparalleled properties [4].

Methods: First, suspension of the Gr was prepared and casted on the electrode surface and dried. In the next step, polymers were synthesized using both chemical and electrochemical methods and were put on the Gr. After that, palladium was fabricated on the electrode surface by a one-step electrochemical method. Several techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were utilized for the characterization of the synthesized materials. The catalytic activities of prepared electrodes were investigated by CV, EIS and chronoamperometry.

Results: As the results show, the presence of polypyrrole-polyaniline/graphene (PP/Gr) as supporting material for Pd catalyst improve the catalytic electroactivities and stability for formic acid oxidation. Besides, PP/Gr represents higher current density rather than each of polypyrrole, polyaniline and grapheme, alone. Also, all fabrication process of catalysts and polymers are fast, easy and eco-friendly. The obtained results suggest the Pd/PP/Gr/GCE catalyst improve the kinetics of formic acid oxidation.

Conclusion: Pd nanostructures supported on PP/Gr/GCE which is prepared by chemically method displays the enhanced electrocatalytic activity but PP/Gr/GCE that is prepared by electrochemically method displays better stability for formic acid oxidation.

Keywords: Palladium nanostructures; Polyaniline/polypyrrole; Graphene; Catalysis; Formic acid electrooxidation.

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A new modified pencil graphite electrode for electrocatalytic oxidation of methanol

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Background: In direct methanol fuel cell (DMFC), methanol is used as a fuel because it can be completely electrooxidized to the final product due to its simple molecular structure. Thus, a great deal of interest exists in the development of materials with a capability for electrocatalytic oxidation of methanol [1,2]. Platinum is used for its stability and activity as an ideal catalyst for methanol oxidation reactions [3]. Many materials have been investigated as catalyst supports for catalysts in DMFCs, such as Multi-walled carbon nanotubes (MWCNTs), chitosan, phosphomolybdic (PMA) and poly (diphenylamine) (PDPA) [4,5].

Methods: In this work, a layer-by-layer (LbL) film assembly was constructed that comprises alternative layers of (PDPA) and (PMA) on the electrode modified with chitosan and MWCNTs. then, the particles of platinum was electrodeposited under constant potential on the previous modified electrode. This procedure is repeated to obtain multi-layers of Pt, PMA and PDPA.

Results: The constructed electrode was characterized using field emission scanning electron microscopy (FESEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry methods. The effects of various parameters on the peak current and peak potential of oxidation of methanol were investigated by modified electrode in H_2SO_4 solution. Chronoamperometry method was used to study the stability of the electrode. The effect of various potential scan rates was tested on the electrocatalytic behavior of the electrode for methanol oxidation reaction.

Conclusion: This study showed that the modified electrode has good electrocatalytic activity and higher peak current density for oxidation of methanol.

Keywords: Fuel cell; pencil graphite electrode; Multi-walled carbon nanotubes; polydiphenylamine

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Electrochemical determination of ribavirin using molecularly imprinted polymer

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Background: Ribavirin is an antiviral drug that was developed in 1972, for the treatment of hepatitis [1]. The most important drug-related dose effects are red blood cell decompression, respiratory distress, renal, and abortion [2]. In fact, the purpose of this research was to construct an electrochemical biosensor based on molecularly imprinted polymer for indirect measurement of ribavirin in biological samples in a short time. Mostly, different methods have been proposed for measuring ribavirin, such as spectrometry [3], chromatography [4], and electrochemical methods [5]. The electrochemical methods were used due to ease of analysis, accuracy, and sensitivity.

Methods: The fabrication of sensor was done by the electropolymerization of ortho-phenylenediamine (OPD) in the presence of ribavirin, as the template molecule and also DNA, on a pencil graphite electrode (PGE) modified with chitosan and multiwalled carbon nanotube (MWCNT). To produce imprinted sites, the template was removed by 0.3 M NaOH solution.

Results: After re-binding ribavirin, the decrease in the peak current of oxidation of Fe^{2+} as a probe was determined using differential pulse voltammetry (DPV). The current variations at 0.5 V were linear with concentrations of ribavirin ranging from 0.1 to 10.0 nM. The detection limit was calculated as 9.1×10^{-2} nM of ribavirin. The effect of some other substances on the electrode response was investigated and the sensor showed high selectivity toward ribavirin.

Conclusion: In this work, a novel sensitive molecularly imprinted electrochemical sensor was prepared for determination of ribavirin using electrochemical deposition of MIP layer together with DNA on the MWCNTs and chitosan. Furthermore, The imprinted sensor shows fast binding kinetics to the template due to their high ratio of surface imprinted sites and has shown large affinity to the template. Eventually, the capability of the proposed sensor was evaluated by determination of ribavirin in biological samples.

Keywords: Molecularly imprinted polymer (MIP); Ribavirin; Deoxyribonucleic acid (DNA); Multiwalled carbon nanotube (MWCNT); Differential pulse voltammetry (DPV).

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Ultrasensitive aptasensor for edifenphos pesticide detection in rice based on sandwich architecture

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Background: Edifenphos (EDI) is one of the most significant organophosphorus pesticides. EDI applies its fungicide acting via the deterrence against choline biosynthesis and synthesis of phosphatidylcholine from the transmethylation of phosphatidylethanolamine. Herein, for the first time, we developed a facile and sensitive method for determination of EDI. The aminated aptamer (APT) was covalently attached on the surface of a glassy carbon electrode (GCE) modified with a nanocomposite composed of reduced graphene oxide (rGO) and functionalized multi-walled carbon nanotubes (f-MWCNTs). In order to promote electron transfer, amplifying signal and increasing stability of the electrode, this nanocomposite was deposited on the GCE by two steps.

Methods: At the first step, GO and f-MWCNTs were deposited on the GCE (f-MWCNTs–GO/GCE). In the next step, electrochemically reduction leads to reduced graphene oxide (rGO) and f-MWCNTs nanocomposites (f-MWCNTs–rGO). Following that, aminated APT was immobilized on the f-MWCNTs–rGO/GCE through covalent coupling of APT and the carboxylate groups of f-MWCNTs–rGO (APT/f-MWCNTs–rGO/GCE).

Results: Due to the synergistic effect of rGO and MWCNTs, an ultrasensitive electrochemical aptasensor for EDI was successfully fabricated. The electrochemical performance of the nanocomposite was demonstrated with CV, DPV and EIS. Using the data from DPV, under optimized conditions, a wide linear range from 0.001 to 1300 nM and the detection limit of 0.1 pM was obtained.

Conclusion: An ultrasensitive electrochemical sensor for EDI based on the APT/f-MWCNTs–rGO was fabricated with desirable detection results in real samples. High sensitivity, very good repeatability, and high stability together with simple procedure for preparation and determination can be presented as the advantages of the proposed electrode.

Keywords: Aptasensor; Graphene oxide; MWCNT; Edifenphos; Cyclic voltammetry

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The Effect of TiO_2 Nanoparticles on the Corrosion Properties of Electroless Ni-Cu - P Composite Coatings

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Background: Today, the electroless process is widely used in various industries. The use of nanoparticles in electroless composites increases the corrosion resistance properties of various substrates. By studying various sources, it is justified by adding TiO_2 nanoparticle in Ni-P-Cu composite that increases the corrosion resistance of the substrate [1-2].

Methods: The precise interval of the parameters of the electroless process was obtained during several experiments by helping with the design express program. Scanning electron microscopy (SEM) was used to study the morphology of Ni–P, Ni–Cu–P and Ni–Cu–P– TiO_2 composite coatings. The anti-corrosion properties of Ni–P composite coatings were investigated in 3.5% NaCl solution by the potentiodynamic polarization technique.

Results: It has been found that Ni–P coating obtained using $CuSO_4.5H_2O$ and TiO_2 nanoparticles with the smooth surface showed higher anti-corrosion resistance.

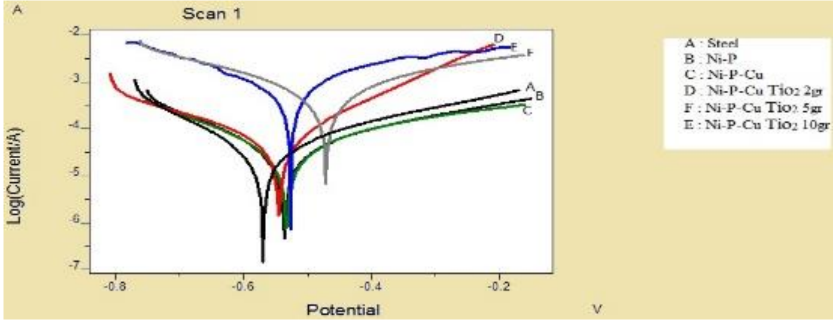

Fig. Potentiodynamic polarization curves of electroless various composite coatings in 3.5% NaCl solution.

Conclusion: Ni-P-Cu composite coating was optimized in a temperature range and pH. It has been shown to have good corrosion resistance, which increased the corrosion resistance by adding TiO_2 nanoparticle to the copozite. In this experiment, it was proved that the formation of suitable deposits on the steel substrate is strongly dependent on the temperature and pH of the electroless bath [3].

Keywords: Electroless Ni, TiO_2 Nanoparticle, Corrosion

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Fabrication of hierarchical $MnMoO_4.H_2O$@Ni-Co-S core-shell nanosheet arrays on nickel foam for high-performance supercapacitor

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Background: The core-shell nanosheet structure of $MnMoO_4.H_2O$@Ni-Co-S significantly increases the amount of active sites for redox reactions, shortens the diffusion pathway for ions and facilitates the effective penetration of the electrolytes for energy storage application. For example, the hierarchical $CoMoO_4$@MnO_2 core-shell nanosheet arrays exhibits the specific capacitance, which is much higher than the pristine $CoMoO_4$ [1]. In particular, Ni-Co-S exhibit much richer redox reactions than that of the corresponding binary NiS and Co_9S_8, which can provide much higher electrochemical activity [2]. In this work, we fabricated hierarchical $MnMoO_4.H_2O$@Ni-Co-S core-shell nanosheet arrays on nickel foam as electrode material for supercapacitors.

Methods: Na_2MoO_4 and $MnCl_2$ was dissolved in water, separately. The nickel foam was immersed in the $MnCl_2$ solution and magnetic stirring in an ultrasonic bath. Na_2MoO_4 aqueous solution was added to $MnCl_2$ solution dropwise under stirring. After that, the product was transferred into an autoclave. The autoclave was in an oven. Then the sample was washed. The electrodeposition was performed by using CV in the electrolyte solution contains $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$ and CH_4N_2S. Then, the sample was dried in an oven.

Results:The $MnMoO_4.H_2O$@Ni-Co-S core-shell nanosheet as electrode material reaches to a high specified capacitance of 5261 F g^{-1} at a current density of 2 A g^{-1}, as well as excellent cycling stability (94.3% capacitance retention after 3000 cycles). These outstanding electrochemical properties demonstrate that the as-prepared $MnMoO_4.H_2O$@Ni-Co-S core-shell nanosheet is efficient electrode material for supercapacitor and has a greatly promising application in the development of high-performance electrochemical energy storage devices.

Conclusion: In summary, we have successfully fabricated the hierarchical $MnMoO_4.H_2O$@Ni-Co-S core-shell nanosheet arrays on nickel foam via a facile two-step method. These enhanced pseudocapacitor performances benefit from the synergistic effect of the hierarchical nanostructure and also provides: 1) large surface area and number of electrochemical reactive sites; 2) faster ion diffusion and electron transport at electrode/electrolyte interface. After further depositing Ni-Co-S, the as-obtained $MnMoO_4.H_2O$@Ni-Co-S hybrid electrode exhibits a high specific capacitance 5261 F g^{-1} at a current density of 2 A g^{-1} and good cycling stability.

Keywords: Core-shell nanosheet, Hydrothermal, Electrochemical deposition, Supercapacitor

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The corrosion behaviour of electrodeposited Pd, Pd-Cd, and Pd-Bi samples in sulphuric acid solution: An electrochemical study

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Background: Palladium-based samples have been used abundantly for different catalytic reactions such as formic acid, methanol, and ethanol oxidation, oxygen reduction, and hydrogen production and storage. These electrochemical reactions can be investigated in alkaline as well as acidic solutions. Therefore, the stability of electrodes in the solution is an important issue [1-4]. In this regard, in the present study, the corrosion of electrodeposited Pd, Pd-Cd, and Pd-Bi samples in 0.5 M sulphuric acid solution is investigated using Tafel polarization, and impedance spectroscopy methods.

Methods: Pd, Pd-Cd, and Pd-Bi working electrodes were electrodeposited on a glassy carbon electrode by the chronoamperometry method at the potential of -0.6 V for 600 seconds. A saturated Ag/AgCl and a platinum plate were employed as the reference and counter electrodes, respectively. The electrochemical experiments were carried out using an Ivium Stat Potentiostat/Galvanostat, model Vertex (Netherland). EDX analyses showed the atomic percentage of Pd as 87.74 and 23.17 in Pd-Cd and Pd-Bi samples, respectively.

Results: The Tafel polarization results and Nyquist diagrams for electrodeposited samples are shown in Fig. 1a, b. According to these results, the Pd sample has the lowest corrosion rate and Pd-Bi sample has a corrosion rate less than Pd-Cd sample. The Nyquist diagrams also confirm the greater resistance (R_{ct}) of Pd sample against corrosion compared to the Pd-Bi and Pd-Cd samples.

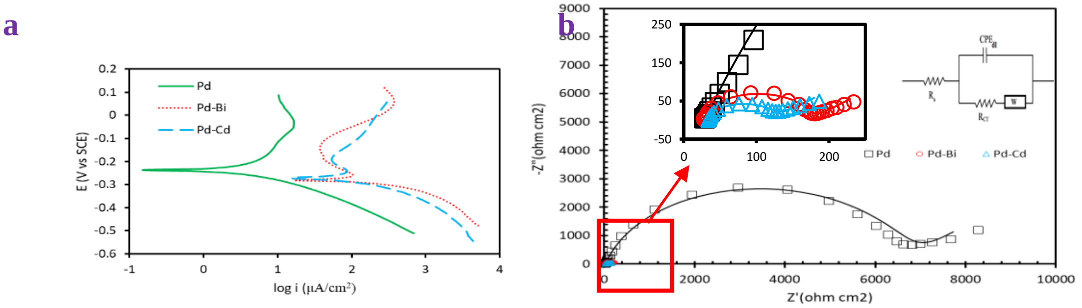

Fig 1. Potentiodynamic polarization curves (a) and Nyquist diagrams (b) of samples obtained in 0.5 M H_2SO_4 solution.

Conclusion: The corrosion and passivation behavior of samples in a sulphuric acid solution was studied by Tafel polarization and impedance spectroscopy techniques. Potentiodynamic Tafel polarization curves and Nyquist diagrams demonstrated that the Pd sample has higher corrosion resistance and smaller corrosion rate compared to the Pd-Bi and Pd-Cd samples.

Keywords: Pd based samples, Corrosion, Tafel polarization, Impedance spectroscopy

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Electrochemical sensor based on carbon nitride/polyaniline nanocompsite for simultaneous determination of dopamine, uric acid, xanthine, and hypoxanthine

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Background: Many studies have been done to introduce g-C_3N_4 as the most stable allotrope [1]. This material has the following characteristics: high chemical and thermal stability, no risk to health, environmentally friendly, and tunable electronic structure [2]. PANI is a good matrix and host for bio-molecules, which makes it useful in the manufacture of sensors. PANI is a good conductive matrix and host for C_3N_4, and the combination of these two substances improves the weakness of weak mechanical strength of PANI and the low conductivity of C_3N_4 [3].

Methods: C_3N_4 was stabilized by electrochemical method on the GCE surface. Next electrodeposition of polyaniline (PANI) on mesoporous polymeric graphitic C_3N_4 (mpg-C_3N_4 /GCE) was performed at ambient temperature and the constant potential of 1.0 V vs. SCE in an aqueous solution containing 50 mM aniline and 1 M HCl. In this way, the obtained modified electrode was PANI/mpg-C_3N_4/GCE. FE-SEM, EDX, FT-IR, XRD, and EIS were used to characterize the nanocomposite.

Results: PANI/mpg-C_3N_4 nanocomposite was used as a high performance sensor for the simultaneous determination of dopamine (DA), uric acid (UA), xanthine (XA) and hypoxanthine (HXA). Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) methods were applied for determinations. The sensor provided one linear responses from 2-200 μM for DA, one from 6-500 μM for UA, one from 12-230 μM for XN, and one from 5-380 μM for HXN. The detection limits were 0.02 μM, 0.16 μM, 0.84 μM, and 0.12 μM, (S/N=3) for DA, UA, XN, and HXN, respectively.

Conclusion: Three-Dimensional mpg-C_3N_4/PANI nanocomposite was synthesized in a completely electrochemical technique. mpg-C_3N_4/PANI nanocomposite was used for the simultaneous determination of e DA, UA, XN, and HXN. Excellent electrocatalytic activity towards DA, UA, XN, and HXN was achieved.

Keywords: Carbon nitride; polyaniline; dopamine; uric acid; xanthine; hypoxanthine

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A nonenzymatic glucose sensor based on carbon nitride/polyaniline/Pt nanoparticles/NiO nanocomposite

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Background: Carbon Nitride (C_3N_4) is an attractive class of N-doped carbon-based materials with 2.7 eV band gap, which has a unique 2-D structure. Studies on carbon nitride began in 1830 when two scientists, Berzelius and Liebig, made a polymer derivative of carbon nitride [1]. Polyaniline (PANI) is an important category of conductive polymers which, due to the existence of a π-conjugation system in it, provides a very large specific surface area and thus enhances electron transfer. Although, it has a weak mechanical strength. It can has synergistic effects along with other nanomaterials and improve the electrochemical sensitivity [2].

Methods: In order to stabilize of C_3N_4 on the GCE surface CV technique was applied. Electrodeposition of PANI on mpg-C_3N_4/GCE was performed at the constant potential of 1.0 V vs. SCE [3]. The Pt nanoparticles were electrochemically deposited on the PANI/mpg-C_3N_4/GCE by CV method. Next, Ni hedgehog-like nanostructures have been deposited on to Pt/PANI/mpg-C_3N_4/GCE by CV procedure. In this way, the obtained modified electrode was NiO/Pt/PANI/mpg-C_3N_4/GCE. FE-SEM, EDX, FT-IR, XRD, and EIS were used to characterize the nanocomposite.

Results: NiO/Pt/PANI/mpg-C_3N_4 nanocomposite was used as a high performance sensor for the determination of glucose. Cyclic voltammetry (CV) and amperometric methods were applied for determinations. The results revealed that the NiO/Pt/PANI/mpg-C_3N_4/GCE exhibited remarkable electrocatalytic performance toward glucose oxidation, with a wide linear range of 0.01-14 mM and a low detection limit of 0.91 μM based on a signal to noise ratio of 3.

Conclusion: NiO/Pt/PANI/mpg-C_3N_4 nanocomposite was synthesized in a completely electrochemical technique. This nanocomposite was used for the determination of glucose. This electrode can effectively analyse glucose concentration in human serum samples, avoiding interference, and is a promising non-enzymatic glucose sensor due to its fast response, good selectivity and stability, low overpotential, high sensitivity**.**

Keywords: Carbon nitride; polyaniline; glucose sensor; Pt nanoparticles, NiO hedgehog-like nanostructure

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Chemically Modified Carbon Paste Electrode for Selective Determination of Fluoride Ions in Solution

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Background: Fluoride (F^-) ion, as one of the most common anions, is useful for dental care, treatment of osteoporosis and water supply treatment in small amounts [1]. Fluoride is one of the most hydrophilic anions and thus design of an ionophore selective towards fluoride is quite challenging. Only a few useful ionophores have been described in the literature that exhibit enhanced potentiometric response towards fluoride anion [2]. The goal of the present work is to devise a highly selective fluoride carbon paste electrode with good response properties, such as slope and response times, using the selective coordination chemistry between fluoride and Zr (IV).

Methods: The modified carbon paste electrode containing Zirconium(IV)-salophen was generally prepared by hand-mixing of 61.0 mg of graphite powder, 7.7 mg of the ionophore and 0.6 mg of TDMACl in a mortar for at least 10 min until the ionophore was uniformly dispersed through the graphite powder. Then, 30.7 mg of Nujol was added and the mixture was mixed until a uniform paste was obtained. The paste was packed in the end of a disposable polyethylene syringe, the tip of which had been cut off with a razor blade.

Results: The modified CPE electrode exhibits a nernstian slope of 28.9 mV per decade for fluoride ion over a wide concentration range of 1.1×10^{-5} - 5.0×10^{-1} M, with a low detection limit of 8.0×10^{-6} M. The electrode has a relatively fast response time (8 s), satisfactory reproducibility and good life time (more than 2 months). The potentiometric response is independent of the pH of the test solution in the pH range 4.0-6.5.

Conclusion: This work revealed that the proposed chemically modified carbon paste electrode based on Zirconium(IV)-salophen can be used as a useful analytical tool and interesting alternative for the determination of fluoride ion. The electrode shows good sensitivity, low detection limit, reasonable selectivity, long term stability and applicability over a wide pH range.

Keywords: Fluoride-ion selective electrode; Carbon paste; Zirconium (IV)-salophen; modified electrode; Potentiometry

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Detection of vitamin D3 with an electrochemical sensor, based on sol-gel molecularly imprinted polymer (MIP) incorporated in multi-walled carbon nanotubes

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Background: As discovered newly, vitamin D sufficiency can decrease prevalence of diseases such as cancer, diabetes, cardiovascular and autoimmune diseases [1]. Hence there is great request for easy and sensitive methods for determination of vitamin D metabolites in medical and nutritional research. In spite of the physiological importance of vitamin D and its metabolites, a few electroanalytical studies had been done on such compounds [2].

Methods: A vitamin D3 selective molecularly imprinted polymer (MIP) and a non-imprinted polymer (NIP) are synthesized by sol-gel polymerization [3], armed with multi-walled carbon nanotubes (MWCNTs), and then mixed with graphite powder and n-eicosane as a binder for construction of carbon paste electrodes (CPEs). Vitamin D3 is extracted in the electrode surface for a certain time and then it is analyzed by square wave voltammetry, which display higher response current for vitamin D oxidation peak. Considerable high recognition capacity in comparison with NIP-CPE is a noble characteristic of the MIP–CPE

Results: A highly sensitive voltammetric sensor for vitamin D3 is designed and generated by using sol-gel imprinted polymer. Various factors, by those the response current of the electrode is mainly affected, are studied and optimized. This sensor shows a linear response range of 8×10^{-8}- 4×10^{-6} M and lower detection limit of 6×10^{-8} M. The sensor is successfully applied for detection of vitamin D3 in human plasma samples.

Conclusion: In this study, we combined the efficient affinity of the sol-gel imprinted polymer to vitamin D with excellent electrochemical characteristic of multi walled carbon nanotube and electrochemical oxidation of vitamin D to produce a novel voltammetric sensor with high sensitivity and selectivity for vitamin D detection in real samples.

Keywords: molecular imprinted polymers; vitamin D; electrochemical sensors.

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A novel non-enzymatic biosensor modified with rGOx/Co_3O_4 nanocomposite for determination glucose by cyclic voltammetry method

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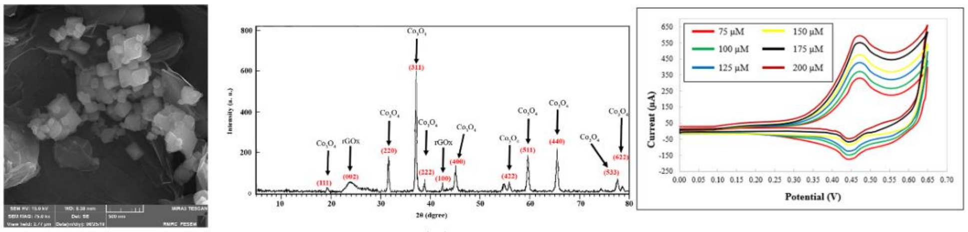
Background: Since reliable and fast monitoring of glucose is essential in areas such as biotechnology, medicine, clinical diagnostics, the food industry and also in the development of renewable and sustainable fuel cells, the extension of electrochemical glucose biosensors has received continuous interest. Cobalt oxide has been proved as a promising material for non-enzymatic glucose sensing because of its low cost, chemical stability environmentally benign nature, relatively good conductivity and electro-catalytic property [1-3].

Methods: In this work, reduce Graphene Oxide/Cobalt Oxide nanocomposite were prepared by a two-step strategy, with a hydrothermal method. Scanning electron microscope (SEM), X-ray diffraction (XRD) and dynamic light scattering (DLS) analysis were applied to characterize the as-prepared sample. Nanocomposite modified electrode showed high catalytic activity for glucose electro-oxidation in alkaline medium. The effects of NaOH concentration and the applied potential were investigated and optimized. Cyclic voltammetry (CV) detection of glucose was performed.

Results: XRD patterns of nanocomposite (Fig. 1b) indicating that the thermal decomposition and oxidization of this cobalt precursor causes its complete conversion to crystalline nanocomposite. The DLS pattern reveals that nanocomposite have an average the diameter of 58.83 nm. The enhanced anodic peak current was observed with increasing concentration of glucose from 75 µM to 200 µM. The detection limit was 976 nM based on the signal-to-noise ratio of 3 (Fig. 1c).



(a) (b) (c)

Fig 1. a) FE-SEM images, **b)** XRD patterns, **c)** CVs of the biosensor in various concentrations of glucose

Conclusion: Nanocomposite show high electrocatalytic activity toward glucose oxidation in alkaline medium and are used as an effective biosensor for glucose detection. These results make Nanocomposite is a good candidate for the construction of a non-enzymatic glucose biosensor in routine analysis. This structural electrode exhibited a good response for the detection of glucose with a high sensitivity. Analysis of real samples revealed the potential of the biosensor for glucose detection in physiological samples.

Keywords: Biosensor Glucose; Nanocomposite; Non-enzymatic; Glassy Carbon Electrode; Cyclic Voltammetry.

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Effect of Electrolyte concentration on the aggregation behavior of cationic surfactant Tetradecyltrimethylammonium Bromide(TTAB) at 298.15 K

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Background: The association of ionic surfactants in aqueous solutions is influenced by the electrostatic interactions between the ionized head groups and their interactions with the surrounding counter-ions and water molecules. Electrolytes normally decrease the electrostatic repulsion between the surfactant head groups and therefore reduce the critical micelle concentration (CMC) of ionic surfactants (salting-out effect) [1-2]. In this manuscript, the conductometric measurements have been used to examine the effect of electrolytes (at different fixed concentrations) on the CMC and aggregation properties of TTAB at 298.15 K.

Methods: The conductivity measurements were performed with a digital conductivity meter (model C860, Consort, Belgium) and a dipping cell with a platinum electrode (cell constant = 1.01 cm^{-1}). The instrument was standardized with potassium chloride (KCl) solutions of the right concentration range. Conductometric titration method involving the titration of a known volume of surfactants stock solution into a fixed volume of aqueous solutions. All the measurements were carried out at 298.15 ± 0.1 K, by circulating water through the outer jacket from a thermostatically controlled water bath (EYELA NTT-1100, Japan).

Results: Firstly, the aggregation point of the TTAB (or CMC) in aqueous and electrolyte solutions were determined from the sudden change in the slope of the specific conductance versus surfactant concentration plot. The results show that in the presence of electrolyte, the addition of TTAB leads to a sharp increase of conductivity at very low concentration and then the values of positive slopes of plots decrease up to the CMC and the value of the specific conductivity decreases. Therefore, the CMC of TTAB decrease with increasing the electrolyte solution (due to salting-out effects). Finally, the standard Gibbs energy of micellization (ΔG_{mic}^{0}) and the degree of counterion binding(α) values were evaluated and discussed with increasing electrolyte concentration.

Conclusion: In this paper, CMC, aggregation number (N), α and the ΔG_{mic}^{0} of TTAB have been measured at various electrolyte concentrations. The results show that the feasibility of the process and spontaneous nature of the micellization increased by increasing electrolyte concentrations.

Keywords: Surfactant, Conductivity, Critical micelle concentration, Binding.

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In-situ Fabrication of Fe-Doped Metal Organic Frameworks/MWCNT Nanocomposite: Electrode Materials for Supercapacitor with Excellent Specific Capacitance and Operational Stability

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Background: Metal organic frameworks (MOFs) are particularly attractive as a promising alternative in the field of energy storage and conversion. In an early report, Domenéch *et al.* showed that Cu MOF and Zn MOF underwent well-defined reduction processes depending on the type of electrolyte [1]. Díaz *et al.* synthesized Co doped MOF-5 and evaluated their electrochemical performance [2]. In this work, a simple and effective precursor conversion method is explored to synthesize Fe-doped MOF/MWCNT nanocomposite for supercapacitors.

Methods: MWCNTs were dispersed in DMF and sonicated. Subsequently, chlorobenzene was added to well dispersed MWCNT/DMF solution and was kept under constant stirring. Then, $Zn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and 1,4-bezenedicarboxylic acid were dissolved in this solution. Further, triethylamine and hydrogen peroxide were added. Subsequently, Ni foam was put in above solution. Finally, Ni foam was washed with DMF and stored in chloroform.

Results: Fe-doped MOF was synthesized by partial substitution of Zn ions with Fe ions during the synthesis process. To synthesize composites of MWCNTs with Fe-doped MOF, MWCNTs were added during the synthesis of Fe-doped MOF. The fabricated supercapacitors showed specific capacitance of 442 F g^{-1}, 871 F g^{-1} and 1925 F g^{-1} (at the current density of 1 A g^{-1}) for MOF, Fe-doped MOF and Fe-doped MOF/MWCNT nanocomposite, respectively.

Conclusion: The fabricated supercapacitors showed specific capacitance of 442 F g^{-1}, 871 F g^{-1} and 1925 F g^{-1} (at the current density of 1 A g^{-1}) for MOF, Fe-doped MOF and Fe-doped MOF/MWCNT nanocomposite, respectively. Simultaneously, the capacitance retention is maintained as high as 92.3%, even after 3000 cycles. These results suggest that the Fe-doped MOF/MWCNT nanocomposite could potentially be applied for supercapacitor.

Keywords: Metal-organic frameworks; Supercapacitor; Fe-doped MOF/MWCNT nanocomposite; capacitance

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Corrosion resistance of Ni—Cu—P with the addition of nano SiC particles

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Background: Since the invention of electroless plating technology in 1946 by A. Brenner and G. Riddell, electroless metal coatings have been used in many fields due to their unique properties. [1].The mechanical and tribological properties of metal coatings can be improved by the incorporation of different solid particles which are categorised as hard such as: SiC, Al_2O_3, Si_3N_4, TiO_2, ZrO_2, B_4C, WC and diamond to enhance the hardness and/or wear resistance of the deposits, or can be dry lubricants such as: graphite (Cg) MoS_2 and PTFE to impart lubricity and reduce the coefficient of friction [2]. SiC is a useful electronic material, which is a high strength ceramic with excellent corrosion and erosion resistance [3].

Methods: In this paper, the tribological behavior and properties of Ni–P, Ni–P–Cu and Ni–P–Cu–nano Sic particles have been investigated. First, the temperature and pH optimal were determined for composite baths Ni–P and Ni–P–Cu composites, and then, by adding various concentrations of nano sic particles, we identified the most favorable mode of composite. Then, at the laboratory temperature, the corrosion resistance was investigated in 3.5% NaCl solution by potentiodynamic polarization technique then the experimental data were compared. The surface morphology of the coatings that were analyzed using scanning electron microscopy (SEM) showed that SiC particles were uniformly distributed by virtue of surfactant addition and mechanical stirring [2].

Results: It has been found that the shift in the corrosion potential (Ecorr) towards the noble direction, decrease in the corrosion current density (Icorr), increase in the charge transfer resistance (Rct) indicated an improvement in corrosion resistance with the incorporation of SiC particles in the Ni–Cu–P composite.

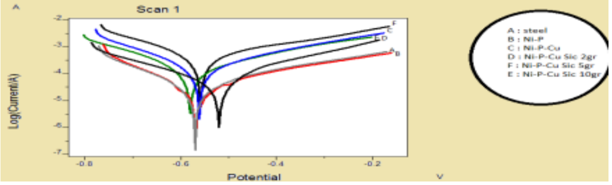

Fig. Potentiodynamic polarization curves of electroless various composite coating in 3.5% NaCl solution

Conclusion: Also the results indicate that in the composite coating of Ni–P–Cu containing 2% by weight of Sic nanoparticles, the properties of coatings such as corrosion and and so on were improved in comparison to other composite coatings.

Keywords: Electroless Ni–P–Cu, SiC particles, Potentiodynamic polarization, Corrosion

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Voltammetric Determination of Theophylline using Carbon Paste Electrode modified with rGO and rGO/NiO Nanocomposite

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Background: Theophylline (TP), is a methylxanthine drug used in therapy for respiratory, asthma and other airway diseases. The safe and effective use of TP relies on careful dosage adjustments based on accurate measurements of concentration in the blood serum. Many methods have been employed for measuring TP. Most often, the procedures involve some extraction, intensive solvent-usage, expensive and are time-consuming. Electrochemical methods are promising due to simplicity, high sensitivity, relatively short analysis time, low-cost instrumentation [1]. Electrochemical analysis based on modified carbon paste electrode (CPE) has proved to be a sensitive and selective method for the determination of various organic molecules [2]. Graphene has unique electronic and mechanical properties such as high electrical conductivity, high surface area, and chemical stability. Combination of graphene with various metal oxides for modification of CPE has been the subject of numerous investigations to improve electrode performance [3]. In this research, a new CPE modified with reduced graphene oxide (rGO) and rGO/NiO nanocomposite was constructed for determination of TP.

Methods: The CPE was prepared by hand mixing of graphite powder with paraffin oil in a mortar and pestle. The modified CPEs were prepared by mixing carbon paste with rGO and rGO / NiO nanoparticles, respectively. The as-prepared pastes were packed firmly to a piston-driven CPE holder and a copper wire provided the electrical contact. Then, the rGO-CPE and rGO /NiO - CPE were used to investigate the electrochemical behavior of TP by cyclic voltametry at various scan rates. To optimize the electrode component, analytical performance of the modified electrodes was evaluated with respect to the quantity of modifiers in the carbon paste.

Results: The CV showed that the oxidation of TP undergoes a one-electron/one-proton reaction.
The anodic peak current increased linearly with TP concentration ranging from 5 μM to 100 μM. The detection limit was 255 nM based on the signal-to-noise ratio of 3.

Conclusion: Modification of CPE by rGO and rGO/NiO nanocomposite could significantly improve the electrochemical response towards TP. Additionally, rGO/NiO - CPE showed a better electrochemical response compared with rGO-CPE. The modified rGO/NiO - CPE have been successfully applied to the determination of TP in human serum.

Keywords: Carbon paste electrode; Electrochemical sensor ; Theophylline

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Electrochemical Investigations of Ganciclovir at Modified Glassy Carbon Electrode and its Determination in Urine and Pharmaceutical Samples

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Background: Ganciclovir has been approved for the treatment of cytomegalovirus infections in immunocompromised patients, and is available for administration intravenously, orally and intraocularly. Ganciclovir has also been shown to be active against herpes simplex virus in human clinical studies [1, 2].

Method: In this study ZnS nanoparticles were synthesized and applied for modification of glassy carbon electrode (GCE). Then, the modified electrode was successfully applied in ganciclovir drug quantification. Field emission scanning electron microscopy (FE-SEM) and electrochemical impedance spectroscopy (EIS) as powerful tools have been used for measuring surface topography and analyzing electrochemical properties of the modified electrode, respectively.

Results: This modified electrode was applied for investigation of electrochemical behavior Ganciclovir by cyclic voltammetry (CV) and determination of it by differential pulse voltammetry (DPV). The linear concentration range of 0.2-100 μM with a detection limit of 0.05 μM (RSD<5%) was obtained for ganciclovir determination with constructed modified electrode.

Conclusion: Mentioned electrode showed advantage such as high sensitivity, good selectivity and durability. This sensor is suitable for the analysis of the trace amounts of ganciclovir in human urine and drug samples.

Keywords: Ganciclovir; cyclic voltammetry; determination

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Determination of Chlorpromazine by Modified Glassy Carbon Electrode

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Background: Chlorpromazine hydrochloride (CPZ) belong to the phenothiazine neuroleptic group. It is generally used as a therapeutic agent for controlling excitation, agitation and other psychomotor disorders in schizophrenia patients and reduces the manic phase of manic-depressive states. It is used for the treatment of hyperkinetic states and aggression and is sometimes given in other psychiatric conditions for controlling anxiety and stress [1].

Although so far various analytical methods, such as spectrophotometry, high performance liquid chromatography, spectrofluorimetry, electrochemiluminescent and so on have been developed for CPZ determination. Among these methods, the electrochemical techniques based on a chemically modified electrode are usually preferred because of their fast response, low-cost, facility and high sensitivity [2]. Here we report a simple electrochemical deposition of Cr nanoparticles onto the GR sheet modified GCE for the determination of CPZ.

Methods: In this study, the determination of chlorpromazine (CPZ) at a glassy carbon electrode modified with graphene and cobalt nano particle is reported. The cyclic voltammetric and amperometric responses of CPZ using the modified electrodes were compared with those of a glassy carbon electrode. The glassy carbon showed a linear response to CPZ in the concentration range of 5 mM to 50 mM with detection limit of 1.753 mM and the modified glassy carbon showed a linear response to CPZ in the concentration range from 10 to 50 µM with detection limit of 0.135 µM.

Results: The glassy carbon showed a linear response to CPZ in the concentration range of 5 mM to 50 mM with detection limit of 1.753 mM and the modified glassy carbon showed a linear response to CPZ in the concentration range from 10 to 50 µM with detection limit of 0.135 µM.

Conclusion: The modified electrode showed excellent reproducibility, accuracy and stability. The modified electrode reported is a promising candidate for use in the electro-analysis of CPZ.

Keywords: Chlorpromazine; Glassy Carbon; Cyclic Voltammetric; Cobalt Nano particle; Graphene.

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Highly efficient Nickle Hydroxide electrocatalyst for oxygen evolution

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Background: The massive consumption of fossil fuel is creating worldwide interest in searching for renewable energy sources. Currently, hydrogen fuel has been regarded as an immense alternative to fossil fuels that can be obtained through water splitting composed of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) [1]. Due to the sluggish multistep proton-coupled electron-transfer process associated with OER, required water splitting voltage is significantly higher than the thermodynamic value (~1.23 V vs RHE) [2]. Therefore, many efforts have been made to reduce this overpotential by using catalysts. Electrochemical water splitting is a sustainable way of producing hydrogen so electrochemical catalysts are widely attracted scientists attention. Among efficient electrocatalysts, Nickel Oxide [3, 4] and hydroxide [5] catalysts show high catalytic activities, which are, recognized as robust water oxidation catalysts.

Methods: Nickel hydroxide films were deposited on ITO electrode through electrodeposit technique. Then, the electrocatalytic activity of modified electrodes was investigated via linear sweep voltammetry (LSV). Moreover, chronoamperometry was used to test the stability of deposited films. Deposited films were characterized by different methods including XPS, XRD and SEM.

Results: In this approach, a very simple, easy and fast electrodeposition method was used to form Nickel hydroxide film, able to catalyze the water electro-oxidation reaction, was demonstrated. Due to investigation of the electrocatalytic activity of the formed ITO/$Ni(OH)_2$ electrodes, water oxidation was conducted in potassium borate electrolyte (pH 10.0) at 1.1 V. The film exhibits an overpotential of 540 mV at 10 mA cm^{-2} in pH 10.0. The catalytic performance of the material is demonstrated by long-term electrolysis at 1.1 V versus saturated calomel electrode (SCE) with a high and stable current density ~ 4.45 mA for pH 10.0 (for at least 5 h).

Conclusion: In this study, Nickel hydroxide film deposited on ITO electrode showed outstanding catalytic activity for water oxidation. Deposited electrode exhibits favorable catalytic properties for electrocatalytic oxygen evolution at pH = 10. A low overpotential of 540 mV at 10 mA cm^{-2} and the low Tafel slope of 53 mV/decade also indicate the favorable kinetic characteristics for electrocatalytic water oxidation, which were outperforming other studies.

Keywords: Water electro-oxidation; Nickel Hydroxide film; Oxygen evolution

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Corrosion behavior of copper in sulphuric acid solution in the presence of a polyethylene glycol

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Background: Metallic copper has a wide range of industrial applications due to its relatively low cost and superior properties such as excellent thermal conductivity, good malleability and easy machining [1]. The use of inhibitors is one of the most effective methods for combating copper corrosion, especially in aggressive solutions [2,3]. In this study, the inhibitory effect of polyethylene glycol (**PEG 200**) on the copper corrosion process in 0.5 M sulfuric acid has been investigated.

Methods: Cyclic voltammetry, linear polarization and weight loss methods were used in order to follow the inhibitive properties of PEG 200 on the copper corrosion process in H_2SO_4 solutions. Electrochemical measurements were performed using an OrigaStat-OGS500 potentiostat. The experimental set-up consisted of a conventional three-electrode. The potentiostat was connected with a Pt counter, Ag/AgCl reference and a copper working electrode with 0.04 mm^2 surface area.

Results: the obtained results showed that PEG 200 acts as a good corrosion inhibitor, even at the low concentration, with a mean inhibition efficiency of 79%. A polarization technique and electrochemical impedance spectroscopy (EIS) data in different concentrations of PEG 200 indicated that this compound is adsorbed on the copper surface, thus blocks its active sites.

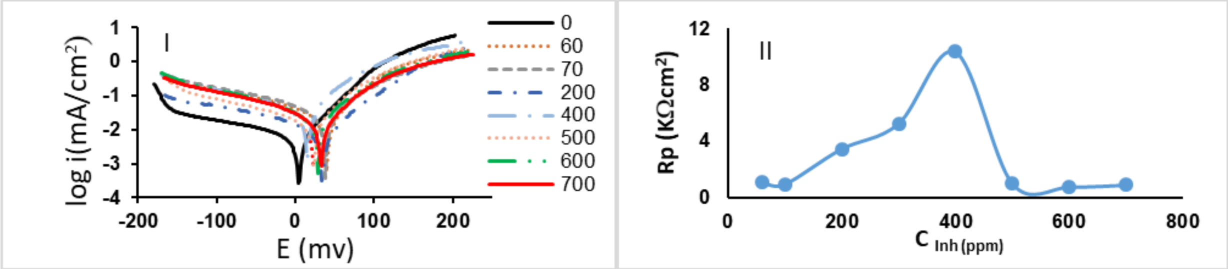

Figure 1 (I): Potentiodynamic polarization curve and (II) Variation of Rp vs. concentration of PEG 200 for copper in 0.5 M H_2SO_4 solution.

Conclusion: PEG 200 shows good inhibitory effect towards copper corrosion in a sulfuric acid solutions. The inhibition effect of PEG 200 is assumed by its adsorption on the copper surface.

Keywords: Copper; Corrosion inhibitor; Poly(ethylene glycol) 200; Weight loss methods

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Voltammetric Determination of Thiosalicylic Acid Using Deep Eutectic Solvent and MWCNTs Modified Carbon Paste Electrode

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Background: Thiosalicylic acid (TSA) chemically identified as 2-sulfanyl benzoic acid is an organsulfur compound. TSA and its derivatives utilized in a number of ways. In metal determination, corrosion study, nanoparticles production used as reagent, used in hair treatment for its growth, as modifiers in fabrication of sensors, as bacteriostatic mediator in some vaccines preparation [1]. Therefore, many analytical methods have been developed to determine of thiosalicylic concentrations. On the other hand, new trends in analytical chemistry encourage the development of smart techniques and methods aligned with green chemistry for the determination of drugs in pharmaceutical products [2]. In this work, deep eutectic solvent/multiwall carbon nanotubes modified carbon paste electrode was developed for the electrocatalytic determination of TSA in aqueous solution.

Methods: A new electrode was modified using multiwall carbon nanotubes (MWCNTs) and the deep eutectic solvent prepared using glucose, choline chloride and water. This electrode was fabricated thorough hand mixing this nanocomposite, graphite powder and paraffin as the pasting liquid, in a mortar and pestle for 15 min until a uniformly wetted paste was obtained. This mixture was packed into the end of a glass tube with a 3 mm inner diameter. The electrical connection was implemented by a copper wire lead fitted into the glass tube.

Results: A comparison of the differential pulse voltammograms of TSA at the surface of this new electrode made of MWCNTs and deep eutectic solvent and the bare carbon paste electrode demonstrated that the electrooxidation of TSA can be catalyzed by the modified electrode. Also, the differential pulse voltammetric determinations showed that under the optimal experimental pH, the MWCNTs and the deep eutectic solvent amounts, the obtained anodic peak currents were linearly proportional to TSA concentration.

Conclusion: A simple and sensitive electrochemical method for TSA determination based on deep eutectic electrolyte combined with MWCNTs was developed. The proposed method exhibited a good performance in terms of sensitivity, detection limit and repeatability. Thus, the approach was successfully applied for the determination of TSA in complex plant matrices.

Keywords: Eutectic deep solvent; Carbon paste electrode; Thiosalicylic acid; Differential pulse voltammetry

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Electrochemical analysis of Tyramine by $Ce_2(MoO_4)_3$ nanostructures modified electrodes

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Background: Tyramine (TA) is a well-known biogenic amine and usually found in fermented food, meet, cheese, eggs, beer and seafood. High concentration analysis of TA inside food samples is essential due to toxic effects and disease. Recent years, developed electroanalytical techniques using various types of chemically modified electrodes have proved to be excellent alternatives for sophisticated instrumental techniques to detect electroactive compounds. Metallic nanostructures due to facile synthesis and probability of size control are one of the best candidates for modifying electrochemical sensors. Among different groups of metallic nanostructures, cerium molybdate was introduced as an effective and sensitive modifier in this study [1, 2].

Methods: Modified carbon paste electrode was prepared based on synthesized cerium molybdate nanostructures. Britton Robinson buffer 0.1M (pH 6) was chosen as the supporting electrolyte. TA behavior was studied using cyclic voltammetry and electrode responses were obtained by differential pulse voltammetry in optimal conditions (scan rate: 0.1 V/s, Estep: 0.01 V). Different techniques such as X-ray, scanning electron microscopy (SEM), ζ-potential, FT-IR and ESI were applied for characterization of $Ce_2(MoO_4)_3$.

Results: The obtained negatively charged modified electrode showed sensitive current response over a wide dynamic linear range of 0.03-10.0 μM ($r^2 = 0.992$) and 10.0 μM-500.0 μM ($r^2 = 0.998$), with detection limit of 0.008 μM. Results showed proposed electrode could successfully be applied in cheese samples to analyze the TA level with satisfactory results (RSD% 2.9%).

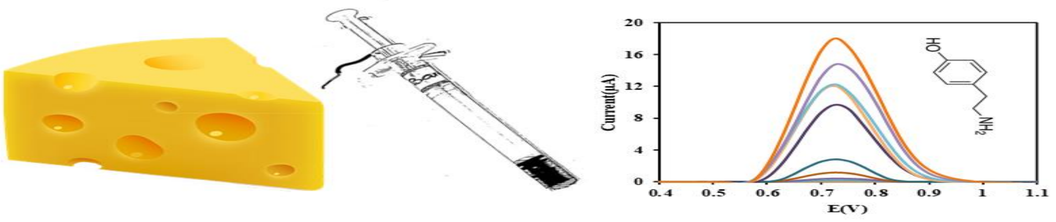

Fig. 1 Differential pulse voltammogram

Conclusion: Repeatability, reproducibility, durability and reusability of the electrode besides its low detection limit and wide dynamic linear ranges are the main advantages of the proposed sensor in comparison with previously reported ones.

Keywords: Tyramine; Electrochemical sensor; Differential pulse voltammetry; Sensors

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Synthesis of the *N*,*N*-Diethyl-1,3-benzothiazole-2-sulfonamide Based on the Electrochemical Oxidation of 2-Mercaptobenzothiazole in the Presence of the Diethylamine

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Background: The organosulfur compounds play a very important role in various fields such as organic synthesis, materials science, agriculture, and medicinal chemistry [1]. Along with this line, recently, oxidative coupling of thiols and N–H compounds has gained a lot of attention because of the eye-catching and promising properties [2].

Methods: The synthesis was carried out in an undivided cell equipped with the carbon and stainless steel as anode and cathode electrodes at the (H_2O: Ethanol; pH 12) mixture. The progress of the reaction was monitored by cyclic voltammetry and thin layer chromotagraphy and the final product precipitated by rotatory system and worked up after 6 h electrolysis. The full characterization of the obtained product by FT-IR, H-NMR, C-NMR, MS, and CHN confirmed.

Results: diagnostic tests have evaluated to obtain better insight into this reaction and interpretation of the appeared diffusion-adsorption pattern that deduced to the proposing of the $E_1C_1E_2C_2$ mechanism. Based on the experimental results and the previous reports [1], a possible reaction pathway was proposed as following: Firstly, dimerization of electrogenerated thiyl radicals, undergoes the electrochemical over-oxidation. Then, the nucleophilic substitution of sulfonothioate by amine would lead to the formation of the desired sulfonamide.

Conclusion: With this in mind, we have developed a mild electrochemical procedure for the synthesis of a sulfonamide compound by employing of the 2-Mercaptobenzothiazole in the presence of the diethylamine, as a metal-free and catalyst-free procedure in room temperature and aqueous solution. The present procedure provides a green and cost-effective method for the synthesis of sulfonamides in high yield with the possibility of extending to the other starting materials.

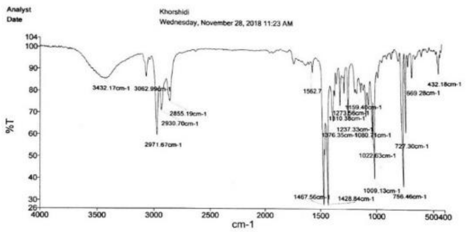

Fig.1.FT-IR spectrum of product.

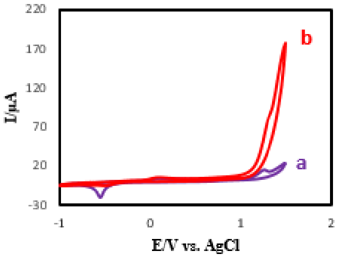

Fig. 2. CVs of 1 mM **MBT** in (Ethanol:H_2O: 20:80: pH=12) at scan rate of 100 mV.s^{-1} onto the GC electrode surface in a) Absent and b) presence of the **diethylamine**.

Keywords: 2-Mercaptobenzothiazole, *N*,*N*-Diethyl-1,3-benzotiazole-2-sulfonamide, synthesis, electrosynthesis

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2- Chemical analysis and industry

Investigation of gallium separation from the Jajarm Bayer process liquor

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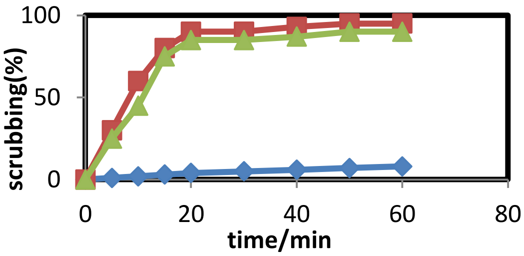
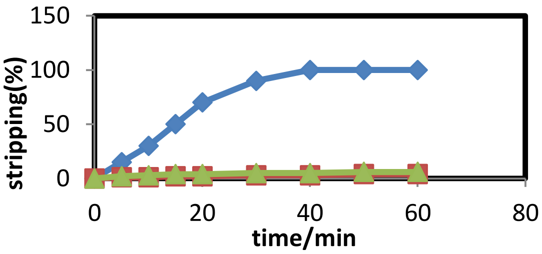
Background: Gallium is an important material used in the electronics industry. In recent years the main way of obtaining gallium is via extraction as a by-product from the Bayer liquor[1]. The composition of the Jajarm Bayer process liquor is containing 164 g/l Na_2O, 86 g/l Al_2O_3 and 146 ppm Ga. Ga in Bayer liquor can be extracted by solvent extraction [2]. In this paper extraction efficiency of Ga is increased by optimizing the parameters affecting the separation.

Methods: The solvent extraction of gallium from a concentrated Jajarm Bayer process liquor was investigated using Kelex100, a 7-(4-Ethyl-1-methyloctyl)-8 hydroxyquinoline as an extractant, ethanol as a modifier and kerosene as a diluent. Back extraction studies of the loaded organic phase were carried out using HCl. Scrubbing step was carried out for removal Al and Na co-extracted into the organic and subsequently stripping of Ga was carried out with diluted acid.

Results: Effect of different parameters such as Kelex100 concentration, mediatore type and percent, diluent type, extraction time and temperature were investigated. Figure 1 represents recovery of Ga (blue line), Al (green line) and Na (red line) in subsequent scrubbing and stripping steps. Under optimal conditions of (Vo :Va = 1.0:1.0) organic to aqueous phase ratio and at room temperature, 83% of gallium was recovered in 96 minutes. The final strip liquor was found to contain 100 ppm of Ga ,along with 8 ppm of Al and 43 ppm Na.





Conclusion: The strip solution can be used to produce Gallium metal of ultra-high purity by electrolysis or pure $GaCl_3$ powder after evaporation. Further removal of impurities from strip solution is under investigation.

Keywords: Gallium ; Kelex 100 ; Bayer Liquor ; Solvent Extraction ; Stripping and Scrubbing

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study of CO adsorption at ambient temperature using Carbon Molecular Sieve

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Background: Carbon molecular sieves (CMS) are carbonaceous materials with a narrow pore size distribution, endowed with a selective adsorption capacity of certain components of a mixture. CMS are commonly prepared from a variety of carbonaceous materials such as cellulosic precursors, coals, carbon fibers, etc. In general, there are two main methods to manufacture microporous CMS; the first one is based on controlled pyrolysis of a carbon precursor and the other one is based on the modification of the existing porous structure by means of carbon vapor deposition technique (CVD) [1-3]. Adsorbent plays a crucial role in the adsorption based gas separation process, it has been found that many porous materials, such as activated carbons, zeolites and metal-organic frameworks (MOFs), have adsorption capacities to a certain extent [4].In this study, CMS was characterized using BET and SEM techniques. Four different mesh of CMS were prepared then measured the adsorption of the samples.

Methods: The adsorption isotherm for adsorbents were measured using a gas adsorption apparatus. A schematic of system was shown in fig1. After loading 2 g adsorbent into a batch reactor, amount of adsorption in different times was measured.

Results: In fig 2.,the adsorption for adsorbent (16-30mesh) was shown in different time.

Fig1. Reactor test system

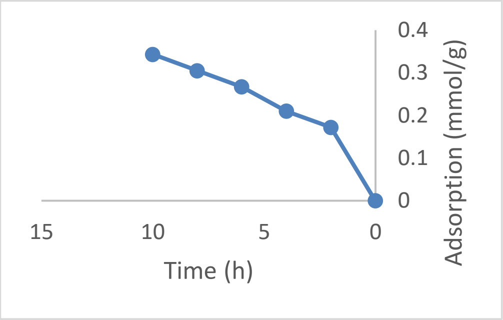

Fig 2. Adsorption in different time

Conclusion: CO adsorption studies on the CMS, at pressure of 2.5 atm and temperature of 30 ^{o}C was done . Maximum adsorption of CO is 0.14 mmolCO/g adsorbent that a high CO adsorption capacity depend on surface area and pore volume of adsorbent.

Kywords : Carbon molecular sieve; Adsorption; CO.

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Investigation of CO_2 at low pressure using Carbon Molecular Sieve

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Background: Carbon molecular sieves (CMS) belong to activated carbons family and can be obtained by various procedures leading to pores narrowing to smaller sizes than 10 Å. Pores narrowing increases diffusion speed for smaller molecules s compared to the larger, resulting in a fast gas separation caused by the differences in molecules sizes [1]. Gas separation by variable pressure adsorption is achieved by the differences between adsorption balances or adsorption speeds of the individual components of a given adsorbent [2,3]. In this study, four different mesh of CMS are prepared. Carbon molecular sievehe was characterized BET and SEM techniques. The samples were tested into reactor.

Methods: The adsorption isotherm for adsorbents were measured using a gas adsorption apparatus. After loading 2 g adsorbent into a batch reactor, amount of adsorption in different times was measured.

Results: Results of BET and adsorption for the adsorbent were shown in table 1 and in fig 1, respectively.

Adsorbent	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
CMS	421	0.234	14.3

Table 1- Surface area, pore volume, and pore size of the CMS

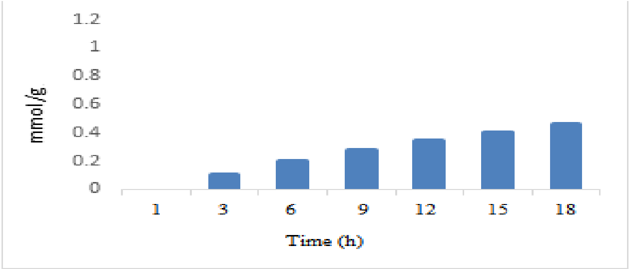

Fig 1. Adsorption in different time for the adsorbent

Conclusion: Adsorption was carried out at ambient temperature and pressure of 2.5 atm. The highest carbon dioxide absorption is 0.71 mmol /g adsorbent that a high CO_2 adsorption capacity depend on surface area , pore volume and pore size of adsorbent.

Kywords : Carbon molecular sieve , Adsorption, Carbon dioxide.

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A novel one step synthesis of tragacanth coated $SiO_2@Fe_3O_4$ magnetic nanoparticles and their use for drug delivery applications

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Bachground: Gum tragacanth is a viscous, odorless, tasteless, water-soluble mixture of polysaccharides obtained from sap that is drained from the root of the plant and dried [1]. In this work a novel method for one step synthesis of magnetic $SiO_2@Fe_3O_4$ nanoparticles coated with

Methods: The core–shell Fe3O4@SiO2 nanocomposites were prepared using a modified method from Stöber et al. [2]. The tragacanth coating was obtained by performing the co-precipitation of Fe^{2+} and Fe^{3+} with ammonium hydroxide and silica in a solution of tragacanth.

Results: The obtained tragacanth coated $SiO_2@Fe_3O_4$ particles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Fourier transform infrared spectroscopy (FT-IR). The nanomagnetic particles were functionalized by ammonium hydroxide. The functionalized nanoparticles were loaded with a drug (metformin) and the drug release was investigated spectrophotometrically at physiological pH (7). The functionalized tragacanth coated displayed good adsorption and in-vitro drug release in phosphate buffer saline (pH 5).

Conclusion: The tragacanth loaded magnetic nanoparticles were succesfuly synthesized and the results indicate that they can be used in separation and drug delivery applications.

Keywords: Tragacanth coated $SiO_2@Fe_3O_4$ nano particles; Magnetic separation; Drug delivery

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Analysis of selenium in aqueous samples: multivariate and chemometrics optimization of dispersive liquid liquid microextraction solidified floating organic drop

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Background: DLLME combined with UV–Vis spectrophotometry was developed for pre-concentration, microextraction and determination of selenium in aqueous samples. different analytical method [1] [2] were used for determination of selenium.

Methods: The experiments were performed using Se (IV) in a vial and DAB solution was added. the pH was adjusted about 2 and was left in bath water for about 6 min to formation of a yellow piazselenol and after 20 min formation complex in room temperature was completed. Then, the solution was neutralized (pH 6.3) with diluted ammonia solution and a mixture of 1-undecanol and ethanol as was rapidly injected into the aqueous sample which caused the formation of a cloudy solution. The mixture was then centrifuged and the organic solvent containing the selenium complex floated on the top of the aqueous solution. The sample vial was transferred into an ice bath. The solidified solvent was transferred into a conical vial where it melted immediately then addition of 50 µL of ethanol and was transferred into the microcell and its absorption was measured at 434 nm against a reagent blank.

Results: In this study, 1-undecanol was selected as main extracting solvent because of low melting point, low water solubility and low vapor pressure and ethanol as dispersive solvent. Optimization of the independent variables was carried out according to chemometric methods in two steps with P.B.D and C.C.D, 100 µL of 1-undecanol (extracting solvent), 212 µL of ethanol (dispersive solvent), pH 6.3, 5 % of salt and 0.0275mol L^{-1} DAB (chelating agent),5.3 min centrifuge,6 min bath water and 10 mL of sample were chosen as the optimum independent variables for microextraction and determination of selenium. Under the optimized conditions, R=0.9980, and linearity range was 60–800 µg mL^{-1}. LOD and LOQ were 13.3 and 40.5 µg mL^{-1}, respectively. The method was applied for analysis of real water samples, such as tap, river.

Conclusion: The method can be used for speciation of selenium in complex matrices such as sea water. It is cost effectiveness, high sensitivity and accuracy, simplicity, reduction in the use of toxic organic solvents, and the use of available and low cost spectrophotometer**.**

Keywords: DLLME; selenium ;solidfied;organic

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Development a new green preconcentration method for quantification of crystalline silica by aerosol sampling filters in occupational environments

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Background: Crystalline free silica is considered as a lung carcinogen and the occupational exposure to its dust is a health hazard to workers employed in industries that involve ores of mineral dust. There is a need for new sensitive methods for in-field of crystalline silica aerosol. The objective of this study was to develop an approach, using supramolecular solvent microextraction to quantify airborne concentrations of crystalline silica (RCS).

***Methods**: for* Monitoring for RCS, sampling the atmosphere was performed where the worker is exposed to the dust by using a portable pump. Samples are then analyzed by a laboratory for their respirable dust concentration and the RCS content.

Results: The variable of interest in the DSLLME method, was optimized with the aid of chemometric approaches. First, in screening experiments, fractional factorial design was used for selecting the variables which significantly affected the extraction procedure. Afterwards, the significant variables were optimized using response surface methodology (RSM) based on central composite design. The calibration curve was linear in the range 0.250 to 1.500 µg, and the intra-assay repeatability and recovery rate were sufficient.

Conclusion: The main benefits of the aerosol into-supramolecular solvent microextraction and solidification of floating drop for determination of RCS in workplaces methodology were low sample consumption, minimum use of toxic organic solvent, short extraction time, rejection of matrix constituent, simplicity and high enrichment factor. Also, in comparison with previous methods, a significant improvement in the LOD and LOQ of colorimetric method of determining respirable crystalline silica can be achieved.

Keywords: airborne dust; air sampling; silica; microextraction; supramolecular

References

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3. Environment and analytical chemistry

nvestigation of the Electrolyte Effect on the Lead Removal from Wastewaters by Using Micellar-Enhanced Ultrafiltration Process

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Background: The discharge of waste stream containing heavy metal ions is a serious problem for many industries because these metal ions are toxic in nature; they are non-biodegradable and cause various health hazards.[1] Between membrane separation processes for removing heavy metal ions, ultrafiltration (UF) process has higher permeate flux and less energy consumption, but the main disadvantage of UF for the treatment of effluents with heavy metals is ionic size of dissolved metallic salts. These ions, would pass easily through the membrane. To overcome these problems, Scamehorn et al. (1986) proposed a surfactant-based UF process.[2]

Methods: In micellar-enhanced ultrafiltration process, the surfactant over its critical micelle concentration (CMC) is added to form micelles in the aqueous stream. Micelles containing solubilized metal ions with sizes bigger than the membrane pore size are rejected by the membrane during the ultrafiltration process.[3] To prepare feed solution, predetermined amounts of surfactant, electrolyte and metal salt were added into ultrapure water and was stirred for 30 minutes. The solution was settled for 10 minutes to allow micelle formation. Then, the solution was fed to membrane module at a flow rate of 0.2 l/min and at the applied pressure of 2 bar. After each experiment, permeate was weighted to calculate permeation flux and the concentration of Lead ions were determined by inductively coupled plasma (ICP).

Results: In this study, the influence of electrolyte addition on permeate flux and Lead removal was investigated. The effect of surfactant concentration and different anions in the presence of electrolyte at different concentrations of lead salts, surfactant and electrolyte was also studied. Results have shown that in the presence of electrolyte, increasing the surfactant concentration leads to flux decline and the permeate flux of lead chloride is lower than lead nitrate.

Conclusion: Lead removal by the MEUF process showed that the addition of electrolyte resulted in improving removal efficiency and decreasing of permeate flux at the same time.

Keywords: Micellar Enhanced Ultrafiltration; Electrolyte; Lead Salts; Surfactant

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Green chemistry analytical method for copper measurement in the Sarcheshmeh mine sulfide concentrate with X-Ray Fluorescence (XRF) spectrometry

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Background: Sarcheshmeh copper complex concentrator unit product is copper Sulfide concentrate. Sampling of this product and measuring its copper content is done routinely by quality control and laboratory units. Copper measurement in Cu-concentrate is carried using classical wet chemical analysis methods [1]. These methods have several disadvantages such time-consuming and producing occupational and environmental pollutions such as acid vapors. For example, in each wet chemical analysis more than 3 liter of NO_x gases enters into the environment. These problems are very important crises in the analytical chemistry and must be overcome by using of new analytical methods. One of the alternative methods proposed for wet chemical analysis is the use of XRF spectrometry green chemistry method [2].

Methods: XRF tube power parameters optimum conditions were obtained in the range of 25-120 for pulse height distribution (PHD) curve with higher height and a narrower width [3]. The calibration curve was plotted in interval (13.38-40.28) %. For validation of this research, 50 samples with known copper grade analyzed by XRF technique. Statistical comparison showed that at 95% confidence level, there is no significant difference and null hypothesis not rejected [4].

Results: By using of XRF method for copper measuring, the analysis time of each sample decreases from about 75 minutes to about 3 minutes. Also, the pollutants and health hazards associated with the wet chemical analysis is omitted. The squared correlation coefficient (R^2) for calibration curve was obtained at 0.9858 (fig.1). The limit of detection (LOD) 0.054 % was calculated based on three times the standard deviation of a sample with five times measurements.

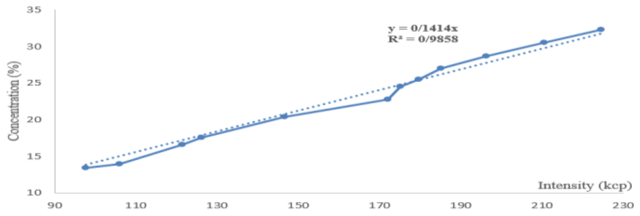

Fig 1.Calibration curve of measuring copper in concentrate samples with XRF

Conclusion: According to this study, the XRF method can be used as an alternative green analytical method for wet chemical analysis in measuring of Cu in sulfide concentrate.

Keywords: green chemistry, XRF spectroscopy, wet chemical analysis, copper sulphide concentrate;

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Synthesis of Silicate Containing Core/Shell Nanoparticles and investigating their catalytic and environmental applications

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Background: Inducing various desirable characteristics into just one synthesized particle seems sometime impossible because of the simple fact that some qualities cannot be accumulated in just one structure. During last three decades many efforts have been devoted to develop materials especially the ones called hybrid nano- and micro-materials that possess two or more features arose from specific materials or precursors. Core-shells are structures that have been devoted to accumulate various materials and characteristics into just one single particle [1-2].

Methods: A synthesis method was developed to produce uniform micro-size spheres of silica coated with MCM-41 mesoporous shell for preparation of SiO_2@MCM-41 core-shell. Lanthanum ion and selenium dioxide, were introduced separately and together into the core-shell structure. The SiO_2@MCM-41, SiO_2@SeO_2-MCM-41, La-SiO_2@MCM-41 and La-SiO_2@SeO_2-MCM-41core-shells were prepared via simple sol-gel method.

Results: It was found that presence of La in the core and SeO_2 in the mesoporous shell, generate very efficient photocatalytic activity of the materials. The prepared photocatalysts were used for degradation of 2,4-dichlorophenol (DCP) as a model compound. The obtained results showed the photocatalytic efficiency was increased in the order of SiO_2@MCM-41 < SiO_2@SeO_2-MCM-41 < La-SiO_2@MCM-41 < La-SiO_2@SeO_2-MCM-41.

Conclusion: Introduction of La^{3+} to the core-shell improved the photocatalytic efficiency which may be assigned to electron-scavenging effect of La^{3+}. Our comprehensive experimental study proved that presence of both SeO_2 and La^{3+} lead to achieve a highly efficient photocatalyst based on SiO_2 core and MCM- 41 shell.

Keywords: Silica; Core-Shell; Photocatalysis; Lanthanum; MCM-41; Selenium dioxide

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Evaluation of Antioxidant Activity and Biosynthesis of Silver Nanoparticles by *Rosa damascene* Aqueous Extract

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Background: Reactive oxygen species (ROS) have been implicated in degenerative diseases such as cancer, inflammation, atherosclerosis and aging as also in food deterioration [1]. A balance between free radicals and antioxidants is necessary for proper physiological function. Many human diseases are caused or negatively affected by free radicals. The natural defence of the human organism against free radicals is not always sufficient mainly due to the significant exposition to free radicals from external sources in the modern world. Many clinical and epidemiological studies show a connection between the antioxidant activity of the substances present in the diet and the prevention from such diseases as cardiovascular diseases or carcinogenesis [1-3]. Fruits, vegetables, grains, teas and some kinds of spices are natural sources of antioxidants. Medicinal plants used in the traditional medicine and healing are one of these sources of antioxidants. In this work antioxidant capacity of *Rosa damascene* aqueous extract has been determined with simple and sensitive electrochemical methods.

Methods: The electrochemical oxidation of leaf extract of *Rosa damascene* aqueous extract has been investigated by cyclic voltammetry and Differential pulse voltammetry (DPV) techniques at biological pH=7.

Results: The results show that *Rosa damascene* aqueous extract oxidize at low potentials in comparison of galic acid, salicilic acid and quercetin as standard antioxidants. The DPPH test (radical scavenging activity) was used for estimating antioxidant effect (Fig.1).

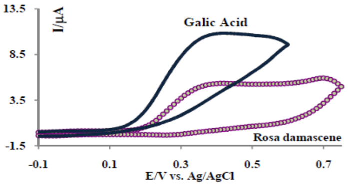

Fig. 1

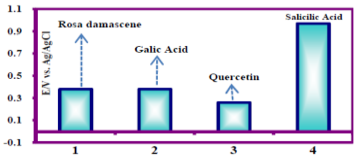

Fig. 1

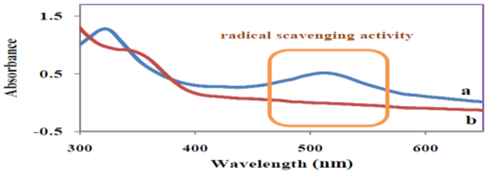

Fig. 2

Biosynthesis of silver nanoparticles has been performed by using *Rosa damascene* aqueous extract. Phenolic compounds in *Rosa damascene* aqueous extract reduces silver ions from silver nitrate to silver nanoparticles. Synthesized nanoparticles were confirmed by UV-Visible absorption spectrum of the reaction mixture (Fig. 2).

Conclusion: We conclude that the *Rosa damascene* aqueous extract has powerful antioxidant activity. Therefore it can be used as a food flavor, natural antioxidant and a preventing agent for many diseases which are caused by free radicals. On the other hand we used of plant extract for making silver nanoparticles that is inexpensive, easily scaled up and environmentally benign.

Keywords: Antioxidant Activity; Silver Nanoparticles; *Rosa damascene*; Free Radicals**.**

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Photocatalytic decolorization of methyl orange in polystyrene waste using TiO_2 as photocatalyst under UV light.

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Background: Azo dyes are dangerous environmental pollutants which unfortunately being used in the textile and plastic material. Their entrance into aquatic ecosystems causes serious problems due to their toxicity and perturbations in aquatic organisms [1]. So far, several methods have been utilized to remove or degrade them from the soil and aqueous environments. However, most of them are ineffective in the treatment of wholly aromatic azo-dyes such as methyl orange in polymer materials. Heterogeneous photocatalytic degradation using TiO_2 as an inexpensive catalyst have been recently introduced. Thus, in this study we proposed to decolorize the methyl orange pigments in polystyrene waste materials to recycle and reuse the regenerated polystyrene.

Methods: to evaluate the efficiency of photocatalytic degradation, methyl orange was dissolved in distilled water at different concentrations. After that the solutions was mixed with different amount of TiO_2 and these mixtures were exposed to UV light under extremely stirring at specific times. The same procedure was used for polystyrene waste having methyl orange.

Results: experiments were done under UV illumination in absence of TiO_2, in the dark with TiO_2 and under UV illumination in the presence of TiO_2. It was found that both UV radiation and TiO_2 are necessary for successful photo-decolorization. Optimal conditions such as methyl orange content, TiO_2 concentration, temperature, irradiation time and pH were determined by comparing the percent degradation of color using the UV-Vis spectrum.

Conclusion: According to the results, no degradation was observed for Methyl Orange in the presence of TiO_2 without UV light and/or under UV irradiation in the absence of TiO_2. The photo-catalytic process was influenced by the initial concentrations of methyl orange, concentration of TiO_2, irradiation time, temperature and pH. Surprisingly, the polymer matrix remained unchanged during the bleaching process.

Keywords: Methyl orange; TiO_2; photo-decoloration; azo dyes; polystyrene waste

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Heavy metals determination in different fish species in Amirkolaye Wetland (Guilan Province)

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Background: The pollution of aquatic ecosystems with heavy metals, have always been a major concern for aquatic organisms and human health.Contaminants such as heavy metals are accumulated along the food chain and them transmitted to human body [1].

Methods:This survey were conduct at summer of 2015 in order to determine the magnitude of heavy metals Cu , Cd, Pb and Zn in muscle tissues of tow fish species *Abramisbrana* and *Esoxlucius* collected from AmirkolayeWetland.The heavy metals were extracted by wet digestion methods (HNO_3/$HCLO_4$) and determined by flame atomic absorption spectrophotometer (FAAS).

Results: The results indicate that the average concentration of heavy metals Cu ,Cd , Pb and Zn in the muscle tissues of *Abramisbrana* were 0.57 ± 0.06,0.08 ± 0.02,0.37 ± 0.08 and 3.34 ± 0.52ppm respectively and in the muscle tissue of *Esox luscious* were 0.94 ± 0.32,0.124 ± 0.07 , 0.65 ± 0.06 and 6.58±0.72ppm respectively.

Conclusion:levels of four heavy metals In *Esoxlucios* compare to *Abramisbrana* were significantly higher but the concentration of heavy metals in both fish species tissues were lower than allowable standards of WHO , UK(MAFF) , NHMRC and FOA.

Keywords: Heavy metal, *Abramisbrana* ,*Esoxlucius* , Amirkolaye Wetland, Atomic absorption

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Adsorption of Heavy Metals onto Modified Silica Aerogels: Modeling and Optimization Using Response Surface Methodology

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Background: Heavy metals such as Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} represent a group of dangerous environmental pollutants that due to their toxic effects on human health [1]. The adsorption process is considered as one of the most promising methods for the removal of toxic metals due to its simplicity, flexibility, and elevated efficiency in industrial applications [2]. Silica aerogels are extremely porous nanostructured materials with high specific surface areas and low density [3].

Methods: The silica aerogels were synthesized and modified with trimethylchlorosilane (TMCS). The adsorbent was characterized with FT-IR, SEM, and BET. The adsorption process of Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} onto modified silica aerogels was optimized and modeled using response surface methodology (RSM). The adsorption isotherm and kinetics were studied.

Results: FT-IR spectrum (Fig. 1a), was approved the successful modification of silica aerogel. The SEM image showed porous structure of the sorbent (Fig. 1b). The surface area and mean pore size were calculated 721.2 m^2/g and 9.2 nm respectively by BET. The best isotherm and kinetics model for adsorption process was Langmuir and pseudo-second order model, respectively. The maximum adsorption capacity of modified silica aerogel for Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} were 268.1, 345.5, 217.1, and186.5 mg/g respectively. The parameters were optimized with RSM (Fig. 1c).

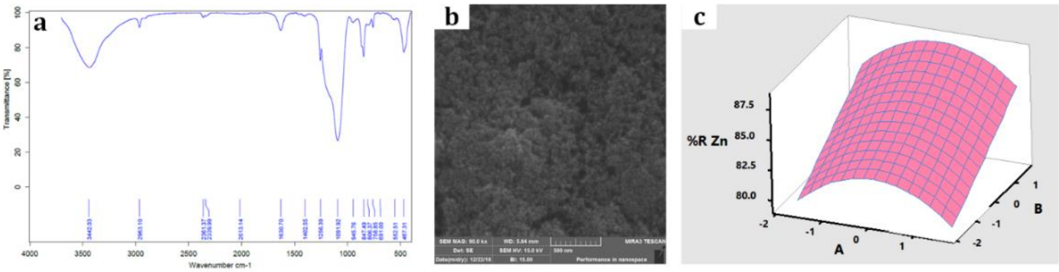

Fig. 1. (a) FT-IR spectrum (b) SEM image of modified silica aerogel.

Conclusion: The high adsorption capacity was obtained due to optimization of parameters and excellent performance of modified silica aerogels for removal of Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}.

Keywords: Modified silica aerogel; Heavy metals; Adsorption; Response surface methodology.

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Synthesis of Fe3O4-Chitosan/MWCNTs Nanocomposite as an adsorbent for removal of food dyes such as sunset yellow on sewage

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Background: Azo paints make up more than 70% of the chemical and artificial colors produced in the world. It is widely used in textile, paper, food, medicine, cosmetics and hygiene industries. Azo compounds are carcinogenic and harmful and are resistant to biological degradation due to its complex structure. The best solution is to remove these compounds from factory wastewaters before entering the environment [1]. In this research, we used nanocomposite chitosan / iron oxide / carbon nanotubes in a few walls to remove sunset yellow from Azo group colors [2].

Methods: Initially, the synthesis of the nanocomposite was carried out by the Hummer method and was used to remove the sunset yellow after synthesis.

Result: In this work, parameters such as PH = 2.5, absorbance value m = .009gr, temperature and time T = 25 and t = 6min were investigated. In optimal conditions and concentration of 10 ppm, removal of 95% of sunset yellow color was observed. In order to investigate the synthesis of the IR spectrum and the XRD pattern.

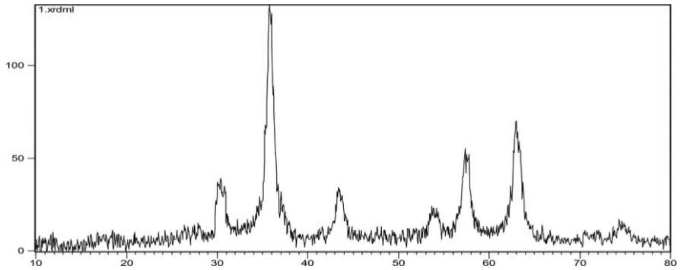

Fig. XRD pattern nanoparticle

Conclusion: In this work, the nanoparticles were synthesized by the Hammer method. The nanoparticle size was reported to be about 14 nm. The XRD spectrum shows the authenticity of synthesis and composite formation.

Keywords: Chitosan, multiwall carbon nanotubes, sunset yellow, iron oxide, azo dyes

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Development of a polymer inclusion membrane based optode for the sensitive determination of Co(II)

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Background: Among the different types of liquid membranes, polymer inclusion membranes (PIMs) have been more considered recently [2]. PIMs are composed of a base polymer which is the skeleton of the membrane and responsible of its mechanical strength, a selective extractant towards the analyte, and often a plasticizer to improve the PIM flexibility. PIMs have been used not only for the extraction-separation aims, they have been also used for the preparation of the chemical sensors [3]. In this work, a PIM composed polyvinyl chloride (PVC) as the base polymer, 1-(2-pyridylazo)-2-naphthol (PAN), as a chromogenic complexing agent, bis-(2-ethylhexyl)phosphoric acid (DEHPA) as an extractant, and tri-*n*-butylphosphate (TBP) has been developed for the fabrication of a cobalt optical chemical sensor.

Methods: A mixture of PVC, TBP, DEHPA and PAN was used for the preparation of the optode. The optimization of the composition of the PIM has been followed by applying the response surface methodology (RSM). The contact time and other parameters including sample solution pH, ionic strength and the temperature were optimized by a univariate sequential optimization procedure.

Results: Fig. 1 shows the visible spectra of the PIM optode contacted with the blank solution and with a solution of 0.5 mg L^{-1} Co(II). The optimal conditions with respect to the sample solution pH, ionic strength, time, and temperature were 6, 0.05 M (Na_2SO_4), 15 min and 27 ºC, respectively. The analytical performances of the developed optode were: the working liner range 0.05-1 mg L^{-1}, limit of detection 0.02 mg L^{-1}, relative standard deviation 4% (n=4, 0.5 mg L^{-1}). The relative recoveries were in the range of 94-110%. The selectivity of the sensor was assessed by the determination of cobalt in the presence of a variety of cations including lead(II), cadmium(II), iron(III), copper(II), nickel(II), magnesium(II) and calcium(II). The proposed sensor was used for the determination of cobalt in some real samples including a tea, a water and a medicine samples. The obtained were comparable to atomic absorption spectrometry method.

Conclusion: A new sensitive polymer inclusion membrane based optode was designed it was successfully was applied for the determination of cobalt(II) in a variety real samples.

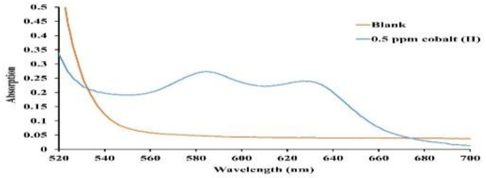

Figure 1. Visible spectra of the optode contacted with a blank and with a 0.5 mg L^{-1} Co(II) solution

keywords: Polymer inclusion membrane; Optode; Cobalt; Determination**.**

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Investigation and Comparison of Removing Cr(VI) from Aqueous Media Using Bacteria and Porous Nano-Adsorbent

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Background: Hexavalent chromium is both toxic and carcinogenic while chromium metal and Cr(III) ions are not considered toxic. Remediation of natural water resources contaminated with Cr(VI) involving a mixed mechanism of adsorption and reduction of Cr(VI) to the less toxic trivalent state, present a clear advantage versus those that only achieve separation of Cr(VI) from aqueous matrices without chemical transformation [1,2].

Methods: Porous nano-adsorbent was synthesized as reported previously [3]. The batch experiments were conducted by adding nano-adsorbent or bacterial culture to Cr(VI) solution.

Results: In order to optimize chromium decomposition percentage in different factors the Response Surface Methodology method was used. In this case, the optimum temperature was 36 ° C and pH 7 and the initial concentration of chromium was 700 ppm. The concentration of Cr(VI) in the sample was determined using calibration curve. The R value for the linear regression was 0.9951 in the range of 2–20 ppm and the limit of detection was 2.5 ppm. The relative standard deviation was 2.45% (n=3). Chromium decomposition was observed 82.53% by bacterium, while chromium removal using nanoparticles was 79.23%.

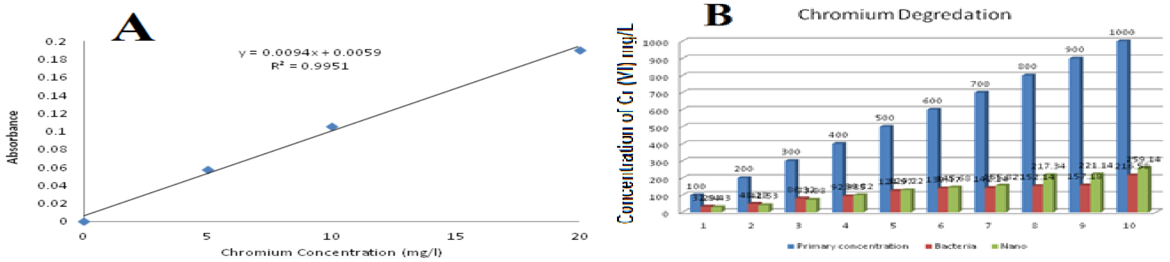

Fig 1. (A) Calibration curve of Cr(VI) in the solution, (B) Comparison of chromium removal by isolated bacterial and nano-adsorbent

Conclusion: According to the results obtained in this work, nano-adsorbent showed a better removal efficiency than that of bacteria for Cr(VI) concentrations more than 700 ppm. Whereas, approximately similar removal efficiency as the lower levels of Cr(VI) concentration.

Keywords: Chromium ions; Biodegradation; Heavy metals; Nano absorbents; Sphingomonas paucimobilis.

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Investigation of quality and quantity characteristicsof municipal house treatment wastewater for evaluation of performance (Case sample: House treatment of eyvan city,Ilam)

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Background: Today, water scarcity in our country, which is considered as an arid and semi-arid climate, is a major problem. In such a situation, reuse of wastewater is one of the ways to save water from the problem of dehydration. Therefore, reuse for agricultural, irrigation, watering and etc. should be one of the main objectives of the sewage treatment project [1]. In general, reuse of wastewater has multiple benefits, such as preserving water resources and reducing environmental pollution, but it is also necessary to address the health hazards of the problem [2].

Method: The sampling (180 sample) from inlet and outlet of the treatment plant under study was conducted during six tandem months. Performance of the wastewater treatment plant was evaluated using determining the indices such as: temperature, coliform, turbidity, remaining chlorine, cations including(Na^+,Ca^{2+},Mg^{2+}), anions(F^-,Cl^-,NO_2^-,NO_3^-,Br^-,PO_4^{3-},SO_4^2), Heavy metals (Zn, Ni, Cr, Cu, Pb, Cd and Co), pH, COD, BOD_5, TSS, TDS, DO and Egg parasites. All the experiments were conducted according to the standard method for the examination of water and wastewater reference and the results were analyzed by excel and SPSS softwares.

Results: The results of this study indicate that the measured values of operational parameters such as:Na^+,Ca^{2+},Mg^{2+},F^-,Cl^-, NO_2^-,NO_3^-,Br^-,PO_4^{3-},SO_4^{2-}, heavy metals (Zn, Ni, Cr, Cu,Pb,Co and Cd), pH, COD, BOD_5, TSS, TDS,DO ,T,turbidity, remaining chlorine, total coliform and Egg parasites , With an average of: 150.3, 79.56, 88.49, 0.16, 48.79, 2.16, 18.12, 0. 081, 0. 95, 73.49, (0 . 152, ≤0.015, ≤0. 015, 0. 016, ≤0. 015, ≤.0.015, and ≤0. 015), 7.76, 13.1, 9.12, 8.51, 412.39, 4.21, 16.76, 1.92, 0. 73, 3, 0. Some of the standards of the environmental organization are: (PH: 6.5-8.5, BOD_5: 30, COD: 60, TSS: 40, DO: 2, NO_2^-:10, NO_3^-: 50, PO_4^{3-}: 6, total coliform: 1000, Egg parasites: 0 and etc).

Conclusion: The chlorine parameter corresponds to an average 0.73 mgL^{-1} in accordance with the environmental organization standards for surface water discharge, but does not meet the requirements for irrigation and agricultural use for wastewater use. Also, theDO parameter with an average 4.21 mgL^{-1} is not consistent with the environmental standards of Iran's environment for reuse in agriculture and irrigation, as well as discharges to surface waters. But other parameters correspond to the standards of the Environmental Protection Agency. Finally, the performance of the city's water purifier is appropriate.

Keywords: Sewage; Eyvan wastewater; Indicators of pollution; Wastewater; Environmental standar

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photocatalytic decolorization of aqueous methylene blue solution by nanostructure magnetite (Fe_3O_4)

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Background: In this study magnetite (Fe_3O_4) nanoparticles were synthesized and were characterized by several analyses. Many methods have been applied for the treatment of dyes wastewater. Photocatalytic reaction has been suggested to be effective to decompose wastewater. The photocatalytic activity of Fe_3O_4 was evaluated by the photodegradation of aqueous methylene blue as a model of pollutant under visible light irradiation [1].

Methods: The Fe_3O_4 nanoparticles were synthesized using the method which is described in Fan et al. work [2]. The stoichiometric amounts of $FeSO_4$, $FeCl_3$ were used as precursors and NaOH as the mineralizer agent. The photocatalytic reaction of aqueous methylene blue solution (10 ppm& pH=9) by Fe_3O_4 as photcatalyst (0.5 g/L) was carried out in a 75 mL beaker under magnetic stirring and irradiation of three 40 W lamps as a visible-light source.

Result:

XRD pattern of samples Fe_3O_4 nanoparticles is shown in Fig. 1. The sample match with the cubic spinel structure of Fe_3O_4 (JCPD card no. 88-0866) with no extra peak observed. The degradation percent of MB shown in Fig. 2.

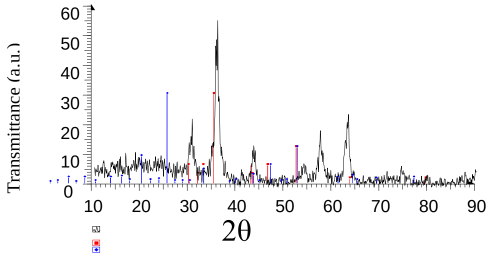

Fig.1. X-ray diffraction pattern of Fe_3O_4

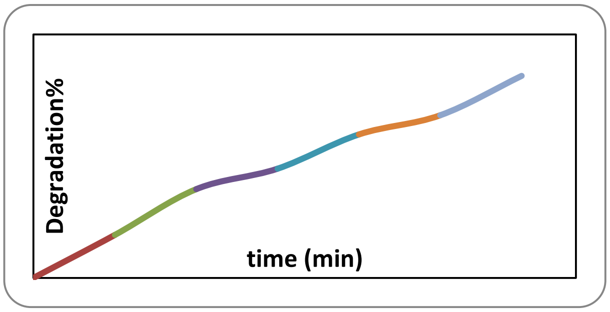

Fig.2. Degradation percent of methylene blue in the presence of Fe_3O_4

Conclusion: This research introduced a method for synthesis of visible light photocatalytic material, namely Fe_3O_4, by hydrothermal method. The photodegradation efficiency for decolorizing methylene blue solution (10 ppm) by magnetite (0.5 g/L) after 360 min illumination was about 83%.

Keywords: Magnetite (Fe_3O_4), Nanostructure, Decolorization, Photocatalysis.

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photocatalytic decolorization of methylene blue solution by nanostructure of sponge magnetite (S-Fe_3O_4)

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Background: In this study sponge magnetite (S-Fe_3O_4) nanoparticles were synthesized and characterized by several analyses. Many methods have been applied for the treatment of dyes wastewater. Photocatalytic oxidation has been suggested to be effective to decompose wastewater. The photocatalytic activity of S-Fe_3O_4 was evaluated by the photodegradation of methylene blue solution under visible light irradiation [1].

Methods: The S-Fe_3O_4 nanoparticles were synthesized using the method which is described in Nian et al. work [2]. The photocatalytic reaction of aqueous methylene blue solution (10 ppm& pH=9) by S-Fe_3O_4 as photcatalyst (0.5 g/L) was carried out in a 50 mL beaker under magnetic stirring and irradiation of three 40 W lamps as a visible-light source.

Result: XRD pattern of samples S-Fe_3O_4 nanoparticles is shown in Fig. 1. The sample match with the standard structure JCPDS cards Fe_3O_4 with no extra peaks. The degradation percent of MB shown in Fig. 2.

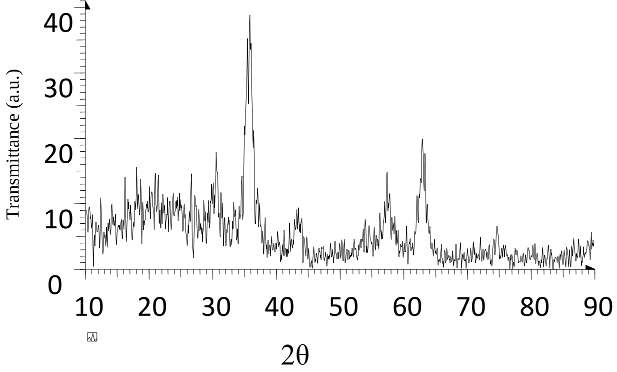

Fig.1. X-ray diffraction pattern of C@Fe_3O_4

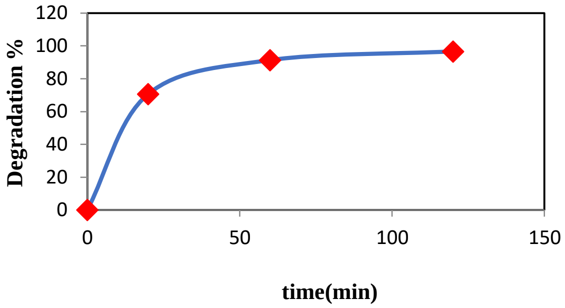

Fig.2. Degradation percent of methylene blue in the presence of C@Fe_3O_4

Conclusion: This research introduced a method for synthesis of visible light photocatalytic material, to prepare sponge magnetite (S-Fe_3O_4) by hydrothermal method. The photodegradation efficiency for decolorizing methylene blue solution (10 ppm) by S-Fe_3O_4 (0.5 g/L) after 120 min illumination was about 97%.

Keywords: sponge Magnetite (S-Fe_3O_4), Nanostructure, Decolorization, Photocatalysis.

Refrences:

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[2] Q. Nian et al., *Journal of Alloys and Compounds*, **2010**, 492, 291–294.

Hydrothermal synthesis and adsorbtion property of perovskite type $LaCoO_3$

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Background: metal oxide have the general formula ABO_3 in which cation B is replaced by transitional elements such as (Fe , Ni , Ti , Mn , Co) and A by rare earth elements, alkaline earth metals and alkaline metals such as (La , Ca , Na). This metal oxides have a very interesting physical and chemical properties. In the present project, nanostructure lanthanum cobaltate ($LaCoO_3$) is produced via hydrothermal method. The adsorption ability of $LaCoO_3$ was evaluated by the removal of aqueous methyl orange (MO) solution as a model of pollutant.

Methods: For synthesis of $LaCoO_3$ nanoparticles, about 0.903 g $La(NO_3)_3.6H_2O$ and 0.592 g of $Co(NO_3)_2.6H_2O$ were dissolved in 100 ml distilled water and hydrothermally treated [1]. The adsorption of aqueous MO solution (25 ppm & pH 2) by $LaCoO_3$ as adsorbent (0.3 g/L) was carried out in a 50 mL beaker under magnetic stirring.

Results: XRD pattern of $LaCoO_3$ nanoparticles is shown in Fig. 1. The sample match with the standard JCPD card number with no extra peak observed. The removal percent of MO is shown in Fig. 2. Since the maximum removal of MO is at pH 2, probably the electrostatic attraction between the dye molecules and $LaCoMnO_3$ surface might be the predominant mechanism [2].

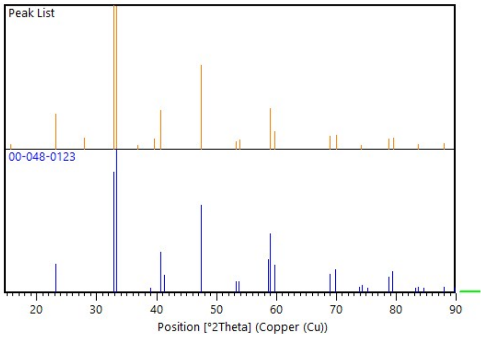

Fig.1.X-ray diffraction pattern of $LaCoO_3$

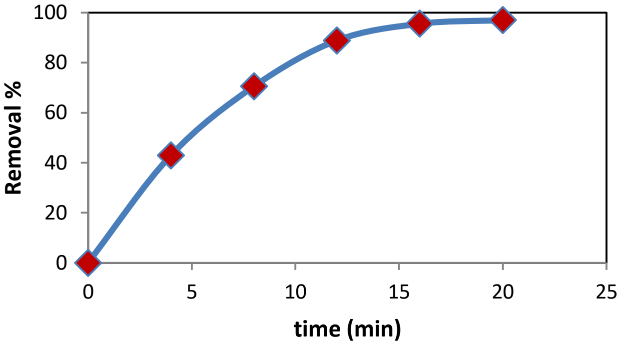

Fig.2. Removal percent of methyl orange in the presence of $LaCoO_3$

Conclusion: This research introduced a method for synthesis of lanthanum cobaltite ($LaCoO_3$), by hydrothermal method. The removal efficiency for decolorizing methyl orange solution (25 ppm) by $LaCoO_3$ (0.3 g/L) after 20 min was about 97%.

Keywords: Lanthanum cobaltate ($LaCoO_3$), Nanostructure, Decolorization, Adsorption

References

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The fast removal of Cd^{2+} from water by hydrothermally synthesized $LaCoO_3$

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Background: The metal oxide have the general formula ABO_3 in which cation B is replaced by transitional elements and A by rare earth elements, alkaline and alkaline earth metals have a very interesting physical and chemical properties. In the present work, nanostructure lanthanum cobaltate ($LaCoO_3$) produced by hydrothermal method. The removal performance of $LaCoO_3$ was evaluated by the removal of cadmium cation (Cd^{2+}) solution as a model of pollutant [1].

Methods:The $LaCoO_3$ nanoparticles were synthesized using the method which is described in Shasha Fu et al. work [2]. 0.903 g $La(NO_3)_3$and 0.592 g of $Co(NO_3)_2$ were dissolved in 100 ml distilled water and hydrothermally treated. The adsorption of Cd^{2+} solution (2.5 ppm& pH=7) by $LaCoO_3$ (0.35 g/L) was carried out in a 50 mL beaker under magnetic stirring.

Results: XRD pattern of samples $LaCoO_3$nanoparticlesis shown in Fig. 1. The sample match with the standard JCPD card number with no extra peak observed. The removal percent of Cd^{2+} with respect to time is shown in Fig. 2.

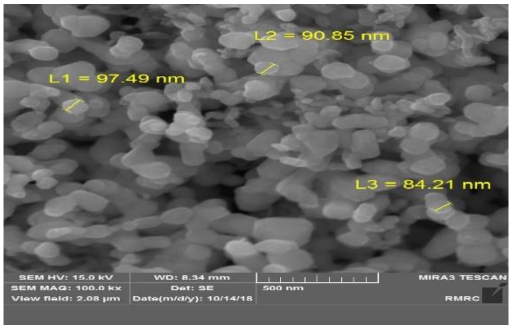

Fig.1.FESEM image of $LaCoO_3$ nanopaticles

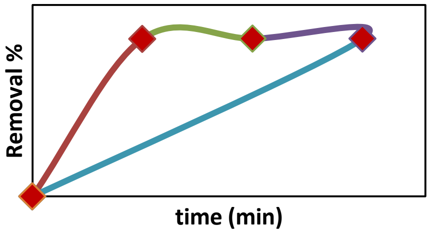

Fig.2. Removal percent of cd^{2+} in the presence of $LaCoO_3$

Conclusion: This research introduced a method for synthesis of lanthanum cobaltite ($LaCoO_3$), by hydrothermal method. The removal efficiency for cd^{2+}removal solution (2.5 ppm) by $LaCoO_3$ (0.3 g/L) after 20 min was about 100%.

Keywords: Lanthanum cobaltate ($LaCoO_3$), Nanostructure, heavy metal ion, Adsorption

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Flow injection analysis-spectrophotometric determination of imidacloprid using grapheme quantum dots

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Background: Pesticides have been dramatically used in agriculture during the recent decades. Leakage of the chemicals to the environment causes pollution of soil, crops, water and bodies of the creatures. Imidacloprid acts as an agonist of acetylcholine, which can suppress the acetylcholinesterase transmission by binding to the post synaptic nicotinic receptors in the central nervous system of insects [1].

Methods: In this work, grapheme quantum dots (GQDs) were prepared using a thermal treatment when citric acid was used as a precursor. GQDs were characterized by TEM, SEM, FT-IR and Raman spectroscopy. Under UV photolysis condition in basic solutions, imidacloprid is decomposed on-line in a flow system through a teflon tubing to produce nitrite. The nitrite content then is reacted in acidic condition with diaminodiphenyl sulfone (dapsone) to form a diazonium cation. After that, the diazonium cation is coupled with GQDs to form an intense yellow colored product. The colored product is detected by colorimetry to estimate concentration of imidacloprid in appropriate samples.

Results: One at a time and central composite design (CCD) optimization methods were applied for the optimization of chemical parameters (hydrochloric acid, dapsone and GQDs). The condition selected by CCD showed more meaningful better sensitivity than one at a time method. Under optimum conditions, calibration curve for imidacloprid was linear in the concentration range of 0.05-8.0 µg mL^{-1}. Also, limit of detection was obtained 0.003 µg mL^{-1}. The relative standard deviations for imidacloprid was found to be 0.4 and 0.2% for 0.50 and 7.0 µg mL^{-1}, respectively. Moreover, this method was applied to the analysis of imidacloprid in real water samples such as lake water and commercial samples of the pesticide.

Conclusion: A rapid, selective, reproducible, accurate and economic imidacloprid determination method was developed using a new laboratory made azo-coupling reagent (GQDs) when a flow injection based method was applied.

Keywords: Imidacloprid; Graphene quantum dots; Photolysis; Determination

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Degradation of ampicillin by magnetite core (Fe_3O_4) metal framework shell (MIL-53 MOF)

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Background: Ampicillin contamination in water sources has been increasingly alarming due to its environmental pollution; however the strategies for ampicillin-containing water treatment are still an enormous challenge [1]. Metal-organic frameworks (MOFs) are a kind of porous material constituted by metal or metal clusters bounded to organic ligands. In recent years, MOFs are being investigated widely as promising materials due to large specific surface areas, tunable pore size and easy functionalization that offer unprecedented potential for MOFs to play an important role in conventional industry catalysis [2]. The combination of magnetism to the usual routes of catalyst design has always been an important method for the preparation and the study of the performance of the catalysts. With the use of additional external magnet, superparamagnetism catalysts in the solid–liquid phase reaction can be easily separated from the liquid system and avoids the loss of the catalysts.

Methods: In this work, Fe_3O_4@SiO_2@MIL-53 (Al) catalyst was synthesized by encapsulating of MIL-53(Al) on the surface of magnetic Fe_3O_4@SiO_2 particles in room temperature. At first the magnetic Fe_3O_4 nanoparticles were synthesized in room temperature. Then Fe_3O_4 nanoparticles were coated by SiO_2 shell for protecting from solvent effect. The hydrolysis of tetraethoxysilane (TEOS) was used for preparation of SiO_2. Subsequently Fe_3O_4@SiO_2 particles were dispersed into the mixture solution of MIL-53 [3].

Result: The structure and properties of the catalysts were characterized by XRD, TEM, SEM, FT-IR, N_2 adsorption/desorption and VSM measurement techniques. The catalytic activity, magnetic recycling and reusability of the catalysts for the photo degradation of one drug such as ampicillin were evaluated. The SEM image and XRD patterns of sample indicated presence of Fe_3O_4, SiO_2 and MIL-53 MOF in new catalyst.

Conclusion: In this study, degradation of 100 ppm ampicillin solution (penicillin group) was investigated using Fe_3O_4@SiO_2@MIL-53 (Al) composite. Investigation of UV-Vis spectra shows conversion of ampicillin to other species.

Keywords: Magnetic; Room temperature synthesis; Metal - organic framework; Ampicillin

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Removal and preconcentration of bortezomib drug from aqueous samples using magnetic multiwall carbon nanotubes

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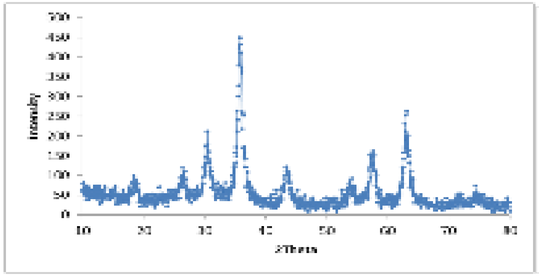
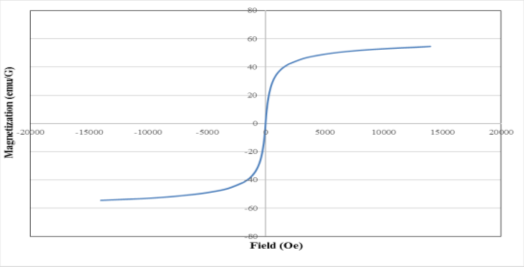
Background: The removal of toxic components in wastewater prior to its disposal is crucial [1]. Various adsorbents have been developed for the removal of organic pollutants (e.g., dyes, pesticides, pharmaceuticals/drugs, and phenols) from [2]. Carbon nanotubes (CNTs), which were discovered by Iijima in 1991 [3], are one of the most widely studied carbon nanomaterials and can serve as excellent adsorbents [4] because of their hollow and layered structure and large specific surface area, which is why CNTs are the most commonly used nano-materials for adsorbing toxic material [5].

Methods: For this purpose, the synthesis of Fe_3O_4 magnetic nanoparticles was carried out using a chemical coagulation method. The structure, magnetic properties and nano-absorbent morphology of FT-IR, VSM, and XRD tools were investigated.

Results: The results showed good synthetic nano-absorbent performance. The effect of factors such as pH, ionic strength, adsorbent amount and contact time on bortezomib adsorption using the Taguchi experimental design was investigated. Optimum adsorption was achieved at a pH 5 and equilibrium was established within 45 min of the process. the Approved kinetic model (second-order R^2: 0.917) and isotherm models (Langmuir R^2: 0.9596 and Temkin R^2: 0.917).





Conclusion: Finally, the process of removing Bortezomib from water samples using a synthesized nano-adsorbent was investigated and the results were satisfactory.

Keywords: Bortezomib; Carbon nano tube; magnetite nanoparticle

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Fabrication of Ag_3PO_4/zeolite composite as photocatalytic degradation of organic dyes

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Background: The presence of organic contaminants in wastewater has been an important problem in many countries since the industry is widely developed. The treatment of highly colored wastewater containing hazardous industrial chemical effluents is one of the growing needs of the present time. One of the best ways to reduce contamination of water is by photocatalytic degradation of organic compounds [1,2].

Methods: In this work, composite of Ag_3PO_4 and ZSM-5 zeolite (APZ) at difference mass rate were synthesized by self-assembly between of component as a nanocatalyst. An APZ were well characterized with the aid of various techniques to study their morphological, physical, and optical properties. The APZ composites were characterized by X–ray diffraction (XRD), Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX), and N_2 adsorption–desorption technique.

Results: As synthesized hybrids was exhibited strong photocatalytic activity for decomposition of Congo red dye (CR). The obtained results revealed that the APZ had strong photodegeration in the visible light region. The kinetics of photodegradation of CR onto APZ composite follow first-order kinetic model. Effect of initial pH of the dye solution on the photocatalytic activity of APZ was studied. Additionally, photodegradation ability and mechanism of the photodegradation of CR by APZ composite were investigation. After five recycles, APZ nanohybrids did not exhibit any significant loss of photocatalytic activity, confirming the photocatalyst was essentially stable.

Conclusion: Here APZ showed good photocatalytic activity by degradation of 99.97% after irradiated for 30 min in the absence of H_2O_2. Thus, this APZ nanocomposite, which has low cost, and green material, might be promising nanostructure for fast removal of high concentration level of organic dyes pollutants from aqueous solutions.

Keywords: Photocatalytic; Zeolite; Silver; Organic dyes; Congo red.

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Magnetic nanofluid based liquid phase microextraction coupled with ETAAS for separation/preconcentration of nickel from water samples

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Background: One of the most considerable environmental pollution in recent years is heavy metals pollution which leads to the pollution of food, soil, and water sources. Nickle enhances the iron absorption of the body and also prevents anemia and osteoporosis. Carcinogenesis, severe allergy, respiratory problems are some health effects of nickel [1]. The mixture of magnetic carbon nanotubes (MCNTs) and deep eutectic solvent (DES) called as "magnetic nanofluid" was used as a new generation of the extraction phase [2]. Magnetic nanofluid based liquid-phase microextraction was applied for separation/preconcentration of nickel.

Methods: To a sample solution containing 10 mL of 100 ng L^{-1} nickel, 20 µL of DES-MNF was added. The mixture was ultrasonicated. Then, the DES-MNF was separated from the solution using an external magnet. The upper phase was taken away. In the back extraction step, 40 µL nitric acid (1 mol L^{-1}) was added to the metal ions-enriched DES-MNF and sonicated for 10 s. the DES-MNF was easily separated by the magnet and 10 µL of the supernatant solution containing metal ions was injected to ETAAS to determine nickel amounts.

Results: In this study the green efficient method of magnetic nanofluid based liquid phase microextraction was applied for separation/preconcentration of nickel and determination ETAAS. The extraction solvent is novel magnetic nanofluid consists of DES based MCNTs which can easily be separated from the media with no need to centrifugation. The influential parameters including the amount of magnetic nanofluid, type and volume of back extraction solvent, ionic strength, and sample volume were studied. The detection limit of 4.5 ng L^{-1}, preconcentration factor of 500, and RSD % of 3.1% were acquired. The potential of the method was considered in water samples which showed high capability of the proposed method for application in the complex matrixes.

Conclusion: In this research study, deep eutectic solvent based magnetic nanofluid based liquid phase microextraction was introduced for extraction of nickel from water samples. Short extraction time, no need to centrifugation, application of green solvent, facile extraction procedure, high enrichment factor, low detection limit are the advantages of the proposed method.

Keywords: Magnetic nanofluid, liquid phase microextraction, nickel, Electrothermal atomic absorption spectrometry

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A new dendrimer-functionalized magnetic nanosorbent for the efficient adsorption and subsequent trace measurement of Hg (II) ions in wastewater samples

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Background: Water contamination originating from the release of heavy metal ions has become a great environmental challenge threatening the life of all living things including human beings [1, 2]. Amongst the heavy metals, the adsorption and measurement of Hg (II) have gained lots of attention. Therefore, the presentation of a reliable and practical method leading up to the accurate determination of Hg (II) from highly complicated matrices such as wastewater samples is of high importance in environmental analysis [3].

Methods: Following the synthesis of a new dendrimer-functionalized magnetic nanosorbent via Michael addition and amidation, the efficient adsorption and subsequent trace measurement of Hg (II) ions in several complicated matrices such as wastewater samples was accomplished using CV-AAS instrument. It should be noted that the characterization of as-prepared nanosorbent was successfully made by several analytical techniques such as XRD, FTIR and SEM.

Results: The calibration plot was linear over the range of 0.25–60 $\mu g\ L^{-1}$ while, the accuracy fell within the range of 88 to 113% in wastewater sample analysis with the corresponding precision range of 3.9-8.2%.

Conclusion: The dendrimer-based nanosorbent was fabricated with some donor functional groups (like N, S and O). The resulting topology of the new sorbent makes it an excellent choice for the efficient adsorption of Hg (II) ions from highly complicated water matrices.

Keywords: Dendrimer, Magnetic nanosorbent, Hg (II), Wastewater, Analysis

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Trace measurement of lead and cadmium in wastewater samples using a novel MOF-based μ-dispersive solid phase extraction

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Background: Herein, a low-cost, reliable, easy-to-perform, sensitive and environmentally-friendly metal-organic framework (MOF)-based μ-dispersive solid phase extraction method (μ-dSPE) for the extraction and simultaneous graphite furnace atomic absorption spectroscopy (GF-AAS) of heavy metal ions such as lead and cadmium in several wastewater samples was developed. It is already believed that the application of the MOF nanosorbents can lead to a high level of improvements in the extraction efficiencies of the pollutants [1, 2].

Methods: Initially, a Zn-based metal organic framework (MOF) was prepared as follows: a solvothermal reaction took place through mixing 4,4'-dipyridylsulfide (dps), Zinc acetate and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) in alkaline water-methanol solution. The sorbent was characterized by FTIR, SEM and XRD techniques and eventually applied for the simultaneous extraction of two well-known heavy metal ions (Pb and Cd) from several wastewater samples. The application of the MOF nanosorbent led to a high level of improvements in the extraction efficiency. After the extraction of the concerning ions, the desorption process using a tiny volume of a desorption solvent (inorganic acid) facilitated with vigorous agitation was achieved. Finally, the desorbed metal ions were measured by a GF-AAS analytical instrument.

Results: The parameters influencing the adsorption and desorption efficiencies were thoroughly evaluated followed by the establishment of the optimal conditions. The established optimal conditions were as follows: pH 6, 5 mg of sorbent, no salt addition, 200 μL of eluent HNO_3. The relative recovery tests on the spiked wastewater samples fell within the range of 91 to 106 %, while the related precisions were determined in the range of 4.6 – 9.0 %.

Conclusion: The MOF-based μ-dSPE method in conjunction with GF-AAS demonstrated to be fast, sensitive, cost-effective, and could be easily administrated in environmental laboratories for the surveillance of the selected heavy metal ions in various wastewater samples.

Keywords: Metal-organic frameworks, Heavy metal ions, Dispersive solid-phase extraction, Wastewater samples

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Implication of magnetically modified reduced graphene oxide as an efficient nanosorbent for the HPLC measurement of two main phthalate esters

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Background: Phthalate esters (PAES), as predominant chemicals in industries, are often incorporated as softening agent. Dialkyl phthalate esters (DAPEs) are one of the phthalates widely used for producing polyvinyl chloride resin, adhesive material and colour. Phthalate esters are also classified as recalcitrant, hazardous and emeging contaminants [1-3].

Methods: Within this study, the synthesis of graphene- magnetic TiO_2 composite by grafting of $Fe_3O_4/SiO_2/TiO_2$ core-shell on the surface of reduced graphene oxide (rGO) was accomplished through a hydrothermal method. The as-prepared composite was applied for the micro-dispersive solid phase extraction (µ-dSPE) of two selected DAPEs known as DMP and DEP from aquatic samples and then HPLC was used for the final measurement of the two mentioned targets.

Results: The influential parameters affecting the efficiencies of the applied µ-dSPE were fully assessed and the optimal conditions were set for DMP and DEP. The method presented the linear ranges in the span of 2-100 ng/ml, while the correlation coefficients were greater than 0.9987. The recovery values ranged between 89.2 and 111.1% with the relative standard deviations (RSD%) falling in the range of 4.8 to 8.9%.

Conclusion: The method proved to be simple, fast and reliable for the extraction and subsequent HPLC detection of trace levels of DMP and DEP from aquatic samples.

Keywords: Phthalate esters, $Fe_3O_4@SiO_2@TiO_2/rGO$, Dispersive solid-phase extraction, Aquatic samples

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Synthesis and characterization of novel nanozero-valent iron based bimetallic nanoparticles immobilized on bentonite as a new nanocatalyst for methyl orange and congo red dyes reduction

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Background: Water pollution is a serious issue which is in result of the rapid development of industries. In the effluents generated from textile, paper, leather, plastics, pharmaceutical and cosmetic industries, there are colored contaminants which are often reported as toxic, hazardous and carcinogenic material. Azo-dyes are an important class of them. Due to its toxicity to many organisms and its suspicious to carcinogenic mutagenicity, MO and CR which are benzidine-based anionic azo-dyes are banned in many countries. However, they are still widely used in several industries. MO and CR are synthetic dyes with aromatic structures and difficulty to biodegrade. It is required, even in trace amount, to develop innovative and low-cost processes to remove these dye molecules. Recently, using of various nanocatalysts for dye removal was considered. Compared to other physicochemical and biological technologies, in this method, the efficiency is higher, there is a selectivity toward nontoxic products, relatively mild conditions are required, and the operation is easier. Various materials have been used for catalytic dye removal to develop effective and selective nanocatalysts.

Methods: Bentonite clay have been used to synthesize bentonite-supported bimetallic Fe/Cu for simultaneous reduction of MO and CR dyes [1, 2]. The synergistic effect between bentonite and nZVI based bimetallic nanoparticles resulting high removal efficiencies. The chief objectives were (1) characterization of the newly synthesized Be@Fe/Cu by BET, TEM, SEM-EDX, XRD, FT-IR, and XRF, (2) modeling and optimization of the parameters that affect the reduction procedure, and (3) elucidation of the most probable reduction mechanism of MO and CR dyes, as well as investigation of the real sample dyes removal.

Results: The results of characterization showed that the nZVI biimetallic was successfully synthesized and immobilized on bentonite. Central composite design (CCD) was used to model and optimized the reduction procedure. Both coefficients of determination (R^2) and adjusted-R^2 obtained from the analysis of variance (ANOVA) were above 0.9, ensuring a satisfactory adjustment of the model with experimental results. Under the defined optimum conditions, the kinetic models parameters were investigated and the results showed the pseudo-second order model has good agreement with the procedure. Finally, under the defined optimum condition, the proposed nanocatalyst was successfully applied for dyes reduction from industrial wastewaters.

Conclusion: The bimetallic nanocatalyst with bentonite as support for MO and CR dyes reduction simultaneously from aqueous solution are reported. The results suggest that the bentonite could effectively lighten the aggregation of nZVI bimetallic nanoparticles and enhance their reactivity towards dyes.

Keywords: Nanocatalyst; Nanozero-valent iron; Bentonite clay; Methyl orange; Congo red; Optimization

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A new and efficient nanozero-valent iron based trimetallic catalyst immobilized on bentonite clay for anionic dyes reduction

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Background: Nanozero-valent iron (nZVI) based materials have been used as tunable reducing composite because of their unique properties e.g. large surface area, high reactivity, strong reductive capacity, eco-friendly, and cost-effective. NZVI is a potential reductive composite because of its sufficient mobility and low toxicity. It can instantaneously adsorb anionic dyes on its surface. Though, the aggregation tendency of nZVI refers to intrinsic magnetic interactions and high surface energy. This limits its dispersibility. Also, in aqueous media, reductive property of nZVI decrease significantly due to quick formation of a Fe oxide and hydroxide layer on its surface. Supporting nZVI on some clays such as kaolin, hematite and bentonite results efficient dispersion of nZVI which prevents its aggregation causing greater reduction performance. On the other hand, oxidation rate and aggregation tendency of nZVI could be reduced depositing Pd as second catalytic metal onto its surface. Also, the activation energy of reduction reaction could be decreased using catalytic property of second metal. It also improves the reduction rate. Recently, it is presented that depositing third catalytic metal on the surface of nZVI based bimetallic catalyst results better performance.

Methods: In this study, nanozero-valent iron (nZVI) based trimetallic nanoparticle immobilized on bentonite was synthesized based on literature [1, 2], and characterized by TEM, FT-IR, XRD, SEM, EDS and BET. The simultaneous reduction of methyl orange and congo red, as two model anionic dyes, by the proposed nanocatalyst was investigated and the dose of nanocatalyst, initial pH, and contact time as parameters which affecting the reduction efficiency were modeled and optimized by response surface methodology.

Results: The characterization results of the synthesized Be@Fe/Cu/Ag nanocatalyst showing successful synthesis of trimetallic immobilized on bentonite. Under the defined optimum value of parameters, the kinetic data for nanocatalyst were fitted well with the pseudo-second order model. The rate constants increase with the increase in temperature, time and dosage of proposed nanocatalyst, but decrease with the increase in initial dyes concentration and pH. The proposed Be@Fe/Cu/Ag system would be a promising process for the removal of the dyes from food industrial wastewater.

Conclusion: The experimental results of the present research indicated that the presence of bentonite clay as support could decrease the aggregation of nZVI besides increasing of their adsorption and reactivity. The structure of Fe/Cu/Ag could improve the electron transport and create active sites with high electron density at the surface enhancing the generation of surface-bonded atomic hydrogen ($[H]_{ads}$) or the direct reduction of pollutant.

Keywords: Nanocatalyst; Nanozero-valent iron; Trimetallic; Bentonite; Anionic dye; Optimization

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Synthesis and identification of copper (II) oxychloride and investigating of its luminescence properties

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Background: Copper (II), is a metal element that can be accumulated in various tissues of all organisms [1]. That is widely used in the formulations for control of mold and other fungal diseases around the world [2]. Copper (II) oxychloride, $Cu_2Cl(OH)_3$ or Dicopper trihydroxy chloride (IUPAC) is one of the most common active compounds of copper fungicides. It is a green solid that is used both as a pigment and as a micronutrient for animal feed [3]. Our aim in this project is the synthesis and identification of copper (II) oxychloride and its use as a catalyst in the luminol-hydrogen peroxide luminescence system.

Methods: Copper oxychloride in atacamite phase was synthesized using aqueous solution from raw materials during laboratory experiments. The green powder was collected. It was then subjected to analysis such as IR, XRD, Atomic absorption to identify [4]. Then the synthesized material will use for luminescence. Solutions with different concentrations of luminol, hydrogen peroxide and the desired sample are made and injected into the device, and its incorporation into various conditions is measured and investigated.

Results: As a result of its synthesis, its infrared spectrum was studied. The bands at 3447, 3360 and 3311 cm^{-1} are assigned to the OH stretching modes. The band at 1621 cm^{-1} is the O–H bending modes. The bands below 600 cm^{-1} are ascribed to Cu–O bonds. The X-ray diffraction pattern was also taken and the results were observed. Strong and sharp diffraction peaks also indicate good crystallinity of the hydrothermal products. Atomic absorption also shows the ratio and percentage of copper element in copper(II) oxychloride.

Conclusion: After synthesis of copper oxychloride and its identification, we intend to use this material as a source of copper for the luminescent hydrogen peroxide system. It is expected that copper as a catalyst in the luminol- H_2O_2 system can enhance luminescence.

Keywords: Copper(II) oxychloride; Fungicide; Luminescence; Atacamite**;** Luminol

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Simple determination of lead(II) and cadmium(II) in environmental water samples using graphite-based dispersive micro-solid phase extraction coupled with micro-sampling flame atomic absorption spectrometry

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Background: Despite the advantages of FAAS, which have caused it to become a widely used technique, it does not have a sufficient sensitivity for determination of most heavy metals in the real samples, and sample preparation could play a key role to address this problem. In general, converting an analyte into a form that is pre-purified, concentrated, and compatible with the analytical system is the main aim in the sample preparation, and it has a critical position in the modern analytical chemistry [1]. In this work a simple graphite-based dispersive micro-solid phase extraction coupled with micro-sampling flame atomic absorption spectrometry for the rapid determination of lead(II) and cadmium(II) in environmental water samples.

Methods: 10 mL of sample solution was transferred to a conical bottom glass centrifuge tube and 100 μL of the 5-Br-PADAP solution (0.5%, m/v) and 1 mL of the buffer solution (pH 6.0) were added to it. Then, 3 mg of adsorbent were added, and the solution was mixed for 3 min to facilitate adsorption of the metal ions onto the adsorbent. After the centrifugation, the supernatant was removed and back-extraction of target anlytes were performed by the utilization of 0.5 mL of an aqueous HNO_3 solution (1 mol L^{-1}). Finally the extractant was analyzed by micro-sampling flame atomic absorption spectrometry.

Results: The method provided a good linearity (in the range of 0.7–400 ng mL^{-1} ($R^2 > 0.997$)). The enrichment factors are suitable (in the range of 29-30), and the method provides low limits of detection (in the ranges of 0.15-0.50 ng mL^{-1}).

Conclusion: An efficient dispersive micro-solid phase extraction was coupled with micro-sampling flame atomic absorption spectrometry for the rapid determination of lead(II) and cadmium(II) in environmental water samples. The method provides a high sample clean-up and a good preconcentration, and, it was successfully utilized for the determination of the target analytes in real samples including the river, dam, and well water.

Keywords: Micro-sampling flame atomic absorption spectrometry; Lead(II); Cadmium(II); Graphite-based dispersive micro-solid phase extraction.

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photocatalytic decolorization of aqueous rhodamine b solution by nanostructure $La_{0.7}Sr_{0.3}MnO_3$

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Background: The interesting characteristics of perovskite oxides (ABO_3) have made scientists to dedicate a remarkable amount of their research to this area. $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) nanostructures have been synthesized via hydrothermal and its photocatalytic oxidation has been investigated to decompose aqueous rhodamine b (RhB) solution under visible light irradiation.

Methods: The $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles were synthesized using the hydrothermal method which is described in our previous work [1]. The photocatalytic reaction of aqueous RhB solution (10 ppm & pH=4.5) by prepared LSMO nanostructures as photcatalyst (0.5 g/L) was carried out in a 50 mL beaker under magnetic stirring and irradiation of visible-light source [2].

Result: The XRD pattern has been provided in Fig. 1. According to the existing peaks, an orthorhombic structure with R-3C space group is attributed to the as-prepared specimen. The degradation percent of RhB shown in Fig. 2.

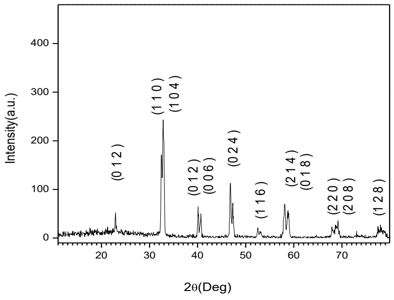

Figure 1. Presentation of the XRD analysis of sample.

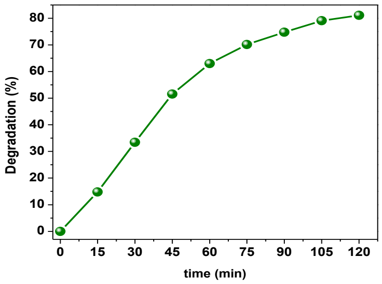

Fig. 2. Degradation percentage of RhB as a function of time in the system

Conclusion: This research introduced a method for synthesis of visible light photocatalytic material, namely $La_{0.7}Sr_{0.3}MnO_3$, by hydrothermal method. The photodegradation efficiency for decolorizing rhodamine b solution (10 ppm) by magnetite (0.5 g/L) after 120 min illumination was about 82%.

Keywords: $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) manganite, Hydrothermal method, Photocatalyst, photocatalytic activity.

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Determination of three antifungal drugs with Ultrasound-air-assisted demulsified liquid–liquid microextraction in water and biological samples

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Background: Antifungal drugs are widely used in different pharmaceutical dosage forms to prevent the conversion of lanosterol to ergostero as the main sterol of the fungal cell [1]. Among the agents used, the imidazole group drugs (azole antifungals) have a wide range of actions [2]. There is a matter of public concern about their environmental impact because of possible negative effects[3]. Different methods based on microextraction have been developed to overcome the limitations of the sample preparations [4]. A novel ultrasound-air-assisted demulsified liquid–liquid microextraction by solidification of a floating organic droplet (UAAD-LLM-SFO) method was applied for the determination of three anti-drugs. In this method, the low-density solvent, 1-dodecanol, was dispersed using air assisted. The ultrasound irradiation enhanced the rapid formation of fine droplets of the extractant in the sample solution, and the contact surface between both immiscible liquids was significantly enlarged. After a few minutes of extraction, an aliquot of demulsifier solvent was injected into the solution to break the emulsion.

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Methods: An aliquot of 10 mL of a sample solution containing 100 µg L^{-1} of each antifungal drug was placed in a glass tube. After adjusting pH to 10, 100 µL of the extraction solvent (1-dodecanol) was rapidly injected using air assisted into the sample solution for 5 times while sonication was used for 30 s. The analytes were extracted into the fine droplets in a few seconds. Then, a 200 µL of acetonitrile as the demulsifier solvent was injected into the solution to break down the emulsion. The mixture was separated into two phases. 1-dodecanol was solidified after 2 min. In finally 20 µL of the extraction solvent was directly injected to HPLC for the analysis.

Results: In this study, 1-dodecanol with a volume of 100 µL was selected as the extraction solvent. The number of suction/injection cycles (5 times in 30 s of the sonication) was selected. The pH value of the solution was selected to 10 for subsequent experiments. Also, the type and volume of de-emulsifier solvent were studied. According to the obtained results, 200 µL of acetonitrile solvent was applied in the subsequent experiments.

Conclusion: In this study, there is some fundamental approaches.
The use of solvents with a density lower than water is an advantage. Air-assisted liquid-liquid microextraction has been developed instead of the disperser solvent. In order to obtain the phase separation without centrifugation step, an aliquot of demulsifier solvent was injected into the solution to break the emulsion.

Keywords: Solidification of a floating organic droplet, Demulsified liquid–liquid microextraction, Antifungal drugs

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Ligandless Liquid–Liquid Microextraction for Preconcentration of Some Heavy Metals in Biological and Environmental Samples with Deep Eutectic Solvent

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Background: Heavy metals are known as one of the most environmental pollutants [1]. They can produce acute or chronic toxicity problems. The direct determination of trace elements in samples are still a sensitive part. Some methods are time-consuming and tedious with the use of large amounts of organic solvents [2]. Deep eutectic solvents (DESs) based on ionic liquids(ILs) are known as green solvents. The formation of deep eutectic solvents is by mixing hydrogen bonding between hydrogen bond acceptors (HBAs) and functional groups of hydrogen donor agents (HBDs). DESs can overcome the drawbacks of hazardous chlorinated solvents, thus they can be an excellent choice in the extraction and separation [3]. In this study, a new technique, air assisted ligandless emulsifcation liquid–liquid microextraction, was introduced in which a mixture of DES and triethylamine (TEA) formed a stable homogeneous liquid as the extraction solvent for preconcentration of some heavy metals from different matrices. The mixture was dispersed in the sample solution and repetitively withdrawn by means of a syringe and then, directed into a tube. Therefore, the contact surface between both immiscible liquids was significantly enhanced.

Methods: To 20 mL of the sample solution containing 50 µg L^{-1} Cd, Pb, Ni and Cu with the adjusted pH of 7, 100 µL of the mixture of TEA and DES at the mole ratio (1:1) as the extractant solvent was added. Then, 100 µL of THF was injected into the homogeneous solution. In order to disperse DES into the sample solution, air-assisted was performed (repeated five times). In this step, the analytes were extracted into the fine droplets of DES. The solution was centrifuged at 4000 rpm for 3 min and the upper phase was diluted with 150 µL of HNO_3 (63%). Finally, 100 µL of the organic phase was injected into the microsampling FAAS system for analysis.

Results: In this study, 100 µL of DES composed of ChCl and 5,6,7,8-Tetrahydro-5,5,8,8-tetramethylnaphthalen-2-ol (TNO) (1:2) as the extraction solvent in the presence of TEA exhibited the highest extraction for all analytes. THF with the volume of 100 µL was selected as an aprotic solvent. Also, the pH of 7 was selected. Finally, by increasing extraction numbers, recoveries also increased up to 5 extraction in 1min.

Conclusion: In this study, there is some fundamental approaches:

The use of DES solvent instead of hazardous chlorinated solvents. The use of TEA as an ion pair to form a complex with ions in the absence of a reagent. The use of air-assisted to disperse the aggregated DES droplets into the aqueous phase and enhance the turbidity of the solution.

Keywords: Deep eutectic solvent, Triethylamine, Air assisted ligandless emulsifcation liquid–liquid microextraction

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Ferrofluid based liquid phase microextraction by use of deep eutectic solvent for preconcentration of cobalt in environmental water samples

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Background: Cobalt is a natural element in the air, water, soil, rocks, plants and animals. When cobalt enters the environment, it does not immediately disappear. Low levels of cobalt are vital to many living organisms, including humans. High concentrations of cobalt in the body cause poisoning and dizzines. [1-2]So, a rapid, reliable and accurate analytical method for the quantification of cobalt in environmental water samples is necessary. Deep eutectic solvents (DESs), which have recently developed by Abbott et al. are new types of eco-friendly solvents. DESs have attracted great attention in chemistry as green ionic liquid analog. With the development of these solvents, they have been used for different targets in analytical chemistry such as extraction solvents, functionalization agents.

Methods: In this work, we report the development and application of DES based ferrofluid as the sorbent for cobalt analysis. The DES based ferrofluid was formed by blending Fe_3O_4 nanoparticles and deep eutectic solvents. By combining DES with Fe_3O_4 nanoparticles that covered with PAN, a highly stable magnetic soft material without any additional stabilizer and that was used for cobalt extraction and preconcentration. The prepared Fe_3O_4 and DES based ferrofluid characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy (FT-IR) techniques.

Results: The effect of experimental parameters, including the amount of sorbent, the pH value of sample solution, extraction time, volume of elution solvent and elution time, were investigated and optimized. Under the optimized conditions, the DES based ferrofluid was successfully used for extraction of cobalt ions in the environmental water samples. The result showed that the method had good linearity (r = 0.990), and the limit of detection (LOD) were 0.033 µg L^{-1}. Recoveries obtained by analyzing the spiked water samples were in the range of 90–102 % and relative standard deviations (RSDs) were 2.6%.

Conclusions: This method was developed for the determination of cobalt ions in environmental water samples. This technique is easily carried out .Furthermore, in comparison with solid phase extraction, it is much faster, because the sorbent is highly dispersed in the aqueous phase and no centrifugation is required for phase separation.

Keywords: deep eutectic solvent; cobalt ion; Fe3O4; Liquid phase microextraction

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Ferrofluid based liquid phase microextraction by use of deep eutectic solvent for preconcentration of cobalt in environmental water samples

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Different phosphorus forms in the surface sediments of Chabahar Bay

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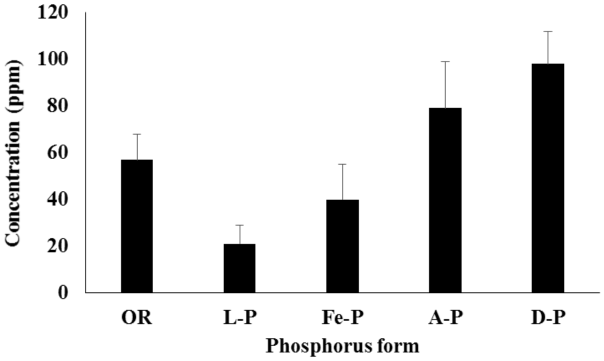
Background: Phosphorus has been recognized as the most essential and critical nutrient in the sediments of terrestrial and aquatic environments[1]. In marine waters, phosphorus is found either in dissolved or suspended forms, each have both inorganic and organic form. In sediments, phosphorus is discovered as loosely adsorbed phosphorus (Loosely-P), Fe-bound, Authigenic-P (Calcium-P and Aluminum-P), Organic-P and Detrital-P. Hence, identification of phosphorus forms in aqua environment is of great importance [2].

Methods: Surface-sediment samples were collected at 7 stations in Chabahar Bay. Samples were carried to the laboratory and then kept at −20 °C prior to analyses. For chemical differentiation of phosphorus, sediments were firstly sieved through a mesh-size screen of 63 μm and then 0.5 g freeze dried sediment of each sample in 50 mL extractant were analyzed using Ruttenberg method [3]. Sequential extraction procedure (SEDEX) with colorimetric detection by UV-Vis was used to determination of loosely-P (L-P), iron-bound P (Fe-P), authigenic-P (A-P), detrital-P (D-P) and organic-P (O-P).

Results: Results revealed that the range of total phosphorus (TP) was between 156 ppm and 374 ppm with a mean value of 295.30 ± 25.13 ppm. Generally, inorganic phosphorus (IP) was between 193 and 342 ppm which comprised 88.6–93.46% of total phosphorus.

Conclusion: In this study for the first time, different forms of phosphorus in the Chabahar Bay was determined by SEDEX method with colorimetric detection by UV-Vis. Findings showed levels of different phosphorus forms in a descending order: detrital P > Authigenic P > Organic P > Fe-P > Loosely P. Around 31.06 ± 4% of total phosphorus was bioavailable phosphorus.



Keywords: Phosphorus forms; SEDEX; UV-Vis; Organic-P; Inorganic-P; Bioavailable-P; Chabahar Bay

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Application of ultrasonic assisted dispersive liquid phase micro extraction combined with dispersive micro solid phase extraction for simultaneous pre-concentration and trace detection of lead and cadmium ions

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Background: Environmental contamination with heavy metals as a worldwide concern menace the human life. Heavy metals are natural components of the seawaters and a large amount of them enter naturally to the rivers and ground waters via various ways such as erosion of mines, dust particles, and volcanic activity. Regional increase of these metals by human-induced industrial processes such as industrial wastes from factories, textile, mining, and other metal smelting process are the major concern [1-3].

Methods: In the present method a hybrid extraction method was utilized for simultaneous detection of cadmium and lead ions. In the first step a liquid phase micro-extraction based on dispersion of organic solvent was used for the fast extraction of complexed ions with dithizone from aqueous solution and in the next step the extraction organic solvent was effectively collected from the solution without any requirement to centrifuge step by using C18-magnetic nanoparticles. Pre-concentrated lead and cadmium ions was monitored by GFAAS at ng L^{-1}**.**

Results: Optimized data for parameters that obtained by Box-Behnken design were: sample's pH: 5.7, ligand/metal concentration ratio: 8, magnetic based sorbent amount: 15 mg and 1-octanol volume: 26 microliter. Relative standard deviation by the hybrid extraction method was observed to be < 6 % for both ions and method detection limit for cadmium and lead ions was 2 ng L^{-1} and 5 ng L^{-1}, respectively.

Conclusion: The findings of characterization tests of the introduced sample preparation method proved that the developed hybrid extraction method is extremely effective for preconcentration of cadmium and lead cations.

Keywords: Hybrid extraction method; Dispersive liquid phase micro-extraction; Dispersive micro solid phase extraction; Box-Behnken design; Cadmium and lead ions

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Highly effective removal of the meloxicam residuals from water by the HKUST-1 metal-organic framework

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Background: Pharmaceutically active substances are an important group of emerging contaminants. Their extended use and the incomplete elimination in wastewater treatment plants have resulted in these contaminants, in their native form or as metabolites, continuously introduced into sewage waters, mainly through excreta, disposal of unused or expired drugs, or directly from pharmaceutical discharges[1]. The pollution of waters and soils with pharmaceutical residues is an emerging environmental issue[2]. To the removal of these residuals, metal-organic frameworks are a good suggestion because of their unique features such as high surface area, ultra high porosity and tunable pore size[3].

Methods: Metal-organic frameworks HKUST-1 synthesized according to previous work and characterized. The ability of this MOF in removal of the non-steroidal anti-inflammatory drug (NSAIDs) meloxicam (MLX) was studied by UV-vis spectroscopy and Adsorption kinetics, Adsorption isotherms, Adsorption mechanism, Adsorption thermodynamics and Reusability of the sorbent was investigated.

Results: The proposed methods showed the good results in the removal of MLX from wastewater in the optimum conditions: pH=7, adsorption time=5 min and 0.7 mg of the HKUST-1 sorbent. The HKUST-1 is able to remove the MLX upper %90 after 4 cycles. The maximum adsorption capacity calculated with the Langmuir equation was equal 526.31 mg g^{-1}. The adsorption kinetics accorded with the pseudo-second-order kinetic model.

Conclusion: In the present work, the removal of MLX was studied using the HKUST-1 MOF. Under the optimum conditions, HKUST-1 has a high capacity for remove of the MLX from wastewater. The adsorption isotherms and kinetics were investigated. These results demonstrate the potential of HKUST-1 using for the removal of organic pollutants from aqueous solutions.

Keywords: metal-organic frameworks; HKUST-1; non-steroidal anti-inflammatory drug; meloxicam; water treatment; removal.

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A Novel SnO_2 Electrode Preparation and its Application in Organic Degradation

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Background: Several studies have revealed that electrochemical oxidation efficiency of organic pollutants depends on the various parameters like the type of anode and electrolyte, anode coating materials and its composition, anode preparation method, applied power and types and concentration of pollutants [1]. Among them, the anode is the most critical component since the oxidation performance and the mechanism of electrochemical reactions mainly depend on the anode material and its coating structure. It follows that design new anodes with high activity, long service life and high stability is critical for the degradation of organic pollutants [2,3].

Methods: A quinoline dye Acid Yellow 3 (AY3), was selected as a model dye. The Coating solutions were prepared in glass beakers as follows: 0.02 g SnO_2 nanoparticles, 0.01 g αFe_2O_3 and a small amount of $NiCl_2$ were dispersed in 50 mL double-deionized water and sonicated for an hour. After the preparation of desired suspensions, the pretreated Ti electrodes were partially immersed in suspension at distance of 10 mm. A constant current density was applied between the electrodes during the deposition time and the deposition took place on the cathode.

Results: Fig.1A and B compares the FESEM images of the Ti/nanoSnO_2-αFe_2O_3 and Ti electrodes. Regarding Ti/nanoSnO_2- αFe_2O_3 electrode (Fig. 1(B)), it can be clearly seen that the Ti plate substrate was homogeneously covered by the nanoSnO_2-αFe_2O_3 layer with a porous morphology, a rough surface and well-distributed α-Fe_2O_3 nano particles on the SnO_2 surface without voids or cracks on the surface after EPD technique. The color removal efficiency was about 99% for degrading 50 ppm AY3 at a current density of 12 mA cm^{-2}, pH=5 and treatment time of 40 min.

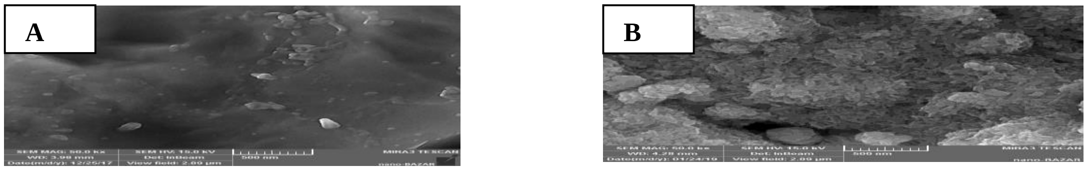

Figure 1. The FE-SEM images of (A) Ti plate substrate and (B) Ti/nano SnO_2- αFe_2O_3 electrode.

Conclusion: A novel Ti/nanoSnO_2-αFe_2O_3 electrode was successfully fabricated using electrophoretic deposition technique. These results confirmed that the good electrocatalytic performance of Ti/nanoSnO_2-αFe_2O_3 makes it a promising anode as low-cost dimensionally stable anodes (DSAs) for treatment of organic pollutants in aqueous solution.

Keywords: Electrophoretic deposition, Electrochemical oxidation, Dye degradation, Ti/SnO_2 anode

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Single particle analysis by inductively coupled plasma mass spectrometry (sp-ICP-MS) as a novel and fast tool for nanoparticle characterization in Environmental Matrices

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Background: Nanomaterials transport of contaminants in the environment is a matter of concern because colloids can travel long distances along surface waters and fractured aquifers [1]. The fate of contaminants in the environment is controlled by complex interactions and transport mechanisms including colloidal, chemical and, hydrodynamic processes. The critical parameters that affect the toxicity of nanoparticles are the particle size which might be related to the larger surface-to-volume ratio, and the surface charge [2].

Methods: Water, soil and peppermint samples collected from Mazandaran and Alborz providence. Samples were stored in refrigerator temperature. Samples were prepared in 1 mM SDS and introduced into ICP-MS in TRA mode. Aqueous suspensions of standard spherical Ag and Au nanoparticles with diameters of 30, 60 and 100 nm and mass concentration of 1.0 mgL^{-1} stabilized with citrate. An Agilent 7700x ICP-MS was used for nanoparticles characteristics. The instrument should be prepared and sat up for analysis.

Results: The sp-ICP-MS technique has been validated for the determination of standard NPs and tested in an inter-laboratory study for the determination of nanoparticles in standard aqueous suspensions. Calculation of particle size, mass concentration and size distribution from the spICP-MS data was performed using a spreadsheet was developed by our group. In sp-ICP-MS, the transport efficiency should be firstly obtained to estimate the nanoparticles content in the particles of the samples. Transport efficiency was evaluated by comparing the signal of dissolved standard of Au of 100 ngmL^{-1} with the signal of a suspension of Au of 60.0 nm at a concentration of 50 ng mL^{-1}.

Conclusion: Under the optimized conditions, natural and engineered nanoparticles were detected in all samples. Limits of detection and quantification of total Ag, Au, TiO_2 and ZnO determined by ICP-MS were 0.01, 0.01, 0.03 and 0.05 ng mL^{-1}, respectively. The recoveries were ranged from 91% - 93% in real samples. The repeatability for the determination of the particle size of a 60 nm Ag based nanoparticles in water samples were 1.4% and 2.3%.

Keywords: sp-ICP-MS; *Metal based Nanomaterials, Environmental Matrices; Method Validation.*

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Determination of Cd in Melissa Oficial L. by Modified Cellulose Nanofibers and Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS)

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Background: Cd is dangerous because it tends to bioaccumulate, i.e. increase its concentration over time in soft tissues [1]. Developing and industrializing result in soil pollution which significantly affects organisms related to soil. High dosage of Pb, Cu, Cr, Zn, Ni and Cd has a bad impact on plant growth also nutrition value of secondary metabolites they produce [2].

Methods: Melissa samples were collected from Mazandaran State. Leaves, roots and steams of plants were washed, air dried and then powdered (mesh 200). Cellulose nanofibers were dissolved in an aqueous solution of NaOH and centrifuged for 30 min for degasification then the sorbent was modified by Cyanex. The sorbent were synthesized by the co-precipitation method. Cd determinations were performed using a Zeeman effect background correcting atomic absorption spectrometer (Model 2-3030 from PerkinElmer, Oberlingen, FRG). The instrument included cornputerised graphic signal processing and was equipped with an AS-60 autosampler, an HGA-600 furnace controller and a PR-100 printer. The effect of different parameters on the determination including contact time, sorbent dosage and solution pH was investigated by atomic absorbtion spectroscopy.

Results: A successful preparation of Cyanex functionalized nanoadsorbents onto CNF for the extraction of Cd were carried out. The recovery of Cd at a spiked concentration of 100 ng kg^{-1} ranged from 89% - 95%. The repeatability and reproducibility for the determination of Cd were 2.6% and 4.9%, respectively.

Conclusion: In this work, the extracted reagents contained a thiol group that served as an important molecule in this work. pH played an important role in determining what pH regime and speciation of the adsorbate in the extraction of Cd.

Keywords: GF-AAS; Cd, Cellulose Nanofibers*; Melissa Oficials L., Method Validation.*

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4-Analytical spectrometry

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Application of a zirconium-based metal-organic framework/ferrite nanocomposite as peroxidase mimetic for spectrophotometric detection of hydrogen peroxide

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Background: *O*-phenylenediamine (OPD) is a colorless, non-fluorescent compound which can be oxidized by molecular oxygen or hydrogen peroxide in the presence of metal ions, forming 2,3–diaminophenazine (DAP) as the main oxidation product [1]. Since the oxidation of OPD by H_2O_2 or O_2 proceeds very slowly, the reaction needs to be catalyzed. The resultant solution of DAP has an orange–red color and exhibits an orange-yellow fluorescence when irradiated by ultraviolet light [2]. The concentration of DAP is usually determined by using UV–Vis spectroscopy.

Methods: In this work, ferrite nanoparticles (NPs) were synthesized using a co-precipitation method and followed by a solvothermal reaction to form zirconium-based metal-organic framework/ferrite nanocomposite (ZrMOF/Zn-$NiFe_2O_4$ NC) and characterized by a combination of physico-chemical and spectroscopic techniques. The prepared NC was used as a nano-catalyst for oxidation of OPD to DAP.

Results: Herein, we report the results of a thorough investigation on the chromogenic oxidation of OPD to DAP in the presence of the synthesized ZrMOF/Zn-$NiFe_2O_4$ NC as the reaction catalyst. The characterization results show successful preparation of the NC. Then, the ZrMOF/$ZnNiFe_2O_4$/OPD system was effectively used for the detection of H_2O_2 under the optimized conditions.

Conclusion: A simple co-precipitation technique followed by a solvotherml method was used for the preparation of ZrMOF/Zn-$NiFe_2O_4$ NC. The NC was tested as a catalyst in the chromogenic oxidation of OPD to DAP by monitoring the absorbance of DAP at 415 nm by means of a UV–Vis absorption spectrometer.

Keywords: Nano-particles; ZrMOF/Zn-$NiFe_2O_4$ nanocomposite; Peroxidase-like activity; Catalyst; Detection; Hydrogen peroxide

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Spectrophotometric Determination of Nabumetone after Pseudo Stir Bar Sorptive Extraction using Molecularly Imprinted Polymer Functionalized Graphene Oxide Anchored Pencil Lead

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Background: In recent years, molecularly imprinted polymers (MIPs) have attracted remarkable attention due to their outstanding advantages, such as predetermined recognition ability, stability, the relative ease and low cost of preparation, as well as the potential of application to a wide range of target molecules [1]. Surface imprinting via grafting the imprinted polymer on the surface of a suitable supporting material in which the template molecules are controlled to locate on the material's surfaces demonstrated great potential for the preparation of MIPs. Today, the synthesis of silver nanoparticles (Ag NPs) using various stabilizing agents has been established and is widely used for the determination of different compounds in various fields [2].

Methods: Graphene oxide (GO) anchored pencil leads (PLs) were prepared through an in situ exfoliation of graphite of PLs using a one-step oxidation procedure based on the Hummers method [3]. In order to functionalize the modified PLs with a MIPs, the polymer synthesis was conducted in the presence of PLs as substrate. For the assay of nabumetone (NAB), the pH of a sample solution containing not more than 2.0 µg of NAB was adjusted at 4.2. Then, modified PLs with MIP was added into the solution and stirred vigorously for 23 minutes. The sorbent was taken out, washed gently with double distilled water followed by treatment with 250 µL methanol/acetonitrile (90/10, v/v) for elution of the analyte. Then, the analyte was quantified through monitoring the decrease of the LSPR peak of silicate sol gel-stabilized Ag NPs at 420 nm.

Results: The analytical performance of the developed method was evaluated under the optimized conditions. The calibration curve showed linearity over the concentration range of 1.5-20.0 µg L^{-1}. A detection limit of 0.20 µg L^{-1} and relative standard deviations of 4.6 and 8.1% were obtained for intera- and inter-day analysis (10.0 µg L^{-1} of nabumetone, n = 6).

Conclusion: The modified PLs were functionalized with MIPs and utilized as a selective and efficient sorbent for pseudo stir bar sorptive extraction of nabumetone. The developed procedure was successfully utilized for the determination of nabumetone in tap water, human urine, and serum samples.

Keywords: Nabumetone; Silicate sol-gel stabilized Ag NPs; Graphene oxide anchored pencil lead; Molecularly imprinted polymer

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Selective Fuorimetric Determination of Sulfadiazine using Graphene Quantum Dots Supported on Silver Nanoparticles

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Background: Graphene quantum dots (GQDs) as a new kind of nanomaterials belong to graphene family with a zero-dimensional network, has increasingly gained interest in scientific research [1]. Importantly, GQDs with the ability to dope or functionalizing with metal nanoparticles have been applied in several fields [2]. Silver nanoparticles could be employed as an electron acceptor in doping with GQDs due to their high extinction coefficient and the broad absorption band. Abundant oxygen-containing groups of GQDs provide a suitable surface for the growing of Ag NPs. The prepared nanocomposite can be used for the determination of various analytical samples [3].

Methods: GQDs were synthesized based on the citric acid pyrolysis method according to the previous literature [4]. For sulfadiazine determination, 1.0 mL of Ag NPs-GQDs and an appropriate aliquot of sulfadiazine solution were added into a centrifuge tube. The solution was diluted to 2.0 mL with distilled water and the mixture was strongly shacked and incubated for 15 minutes at room temperature. The Ag NPs-GQDs fluorescence intensity in the presence of sulfadiazine was measured at 470 nm (F). The fluorescence intensity of a blank solution (containing the same ingredients except for the analyte) was also measured at 470 nm (F_0). The relative fluorescence intensity ($F/F_0 - 1$) was applied to calculate the signal output.

Results: Quantitative detection of sulfadiazine was evaluated under optimum conditions. A good linear relationship between the sulfadiazine concentration and fluorescence signal was achieved in the concentration range of 0.04-22.00 µmol L^{-1}. Moreover, the limits of detection (LOD) and quantification (LOQ) were found 0.011 µmol L^{-1} and 0.037, respectively.

Conclusion: A rapid, selective, and cost-effective fluorimetric method has been proposed for the determination of sulfadiazine in human serum, urine, and mineral water samples. The method has the advantages of the low detection limit without any need for a complex preparation process.

Keywords: Sulfadiazine; Nanosensor; AgNPs- GQDs; Fluorescence intensity; Fluorescence resonance energy transfer (FRET).

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An Optical Nanosensor Fabricated by Graphene Oxide Quantum Dots Embedded Silica Molecularly Imprinted Polymer for Sensitive Detection of Ceftazidime Antibiotic

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Background: Ceftazidime is an antibiotic, which is used to treatment of bacterial infections. Determination of this antibiotic is important because of its dangerous side effects. Currently HPLC and HPLC-Mass are the most common determination methods for ceftazidime [1]. Thus, reporting a simple, rapid, and low cost method to detect ceftazidime is crucial. Molecularly imprinting is a technique for the formation of molecularly imprinted polymers (MIPs) based on polymerization around target molecule. This work is introduced an optical nanosensor based on graphene oxide quantum dots (GOQDs) embedded SMIP. The introduced chemical nanosensor was used to analysis of ceftazidime in a urine sample and showed a remarkable recovery.

Methods: As mentioned in former reported article, citric acid was an initial material to synthesis of GOQDs by pyrolysis method [2]. In order to synthesis of GOQDs-SMIP in the first step, APTES was added into GOQDs. The GOQDs functionalized with APTES. Next, ceftazidime as a template molecule was added to APTES-GOQDs in the solution. Steps of the synthesis was followed by adding TEOS and the catalyzer. At last, the template was removed from the polymer.

Results: The linear range of GOQDs-SMIP and GOQDs-SNIP was 0.182-1.274 µg L^{-1}. The coefficient of determination (R^2) for the GOQDs-SMIP and GOQDs-SNIP were 0.994 and 0.986. The LOD for detection of ceftazidime was 0.063 µg L^{-1} Fig. 1. This low LOD proved that the proposed optical nanosensor was applicable and sensitive in the determination of trace level of ceftazidime. The proposed fluorescent probe exhibited quenching in response to different concentration of ceftazidime in urine sample. Based on calibration curve the concentration of spiked ceftazidime was found 0.039 µmol L^{-1} which the accuracy was 99.2%. The percent of error was 0.9 %.

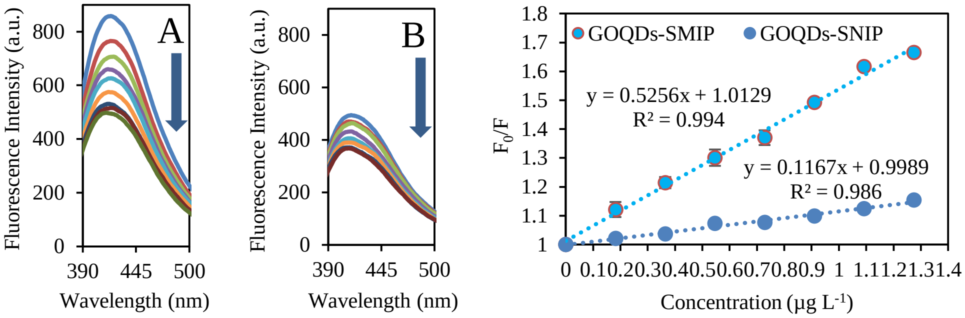

Fig. 1 Fluorescence spectra of GOQDs-SMIP (A) GOQDs-SNIP (B) and calibration curve (C)

Conclusion: This fluorescent probe was consisted of the properties of SMIP and GOQDs such as high specificity and the strong fluorescence emission, which produced for the first time an optical nanosensor to highly sensitive and selective determination of ceftazidime at trace levels.

Keywords: nanosensor, graphene oxide quantum dots, molecularly imprinted polymers, ceftazidime

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Investigating the effect of solvent extraction kind on the determination of traces of Co(II) after pre-concentration by single drop microextraction

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Background: The analysis process steps include: sample preparation, separation, identification, measuring and data analysis. The purpose of research is considering the role of cobalt in biological body and importance of measuring of this element in biological and aqueous sample. The purpose of this work, developing method which accurate with green chemistry principles and according to environmental that is simple, effective and low cost for measuring cobalt. In this work is investigated the effect of solvent extraction kind, ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate $[C_8MIM][PF_6]$ or carbon tetrachloride CCl_4. It is investigated for measuring the trace of cobalt in water solution using single drop microextraction. Micro extraction in which the volume of the extractor phase is very small relative to the sample volume [1].

Methods: Before each extraction, the microsyringe was washed with ethanol solvent in order to eliminate the bubble in the needle and air dried. A 10 ml of aqueous sample containing Co and 2.4% (m/v) APDC were mixed in the buffer solution, is poured into a cylindrical container. In order to rotate the solution, a magnet was inserted to it and placed on stirrer. The trace analytes were extracted into the $[PF_6][C_8MIM]$ or CCl_4 drop from the sample solution. In order to hang a droplet larger than the tip of the microsyringe, a polypropylene rubber tube was attached to it, as a result, increased the surface and volume of the droplet. After the extraction, the droplet was retracted into the microsyringe. Then, 0.4 ml of ethanol solvent was adapted to properly dilute the concentrated sample and transported to spectrophotometer for determination. As shown in Fig1.

Results: Under optimum conditions such as pH of working solution (pH=6), amount of chelating agent (2.4% m/w), volume of microdrop (20 µl), microextraction time (30 min) and stirring rate (300rpm), the below results are achieved. As shown in Table.

Extraction solvent	Calibration curve	Limit of detection	correlation coefficient	RSD	Enrichment factor
Ionic liquid	**0.4-6 mg/L**	**0.08 mg/L**	**0.997**	**1.4%**	**25.95**
Carbon tetrachloride	**0.5-12 mg/L**	**0.04 mg/L**	**0.9976**	**3%**	**19.17**

Conclusion: The enrichment factor has been increased by using ionic liquid Because CCl_4 has a higher vapor pressure than ionic liquid, some of it may evaporate during the extraction process, so the repeatability in the drop volume decreases, which will reduce the repeatability of the amount of extracted .

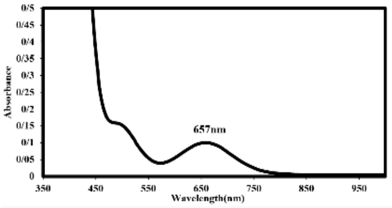

Fig1. The spectrum obtained from the cobalt (II) complex in optimal conditions

Keywords: Pre-concentration; Single drop microextraction; Ionic liquid; Trace.

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Determination of Mercury (II) Ion by Colorimetric Sensor using Green Synthesized of Silver Nanoparticles Functionalized Date Palm Extract

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Background: A simple, low cost, rapid method for colorimetric determination of Hg^{2+} based on surface plasmon resonance peak of silver nanoparticles green biosynthesis by using Date palm (Phoenix Dactylifera) fruit extract in real environmental samples was developed. The detection limit of the present method was determined to be 3.7×10^{-8} M with a linear response range of 2.5×10^{-7} 1.7×10^{-5} M, which is much lower than the standard value defined by the Environmental Protection Agency (EPA).

Methods: Some of fruit were crushed into fine pieces with sterilized knife. The fruit of Date palm were taken into the beaker containing double distilled de-ionized water and then the solution was stirred for 30 min. The extract is used as reducing agent as well as stabilizing agent. The prepared DP-AgNPs were characterized by Fourier transformed infrared spectroscopy, transmission electron microscopy, X-ray diffraction, and UV-Vis spectroscopy [1].

Results: The difference in absorbance (ΔA) at 405 nm, after addition Hg^{2+}, was calculated to optimize different parameters. The obvious color change from yellow to colorless was observed with the naked eye and the absorbance were recorded after 5.0 min by UV-Vis spectra.

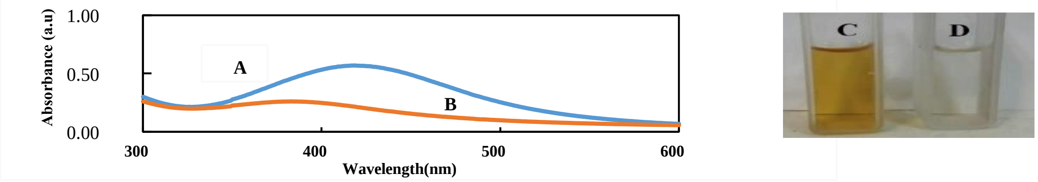

Figure 1. a) UV-Vis spectra of DP-AgNPs , b) DP-AgNPs in the presence of 4.8×10^{-6} M Hg^{2+},c) and d) the color changes of silver nanoparticles in the absence and presence of Hg^{2+}, respectively

Conclusion: Hg^{2+} in aqueous media were detected by date fruit extract functionalized DP-AgNPs via a colorimetric method with good selectivity and sensitivity. The distinct color change of DPAgNPs can be detected by naked eyes. Analysis with small sample volumes with low cost and detection of Hg^{2+} with good selectivity in low response time in aqueous solutions are the unique characteristics of the proposed colorimetric sensor.

Keywords: Silver nanoparticle, Colorimetric Sensor, Mercury ion (II), Green synthesis, Date palm

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A novel fluorescence sensor for mercury based on Förster resonance energy transfer assembly using carbon quantum dots and silver nanoparticles

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Background: Förster resonance energy transfer (FRET) is a unique technique for probing subtle changes in molecular conformation, association, and separation between donor and acceptor. The intrinsic mechanism of FRET is that the donor fluorophore is excited by absorbing a photon, and then the energy is transferred to a nearby acceptor molecule through a non-radiation pathway [1, 2]. Carbon dots (CDs) have attracted more and more interests due to their excellent properties as small size (2–10 nm), nontoxicity, biocompatibility and feasible cell permeability, which have been extensively applied to analytical detection and imaging. In the present study, we have designed a FRET assembly among carbon dots (CDs) and silver (Ag) nano-particles (NPs) as perfect donor and acceptor, respectively and successfully applied as mercury sensor.

Methods: The carbon dots were synthesized by a hydrothermal method. Citrate-stabilized Ag nanoparticles were synthesized and used as acceptor. Novel synthesized carbon dots were characterized by FT-IR, carbon NMR, hydrogen NMR, TEM and SEM. The spectral information demonstrate the well synthesized carbon dots with the size of less than 10 nm. UV-Vis spectra were also used to show the possibility of the FRET assembly between Ag NPs and carbon dots.

Results: Due to FRET assembly between Ag NPs and carbon dots, the fluorescence emission intensity of carbon dots decreases by the addition of Ag NPs. The suggested system was applied for mercury determination. All related parameters which can affect the efficiency of the method were optimized. After the optimization, Hg determination was applied with the proper selectivity and accuracy in the concentration range of 0.25 ppb-0.25 ppm, with a detection limit of 0.07 ppb.

Conclusion: A new carbon dot was applied for the construction of FRET assembly as donor. As a result, determination of mercury ions in real samples were carried out by the accurate, fast and inexpensive method which has been rarely applied, so far, for the measurements of heavy metals.

Keywords: Förster resonance energy transfer; Fluorescence; Carbon dots; Silver NPs; Mercury; Optical sensor

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Comparison of some magnetic nanoparticles based on iron oxide for separation and determination of cadmium metal ion by atomic spectrometry in the seawater samples

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Background: Magnetic nanoparticles based on iron oxide (Fe3O4) can be synthesized easily and separated with magnetic bar. On the purpose of determining heavy and dangerous metal of cadmium, for the first time, five types of magnetic nanoparticles based on iron oxide were used for separation, detection and measurement of heavy and dangerous metal ion of cadmium. The used complex ligand was 4-(2'–thiazolylazo) - resorcinol (TAR) which has a thiol group with strong tendency to silver and gold ion metals. In order to increase the specific surface, absorption and extraction of cadmium ion, the magnetic silica nanoparticles (MCM-41-Fe_3O_4) was used.

Methods: Fe_3O_4 nanoparticles, Fe_3O_4@Ag were prepared according to our previous work and Fe_3O_4@Au were prepared according to the reference [1]. For placement of TAR Ligand on the synthesized nanoparticles, various solutions of TAR with different concentrations of 0.1 mM to 10 mM in solvent of water/ ethanol (50/50 v/v) were prepared. At 25 °C, the TAR solution was added to 10 mg of nanoparticles in 10 mL of ethanol for 12 h. For preparation of MCM41-Fe_3O_4@Au-TAR and MCM41-Fe_3O_4@Ag-TAR, at first magnetic MCM-41 (MCM-41-Fe_3O_4) was synthesized [2] and then $HAuCl_4 \cdot 4H_2O$ solution and $NaBH_4$ (as a reducer agent) were added. The synthesized nanostructure (MCM-41-Fe_3O_4@Au-TAR) then was added to the cadmium ion solution and after 10 min extraction performed using a magnet bar. The separated mixture was washed 3 times with distilled water and finally dissolved in 2 mL of 1.0 mol. L^{-1} HNO_3 in methanol. The extracted solution was introduced into a flame atomic absorption device for determination of cadmium ion.

Conclusion: In this research, a comparison was performed among six types of magnetic nanoparticles for adsorption and preconcentration of cadmium metal ion. The results indicated that the magnetic nanoparticles of MCM41 had the best response due to possessing the extremely high specific surface area. Subsequently, the suggested method revealed a low detection limit of 0.11 nM for determination of cadmium metal ion using flame atomic absorption spectrometry technique. Also, the applicability of the proposed method was examined on the real samples of sea, wastewater water and urine samples.

Keywords: Magnetic nanoparticles; Complex ligand of TAR; Magnetic silica nanoparticles;Cadmium ion

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Determination of Lead metal ion using the nano-adsorbent of magnetic functionalized graphene oxide nano sheets - Humic acid and flame atomic absorption technique

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Background: The functionalization of magnetic graphene oxide nano sheets and binding humic acid as a lead-metal complex ligand have been investigated in this paper. Nano sheets of graphene oxide by possesing the high surface area as well as various carboxylic acid groups which can be activated easily by activator agents are the suitable choice for extraction of heavy metals. Humic acid, as a lead metal complex agent, has an amino functional group, which can be binded to the modified graphene oxide from one side. In this work, we optimized three main effective parameters such as pH, nano-adsorbent concentration and metal adsorption time by nano-adsorbent. The effect of these factors on the measurement of lead metal was investigated.

Methods: 10 mg of magnetic graphene oxide nano sheets was poured in 5 ml of NHS / EDC solution (0.05M / 0.05M) and it was stirred for 24 h to activate the carboxyl groups of graphene oxide nano sheets. Then, humic acid-ethanol solution (5% w/w) was added to the graphene oxide nano sheets activated and stirred for 12 hours. Then, the synthesized nanostructure was added to the lead ion solution and after 10 min extraction was performed using a magnet bar. The separated mixture was washed 3 times with distilled water and finally dissolved in 2 ml of 1 mol. L^{-1} HNO_3 in methanol. The extracted solution was injected into a flame atomic absorption device for determined lead ion.

Conclusion: In this study, we introduced a new method for trace determination of the heavy and toxic metal ion of lead in real samples by combination of nanotechnology and using a natural and biodegradation ligand. The nano - absorbent of graphene oxid-Fe_3O_4 - humic acid was designed to extract the trace amount of lead metal ion (0.07 μM) in the simulated samples. The extracted lead metal ion was injected to a flame atomic absorption device and the linear range of 0.2 - 12 μM for determination of lead was obtained.

Keywords: Functionalized; Magnetic graphene oxide;Flame atomic absorption;Humic acid;Fish; Oysters.

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Cysteine modified Ag_2S quantum dots as a resonance Rayleigh scattering sensor for selective determination of egg allergen Ovalbumin

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Background: Considerable attention has been attracted to quantum dots (QDs) as fluorescence and resonance Rayleigh scattering probes [1]. The biocompatibility, nontoxicity and small size is also important for labeling QDs. The use of QDs in biological labeling may be limited due to their large size, which would interfere with both the recognition between QD labeled bioprobes and target molecules. Thus, it is a great challenge to construct new QDs with less toxicity and small size for biodetection [2]. Ovalbumin is the most abundant protein in egg white comprising 58% of the egg white proteins. Therefore it can be used as a marker for the presence of egg contamination in food products. Under the current regulations, egg should be mentioned in the ingredient list on the food product label because the most common allergens in egg are chicken egg white proteins; ovalbumin, ovomucoid and lysozyme [3]. The quantum dots of silver sulfide coated with cysteine (Ag_2S-Cys QDs) were synthesized and used as a novel Rayleigh scattering (RRS) sensing system for measuring ovalbumin.

Methods: The Ag_2S-Cys QDs was synthesized during the two-step process. In the first stage, the silver-cysteine complex was formed under N_2 gas. Then, by adding sulfide ions to the silver-cysteine complex, the Ag_2S-Cys QDs were formed. The synthesized quantum dot and ovalbumin showed a very weak RRS peak. However when they were mixed at a suitable pH, silver sulfide and ovalbumin formed a complex and as a result, the RRS peak intensity was increased. This increase in signal was considered as the sensing response for ovalbumin.

Results: The effects of various factors such as pH, buffer type, Ag_2S-Cys QDs volume and time on the response of the system were evaluated and the optimum values were obtained: pH=5, 500 µL citrate buffer, 300 µL Ag_2S-Cys QDs, and 15 min for reaction time.

Conclusion: A RRS bioassay for ovalbumin determination was established. The increase in analytical signal was linearly proportional to the concentration of ovalbumin in the range of 20-1700 ng mL^{-1} under optimum conditions. The limit of detection was 7.14 ng mL^{-1} and the relative standard deviation for eight replicate measurements of 800 ng mL^{-1} of ovalbumin was 2.85%. The proposed method was successfully applied to determination of ovalbumin in cake and egg white samples with satisfactory results.

Keywords: Ag_2S quantum dot; Rayleigh scattering sensor; Ovalbumin.

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Developing a Miniaturized Cell Spectrophotometer Toward Single Cell Detection

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Background: There is a growing demand to create a battery- operated, portable, and low-cost device to do the *in-situ* measurments. However, designing a system to accomplish the point-of-care (POC) applications is still a difficult task because the existing systems need to consume low power and have a small size to do the whole stimulation and detection process of spectroscopy method [1,2].

Methods: Figure 1.A shows the miniaturized optical spectroscopy system. This optical sensor consists of an LED and LED driver, a black-plastic cap with a fiber and two tiny optical lenses to send and receive the light, a micro-spectrometer detector, and three compact layers of printed circuit boards (PCBs). The dimension of the fingertip spectrometer is 20.1 mm × 12.5mm × 10.1mm, and weights 5g (Fig. 1B). The device is used for the detection of cells tagged with Alexa Fluor488 and DAPI (Fig. 1C). It detects wavelengths ranging from 340nm to 850nm.

Results: These experiments are performed with several concentrations of cell to show the quantitative detection capability of the device. The results of this step including examined concentrations, their peak amplitude and wavelength, and source light are shown in Fig. 1D. The results exhibit that each concentration of targeted cells stained by the Alexa Fluor 488 produces a different peak wavelength. The minimum concentration detected by the proposed device is 89µM, and the linear detection range is in the concentration range of 89µM to 1mM.

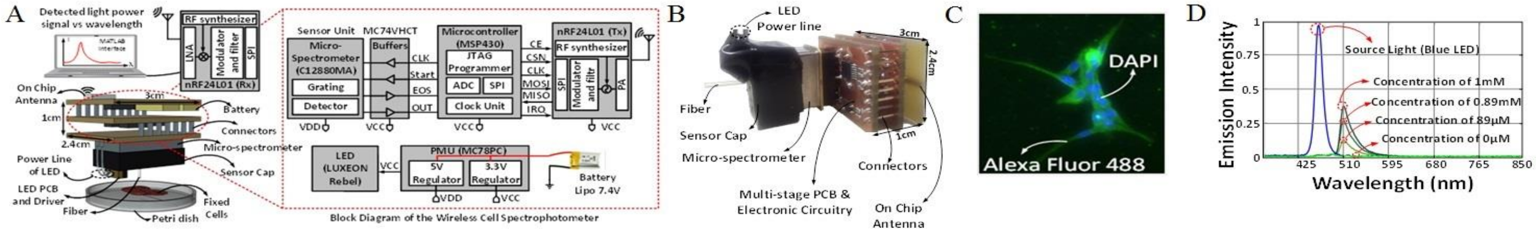

Fig.1. A) schematic of the device. B) Experiment setup. C) Test cells tagged with Alexa Fluor488 and DAPI. D) The results of different concenteration.

Conclusion: a wireless cell spectrophotometer interface for detecting tubulin protein as the primary antibody of VERO E6 cells tagged with DAPI and Alexa Fluor 488 as the secondary antibody, using commercial off-the-shelf components and a mini-spectrometer (C12880MA) is developed and utilized successfully.

Keywords: Miniaturized spectrophotometer; African green monkey tagged cells; Tubulin Protein Determination; Low power, Wireless, Point-Of-Care.

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Alizarin Red as a single colorimetric chemosensor for sequential determination of Cu^{2+} and arginine in aqueous media

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Background: Many of metal ions can play important roles in the detection of amino acids, for example, (1) they can represent the active sites for the interaction with amino acids. In the development of probes for amino acids, metal ions can serve as the binding site. (2) The metal center can interact with amino acid and give a convenient route for achieving strong binding. (3) Metal ions can also be used profitably as structural elements that help to bind the amino acids without exerting any direct interaction with amino acids [1, 2].

Methods: Herein, we have reported the application of Alizarin Red (ALR) as a colorimetric sensor of Cu^{2+} that the resulting interaction (ALR -Cu^{2+} complex) indicated photophysical changes upon the addition of Arginine (Arg) among other amino acids.

Results: The metal ions examined and color of ALR solution after addition of Cu^{2+} changed from orange to purple in aqueous media(10.0 mmol L^{-1} HEPES buffer solution, pH=7.0). The addition of Arg to ALR -Cu^{2+} complex showed significant color changes as well as the absorption bands at 500 nm. The ALR-Cu^{2+} complex solution showed a linear relationship to Arg concentration over the range from 1.19 to 107.9 μmol L^{-1}-.

Conclusion: Synthetic receptors are rather difficult to synthesize or are expensive instruments for detections. Taking this dilemma into consideration recently, we have undertaken an extensive research program to explore easily available dyes demonstrated a high chromogenic receptor for cations, anions, and amino acids [3-5]. In the current study, our group developed a simple and cost-effective colorimetric probe based on ALR for detection Cu^{2+}. Then, the interaction of ALR-Cu^{2+} complex could be used to selective, fast, and efficient sense arginine over available other amino acids. Importantly, the sensor can be successfully applied for the determination of Cu^{2+} and Arg in environmental, pharmaceutical, and serum samples

Keywords: Colorimetric chemosensor; Aqueous media; L-Arginine; Cu^{2+}.

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Single sensor for multiple analyte: Indigo Carmine as a selective colorimetric chemosensor for sequential determination of Hg^{2+}, Arginine and Glutathione in water media with biological applications

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Background: Amino acids (AAs) are important components in a range of chemical and biological systems. Their role as building blocks in living systems, has prompted increasing interest in their detection in various fields, such as chemistry, biochemistry and clinical chemistry [1]. The detection of environmentally and biologically relevant important analytes including amino acids has nowadays received considerable attention because of the involvement in a wide variety of biological processes [2].

Methods: Our approach is to use Indigo Carmine (IC) and IC–Hg complex, that the behavior of this dye has been studied for the first time in chromogenic sequential sensing of arginine (Arg), and glutathione (GSH) and for Hg^{2+} as a cationic species in an absolutely aqueous media.

Results: IC an efficient colorimetric chemosensor was afforded with a chromogenic selectivity for Hg^{2+} over other cations. The complex of Hg^{2+} with IC also displayed ability to detect Arg and GSH with color changes.

Conclusion: Synthetic receptors are rather difficult to synthesize or are expensive instruments for detections. Taking this dilemma into consideration recently, we have undertaken an extensive research program to explore easily available dyes demonstrated a high chromogenic receptor for cations, anions, and amino acids [3-5]. In this work, we disclose a new approach toward this goal. IC has been identified as highly sensitive probe for Hg^{2+} which responds at 0.21 µmol L^{-1} concentration levels. The complex of Hg^{2+} with IC also displayed ability to detect up to 0.15 and 0.3 µmolL^{-1} Arg and GSH, respectively. This novel method eliminated the need of separation processes, chemical modifications, organic co solvents, and sophisticated instrumentations.

Keywords: Colorimetric chemosensor; Hg^{2+}; Arg; Glutathione; Indigo Carmine, Aqueous media, Sequential sensing.

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Development of a highly sensitive and selective bulk optode for determination of Hg(II) based on a synthesized ionophore and chromoionophoreI

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Background: Today, measuring small amounts of organic and inorganic species, especially ions of heavy metals is very important in various environmental [1] and other fields, so different methods have been introduced. Among a wide range of methods, optical sensors have highly been regarded in the analytical chemistry [2-4]. Optodes enjoy several advantages such as good selectivity, high sensitivity, relatively fast response time, large response range, long life, low cost, small size, method of preparation and easy work that are influenced by the technique the membrane were stabilized reagent [5].

Methods: An optical sensor is introduced for the determination of mercury ions. The sensor is based on the interaction of Hg(II) with newly synthesized 1,15-diaza-3,4,1,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido)cyclooctade-cane-2,14-dione [6] as ionophore in plasticized polyvinyl chloride membrane incorporating chromoionophoreI as proton-selective indicator and sodium tetraphenyl borate as lipophilic anionic sites.

Results: The PVC membrane composition plus the other experimental variables being optimized, the detection limit is 3.81×10^{-11} M Hg(II), with a widely linear range 1×10^{-10} to 1×10^{-4} M and a response time <45s. The sensor can be easily and completely regenerated by dilute nitric acid solution.

Conclusion: The sensor showed excellent selectivity for Hg^{2+} with respect to several common alkali, alkaline earth and transition metal ions. The results obtained for the determination of mercury ions in river water samples using the proposed optode was found to be comparable with the well-established cold-vapor atomic absorption method.

Keywords: Bulk optode; ChromoionophoreI; 1,15-diaza-3,4,12,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido) cyclooctadecane-2,14-dione; Mercury(II)

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Combining the Dispersive Liquid-Liquid Microextraction and the Liquid Antisolvent Precipitation Methods to Develop an Efficient Extraction Method

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Background: In this work, an extraction method has been developed based on the dispersive liquid-liquid microextraction (DLLME) and liquid antisolvent precipitation (LAP) methods. In DLLME, an extraction solvent is mixed with a dispersive solvent and this solvent mixture is then rapidly injected into the aqueous sample [1]. The rapid injection of the extraction-dispersive solvent mixture produces a cloudy solution, formed of microdroplets of extraction solvent dispersed in the aqueous sample. Partitioning of analytes into the extraction phase is instantaneous due to the very high collective surface area of the droplets. This leads to very high enrichment factors and very low solvent consumption, relative to other liquid or solid phase extraction methods. On the other hand, LAP involves the formation of analyte particles in the solution by adding an antisolvent to the sample solution [2]. The driving force of a LAP process is the supersaturation of the solution produced by mixing the analyte solution and the antisolvent.

Methods: In the newly developed method, the extraction solvent in DLLME has been replaced with the antisolvent of LAP. Upon optimization of the chemical conditions such as pH, contact time, and temperature, the solubility of the analyte in the antisolvent is minimized so the analyte precipitates on the surface of the antisolvent nanodroplets which act as the nucleation site. Then, the precipitate is separated using centrifugation and is dissolved in a solvent for further UV-vis determination experiments. To evaluate the method efficiency, two model analytes (i.e. doxorubicin and methylene blue) were extracted and determined under the optimized conditions.

Results: The results showed that the method provides high efficiency in the determination of the investigated analytes in terms of the analytical figures of merits. The dynamic linear ranges for doxorubicin and methylene blue were 0.1-10 μM (LOD: 36 nM, R^2: 0.999, recoveries: 98.8%-95.3%) and 0.1-5 μM (LOD: 39 nM, R^2: 0.997, recoveries: 106.7%-108.2%), respectively.

Conclusion: In this work, a new efficient method for the extraction and determination of two model analytes was introduced which in the method, sensitivity was significantly improved while very low volumes of extraction solvent was used.

Keywords: Dispersive liquid-liquid microextraction; Liquid antisolvent precipitation; Separation; Determination; Doxorubicin; Methylene blue.

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A Novel Colorimetric Sensor for Determination of Cysteine based on Biosynthesized Silver Nanoparticles

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Background: Cysteine is an important amino acid containing a free thiol moiety in living systems. This sulphur-containing amino acids are essential biomolecules required for the normal growth of cells and tissues in living systems. For instance, a variance in normal levels of cysteine is implicated with several health problems such as slowed growth, hair depigmentation, lethargy, liver damage, muscle and fat loss, skin lesions, and weakness. Several analysis methods for the determination of Cysteine and L-Cysteine have been developed, such as high-performance liquid chromatography (HPLC) method, spectroscopic method, fluorescent and colorimetric analysis. Among the developed analytical methods, colorimetric assay has been attracted an ever increasing attention for point-of-care detection due to the advantages such as low cost, simple operation and feasible readout [1].

Methods: Herein we used biosynthesized silver nanoparticles (AgNPs) as a colorimetric sensor for detection and determination of L-Cysteine. AgNPs were synthesized by using curcumis melo juice as reducing and stabilizer agent, these AgNPs shown a sharp and intense surface plasmon Resonance band near 405 nm with yellow color. The as prepared AgNPs were characterized by Uv-Visible spectroscopy, X-ray diffraction, Fourier transformed infrared spectroscopy, transmission electron microscopy [2].

Results: The series of difference in absorbance of AgNPs before and after addition of cysteine were recorded for optimization condition (Tris-HCl buffer pH=7.0, response time 10 minutes), after addition of cysteine a color change was observed (yellow to light pink).

Conclusion: In this study a simple, safe, cost effective colorimetric sensor base on biosynthesized AgNPs were represented. This sensor had shown a good selectivity toward cysteine in compare other amino acids, special methionine and glutathione, with linear range 0.9 µM to 15.0 µM and limit of detection 0.3 µM. This sensor was used to measure cysteine in artificial urine sample.

Keywords: Colorimetric detection; Green Chemistry; Nanotechnology; Aminoacid.

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Colorimetric Determination of Cr (III) Ion based on Surface Plasmon Resonance Peak of Tartaric Acid-Capped Gold Nanoparticles

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Background: Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. Heavy metals include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), silver (Ag) and the platinum group elements. Chromium (Cr) potentiates the action of insulin and has been shown to restore glucose tolerance in malnourished infants. Several studies have shown that chromium supplementation lowers circulating glucose levels, increases plasma insulin, and produces a favorable profile of plasma lipids. It has been suggested that these effects may be due to a low molecular weight chromium-binding substance that may amplify insulin receptor tyrosine kinase activity in response to insulin [1].

Methods: First, 50.0 mL of 0.0400% $HAuCl_4$ solution was reduced by 6.0 mg $NaBH_4$ at room temperature in the dark for 25.0 min to yield colloidal gold particles. Then 1.4 mL L-tartaric acid 50.0 mM (L-Ta) solution as capping agent was added into the above solution, further stirred for 15.0 min [2]. TA was used as second capping agent for selective response to the chromium ions (Cr^{3+}). These AuNPs had shown a sharp and intense surface plasmon Resonance band near 540 nm with wine red color. The as prepared AuNPs were characterized by Uv-Visible spectroscopy, X-ray diffraction; Fourier transformed infrared spectroscopy, transmission electron microscopy

Results: To obtain optimum condition a series of difference in absorbance TA-AuNPs before and after addition chromium ions (Cr^{3+}) were recorded. Under optimum condition (borate buffer pH=7.0, response time 2 minutes) after addition Cr^{3+} ions, a color change from wine red to colorless was observed.

Conclusion: In this work we used TA-AuNPs as colorimetric sensor for detection and determination of Cr^{3+} ions. This sensor shown good selectivity and linear range 3.3µM to 16.0 µM with limit of detection 0.4 µM.

Keywords: Colorimetric detection; Green Chemistry; Nanotechnology; Heavy metal.

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A fully integrated lab on a smartphone: A compact miniaturized smartphone-based analytical device for point-of-care testing using a fluorescent nanopaper

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Background: The ubiquitous availability, ease-of-use, and other fascinating features of smartphones technology make them as promising platforms in (bio)sensing technology [1]. Despite recent progress in this filed, most exciting smartphone-based (bio)sensors have been limited to sensing and data analysis applications and other sample preparation steps including mixing, separation, centrifugation etc., are typically performed by usual laboratory equipment. Herein we developed an easy-to-use, cost-effective, portable, compact and miniaturized analytical device, which integrated the all main steps of a routine analytical procedure including mixing, separation, centrifugation as well as detection, onto a smartphone platform. To verify the applicability of the developed smartphone-based analytical platform it was utilized for point-of-care testing (POCT) of Phenylketonuria (PKU) through determination of L-phenylalanine (Phe) in blood samples using a carbon dots embedded in bacterial cellulose (BC) nanopaper.

Methods: The developed 3D-printed platform consists of three parts: detection part with a dark chamber with defined places for lamps and smartphone camera and a mobile application to measure the analytical signals; centrifugation part to separate (bio)chemicals and blood plasma; and stirring part for mixing purposes, which all integrated onto a smartphone platform.

Results: Using the 3D-printed smartphone-based analytical platform, the total process of blood plasma separation (>90% in less than 1 min), mixing(up to 1500 rpm), washing, centrifugation (up to 2500 rpm) and detection are fully performed using a smartphone. The developed smartphone-based assay kit for PKU diagnosis demonstrated two linear calibration intervals in the concentration ranges of 2–100 mg L^{-1} and 100–400 mg L^{-1} of Phe with a LOD of 1 mg L^{-1} and a RSD of 1.5% for 8 replicate measurements of 100 mg L^{-1} of Phe. The clinical applicability of the developed smartphone-based analytical platform was validated through comparing the results obtained from our developed device with the reference laboratory results for determination of Phe concentration in blood samples.

Conclusion: Building upon the interesting features of the developed lab on a smartphone as an easy-to-use, cost-effective, portable and miniaturized analytical device, it can be exploited in routine clinical/chemical laboratories and POCT, especially in resource-limited settings.

Keywords: Smartphone; miniaturized platform; point-of-care testing;nanopaper

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A tartrazine optical nanosensor fabricated by carbon dots embedded silica molecularly imprinted inorganic polymers for detection of artificial Saffron

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Background: Tartrazine (TZ) is a lemon yellow azo dye which is used in food industries. Although its usage, it can cause some disorders and toxicities in human body. Hence, finding a sensitive and selective sensor for simple and quick determination of TZ in food samples can be interesting. Currently, UV-vis, chromatography, electrochemical sensor and mass spectrometry were reported for analysis of TZ. These days, carbon dots (CDs), a new category of fluorescent nanomaterials has too much attention in fabrication of optical-nanosensors due to their high water solubility, eco-friendliness, low toxicity, photo-stability, symmetrical emission and simple synthesis[1]. In this study, fluorescent of CDs was applied as a probe to detect TZ. To have a selective detection it embedded in silicate based molecularly imprinted polymers (MIPs). Finally, proposed method was successfully applied for the detection of original and artificial saffron.

Methods: CDs was synthesized based on thermal pyrolysis method[2]. In order to coating CDs by MIP, individual proportion of APTES, TEOS and catalyzer were used. In order to eliminate template molecules, synthesized CD-MIPs were washed several times. Experimental conditions such as temperature and pH incubation time optimized for more sensitivity. Different concentration of target molecule can cause quenching emission. FT-IR, UV-vis, Fluorescence spectroscopy, TEM and SEM were used to characterization of CD-MIPs.

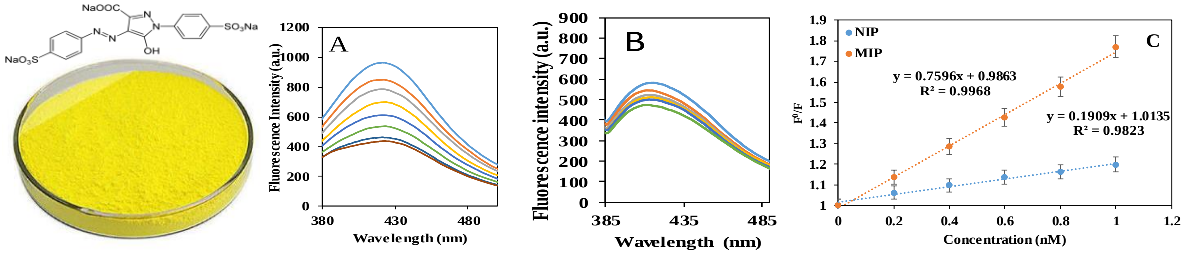

Fig. 1: (A) MIP (B) NIP spectrums and (C) calibration curve

Results: The synthesized CD-MIPs showed a remarkable response in linear range 2.36-10.68 µg L^{-1} with determination coefficient of 0.997 and detection limit 0.71 µg L^{-1}. RSD% for real sample is 3.5%.

Conclusion: In this work, a newly fabricated fluorescent nanosensor was introduced for detection of tartrazine in food samples. Selectivity, sensitivity, low detection limit, applicable linear range, cost effectiveness and facility of the method are some of highlighted features.

Keywords: Tartrazine; Food color; Fluorescence nanosensor; Carbon dots; Molecularly imprinted polymer

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An approach for determination of poly vinyl alcohol impurity in polymeric microballoon used in emulsion explosives

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Background: the use of micro balloon is important in the detonation properties of emulsion explosives (EMXs). The use of sensitizers with very light wall is important because It enables the development of models for the detonation mechanism of condensed explosives. Second, the addition of polymer micro balloons to (EMXs) makes it possible to produce compositions with a wider range of detonation characteristics than the characteristics of EMXs with other sensitizers [1]. Poly (vinyl alcohol) (PVA) is a polymer of great interest for various applications and starting materials for micro balloone[2]. There are various methods for determination of (PVA) such as gel filtration chromatography [3].in this work, we developed an easy and fast spectrophotometric method for determination of (PVA) in microballoones samples.

Methods: Poly vinyl alcohol (PVA)forms green complex with triiodide in the presence of acid boric. An aliquot of the solution containing 10-100 mg/L of (PVA), was transferred to the 10 mL balloons, the complexing reagent triiodide was add, and the complex was made in the presence of acid boric. The resulted product was diluted to volume with water and measurements was done at 665 nm against a reagent blank as the reference.

Results: Before proceeding with the analysis real samples, an optimization study was needed to ensure that the maximum efficiency was attained.Various factors and reaction conditions such as acid boric and reagent concentration, molecular weight of (PVA), pH, ionic strength werestudied and optimized. Under the optimization conditions the method was linear in the range of 10-100 mg/L. the detection limit was 5 mg/L.The recovery percent for the determination of (PVA) in micro balloons were closed to 100%.

Conclusion: This is for the first time that (PVA) was determined in micro balloons samples. A comparison of the proposed methodwith the previouslyreported methods for determination of (PVA) indicates that the proposed method issimpler than the existing methods. Proposed method gives a very rapid, simple,sensitive,and low cost spectrophotometric procedure for determination of (PVA) in a wide dynamicrange that can be applied to micro balloons samples.

Keywords: Poly vinyl alcohol; Triiodide; Micro balloon; Spectrophotometric determination

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A fast and simple approach for determination of titanium dioxide (TiO_2) in double base solid propellants based on UV-Vis Spectrophotometric method

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Background: Burning rate catalysts or burning rate modifiers are classes of materials that improve the burning rate of the propellant by adjusting the rate of burning at the burning surface. One of these catalysts is titanium dioxid (TiO_2) that has important roles in grain tailoring and also in desirable thrust-time curves. Its main role is reducing dependency of burning rate to temperature and chamber pressure, because creating plateau and mesa zones that modify ballistic properties [1]. Different method including of atomic absorption spectrometry [2] and inductively coupled plasma [3] have been reported for determination of (TiO_2). Therefore, we developed an easy and fast spectrophotometric method for determination of titanium dioxid in double based solid propellants.

Methods: The method is based on derivatization of (TiO_2) with hydrogen peroxide in the present of sulfuric acid and ammonium sulfate mixture. An aliquot of solution containing of 10-125 mg/L of (TiO_2) was mixed with hydrogen peroxide and the colored product was diluted to volume with the mixed solution of acid sulfuric and ammonium sulphate solution.The solution was transferred to a 1.0mL quartz cell forabsorbance measurement at 407 nm against a reagent blank as the reference.

Results: Various factors and reaction conditions such as hydrogen peroxide concentration and time of reaction,the effect of temperature on reaction were studied and optimized. Linearity was obeyed in the range of 10-125 mg/L of (TiO_2) and the detection limit of the method was 5 mg/L.The interference effects of some cations and anions were also tested. The proposed method was successfully applied to the determination of in double based solid propellant. The recovery percent for the determination of (TiO_2) in double based solid propellants were closed to 100%.

Conclusion: This is for the first time that (TiO_2) was determined in double based solid propellant samples. A comparison of the proposed method with the previously reported methods for determination of (TiO_2) indicates that the proposed method issimpler than the existing methods.The proposed method gives a very rapid, simple, sensitive and low-cost spectrophotometric procedure for determination of (TiO_2) in a wide dynamic range that can be applied to double based solid propellant samples.

Keywords: Titanium oxide, Spectrophotometric determination, Double based solid propellant

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Application of Cloud Point Extraction Technique to Preconcentration and Spectrophotometric Determination of TNT in Water Samples

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Background: The nitroaromatic compounds (NACs) are a group of explosives materials which have been widely used in army purposes, industries, mining and agricultural activities. A particular type of NACs is 2,4,6-trinitrotolune (TNT), that is commonly applied in the preparation of landmines for military and terrorist activities.Therefore, rapid detection and identification of TNT is a preference in criminology laboratories, improvised explosive device (IED), contaminated military sites and homeland defense applications [1].Various methodologies have been reported for identification or determination of TNT, including optical colorimetric sensors [2], fluorescent polymers[3].In this work we developed a new method for determination and preconcentration of TNT based on derivatization of it with tetra propyl ammonium hydroxide.

Method: The method is based on the color reaction of TNT with tetra propyl ammonium hydroxide in neutral media and cloud point extraction of the produced dye with Triton X-100, in the presence of NaCl electrolyte.The surfactant rich phase of this procedure was dissolved and diluted to 1.0 mL with ethanol and transferred to a 1.0mL quartz cell for absorbance measurement at 495 nm against a reagentas blank as the reference.

Results: Various factors and extraction and reaction conditions such as surfactant concentration and reagent concentration were studied and optimized. Linearity was obeyed in the range of 0.2-7 µg/mL of TNT and the detection limit of the method was 0.08 µg/mL. Preconcentration factor and enrichment factor were 4.1 and 3.86, respectively. The interference effects of some cations and anions were also tested.The proposed method was successfully applied to the determination of TNT in drinking, river, wellwater samples.

Conclusion: The proposed method gives a very rapid, simple,sensitive, and low cost spectrophotometric procedure for determination of TNT in a wide dynamic range that can be applied to water samples.The surfactant has been used for preconcentration of TNT,and thus toxic solvent extraction has been avoided. Triton X-100 was chosen for the formation of the surfactant rich phase. A comparison of the proposed method with the previously reported methods for determination of TNT indicates that the proposed method is simpler than the existing methods and that it provides a wider dynamic range and a lower limit of detection.

Keywords: TNT, Triton X-100, tetra propyl ammonium hydroxide, cloud point extraction, spectrophotometric determination

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Layered double hydroxide–assisted photogeneration of reactive oxygen species in luminol-based chemiluminescence system for trace determination of bisphenol A

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Background: Bisphenol A (BPA) is found in most of the water sources around the world and its toxicity is widely reported in literature [1]. Hence, it is very important to determine it in water samples as a substance that is related to human health. Among conventional analytical methods, chemiluminescence (CL) methods have attracted many attention because of a number of advantages, such as simplicity of the instrumentation, low operating costs, high sensitivity, wide linear range and the high selectivity [2]. The present work aimed to provide a new, simple, precise and efficient method based on layered double hydroxide (LDH)–assisted photogeneration of reactive oxygen species (ROS) as oxidants in luminol-based CL system for sensitive and selective detection of BPA in water samples.

Methods: The CoZnAl LDH was prepared by a co-precipitation method and characterized via X-ray diffraction analysis, scanning electron microscopy, Fourier transform infrared spectroscopy and diffuse reflectance spectroscopy. Several parameters affecting the analytical signal such as concentrations of luminol, NaOH and LDH as well as irradiation time were optimized. For CL measurements, an aliquot of 500 µL CoZnAl LDH sol solution and appropriate volume of real sample or standard solution were transferred into the CL cell and volume was reached to 2.0 mL with deionized water. Then, light irradiation of the mixture was carried out for 5 min under stirring. Finally, the CL reaction was progressed by injection of 1.0 mL of 1.5×10^{-3} mol L^{-1} luminol solution into the reaction cell and recording of CL intensity-time profiles at λ=425 nm.

Results: This simple CL approach showed a limit of detection of 30 pg mL^{-1} and exhibited a linear response in the concentration range from 0.1 to 20 ng mL^{-1}. The intra- and inter-day relative standard deviations were 2.7% and 4.1%, respectively and relative recovery values were obtained between 97.3 and 104.6% for the spiked water samples.

Conclusion: The presented method is based on the inhibitory effect of BPA on the chemiluminescence signal of the LDH-assisted luminol-based CL system in which the photogenerated ROS acts as oxidants in luminol-based CL system. It demonstrated high specificity, low detection limit and real sample analysis applicability.

Keywords: Bisphenol A; Layered double hydroxide; Photocatalyst; Light-initiated ROS generation; Chemiluminescence

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Application of NMR spectroscopy for investigation embryo culture medium samples during in vitro fertilization

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Background: The most important factor for a successful pregnancy after in vitro fertilization (IVF) is embryo quality. We present here a new metabolomic methodology to predict embryo implantation ability in IVF using 1H NMR spectroscopy. The culture medium is the immediate environment of the embryos in vitro, and a change of the substances in the culture medium is possibly related to the embryo quality [1]. One of the most common and widely used spectroscopic techniques for metabolomics is NMR spectroscopy. Based on magnetic properties of atomic nuclei, this technique provides a multivariate analysis approach by non-destructively examining intact tissue and biological fluids. NMR is intrinsically rich in information, offering structural and quantitative information simultaneously, with metabolite identification capabilities of even the most complex of mixtures, without the need of separation or sample preparation. An important aspect of NMR spectroscopy is that the fundamental physicochemical mechanism is completely different from other analytical techniques and provides a different scientific perspective [2].

Methods: A total of 35 patients scheduled at the gynecology clinic of Imam Khomeini Hospital in Tehran University of Medical Sciences, Tehran, Iran. Following the removal of the embryos in preparation for transfer, the culture medium on the third day was placed individually into labelled cryo-vials, snap frozen in liquid nitrogen, being stored at -80^{o}C. NMR spectra were recorded with a Bruker DRX-500 Avance instrument. Supervised classification method was applied to the spectra using soft independent modelling of class analogies (SIMCA) algorithm.

Results: Glutamate concentrations determined by 1H NMR were significantly higher in spent culture media of embryos that resulted in pregnancy and delivery compared to those that failed to implant. Similarly, viability indices calculated by 1H NMR using the weighted coefficients of glutamate and alanine/lactate ratio quantities were higher for embryos that implanted and resulted in a delivery. Classification accuracy of 96% was obtained using SIMCA algorithm.

Conclusion: Our results can allow building a quick, useful and feasible model in order to identify embryos with a high pregnancy rate and embryos unable to achieve successful pregnancies.

Keywords: Metabolomics; NMR spectroscopy; Embryo viability; Culture media; IVF

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Simultaneous Determination of some Common Food Dyes by Digital Image Analysis

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Background: Extraction of meaningful information from digital images by digital-image processing techniques is called image analysis and used for different purposes. Several techniques have been used for obtaining digital images such as digital color cameras and scanners [1, 2]. In recent years, mobile phone technology has rapidly advanced in terms of computational power and camera-resolution. They are portable, inexpensive, can provide simple and fast images. Recently, and then have been used as portable analytical devices [3, 4].

Methods: A simple and relatively fast method using digital images, obtained with a Smartphone, has been described. The method was used for determination of some food dyes, carmoisine, brilliant blue, sunset yellow, and quinoline yellow. To prepare the color spots of the dyes, the prepared solutions (30 µL) were spotted on Whatman paper, left for a while, and a digital image was taken using Smartphone camera. The images were saved in the bitmap format composed in the three channels of the RGB model using android RGB producer software. The magnitude of each component (red, green, and blue) was determined, and the color value was calculated by subtracting the suitable RGB channel intensities of samples from those of the white sheet. The parameters affecting the experimental results were optimized.

Results: Under the optimal conditions, the method provided acceptable linear ranges (30-250 mg/L) with correlation coefficients higher than 0.998, suitable precision (relative standard deviation ≤ 5%), and limits of detection between 5.43 and 7.64 mg/L.

Conclusion: The method has been successfully used for the simultaneous determination of four common food dyes, namely, carmoisine, brilliant blue, sunset yellow, and quinoline yellow, in binary mixtures without a need for any prior separation steps. The results demonstrated good performance of the Smartphone as an analytical instrument. The proposed method is inexpensive and the experimental setup and operating conditions are simple.

Keywords: Food dye; Image analysis; Simultaneous determination; Smartphone;

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Mesoporous functionalized based on carboxylic acid for drug loading

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Background: In recent years, substantial researches have been done in developing systems with porous materials like MCM-41 for drug delivery [1,2]. These materials have some significant properties such as stable structure of the porosities, their homogeneity, the high specific surface area, the adjustable size of the pores, the narrow range of the size distributions of the porosities, the minimum toxicity, the high stability, the biodegradability and the biocompatibility which have made them superior to the other drug carriers. Vallet-Regi *et.al* mesoporous MCM-41 have used for drug delivery of ibuprofen [3].

Methods: MCM-41 was synthesized and then functionalized via grafting by carboxylic acid group to obtain MCM-41@CA. Simple mixing performed the drug loading.

Results: The potential effect of parameters such as loading time, ultrasound irradiation and the dose of adsorbent were investigated by Box-Behnken design. The data of F_{values} linear, square and interaction regression F_{values} for MCM-41 and MCM-41@CA were obtained. Based on results it can be judged that the model is significant.

Conclusion: The highest effect is related to the dose of adsorbent, the mutual interaction effects between dose of adsorbent and ultrasound irradiation, dose of adsorbent and drug loading time, and ultrasound irradiation and drug loading time were statistically significant for drug loading.

Keywords: carboxylic acid group, Box-Behnken design, drug loading.

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Cu nanoparticles embedded on graphitic carbon nitride for spectrophotometric determination of fenitrothion and oxyfluorfen pesticides

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Background: Pesticides, a class of agricultural chemicals, are employed for pest control. Fenitrothion phosphorothioate known as a contact insecticide. This pesticide is used to restrain the sucking and feeding insect pests on cereals, rice and vegetables [1]. Also, oxyfluorfen is a contact herbicide used for controlling grassy weeds in a variety of field crops [2]. On the other hand, the pesticides have to be carefully used since they are dangerous for public health.

Methods: In this study, graphitic carbon nitride decorated by copper nanoparticles was prepared by using sodium borohydride for formation of Cu nanoparticles from the adsorbed Cu (II) on the graphitic carbon nitride. The catalyst was characterized by SEM, EDX-mapping, XRD and FT-IR. By using the catalyst, trace amounts of fenitrothion and oxyfluorfen were reduced to their amines in the presence of sodium borohydride. Then, the formed amines were diazotized and coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride in sodium dodecyl sulfate micellar solution to form the corresponding azo dyes to develop a sensitive colorimetric analytical method.

Results: Under optimum conditions, calibration curves were linear over the concentration ranges of 1-100 µmol L^{-1} and 1-40 µmol L^{-1} of fenitrothion and oxyfluorfen, respectively. Also, limit of detections were obtained 0.59 µmol L^{-1} (for fenitrothion) and 0.64 µmol L^{-1} (for oxyfluorfen). The relative standard deviations were found to be 4.7 and 5.1% for 20 µmol L^{-1} fenitrothion and oxyfluorfen, respectively. Moreover, this method was applied to the analysis of these pesticides in real samples such as lake water and commercial samples of the pesticides. As well, two HPLC methods as the standard reference methods were applied on the analysis of the samples. The results of the established method were in good agreement with the results of the HPLC methods.

Conclusion: An accurate, rapid and economic determination method was developed for fenitrothion and oxyfluorfen by using a new catalyst. The catalyst, graphitic carbon nitride decorated by copper nanoparticles, reduced the nitroaromatic pesticides to their related amines. A diazotization-azo coupling reaction was developed for accurate determination of the pesticides.

Keywords: Fenitrothion; Oxyfluorfen; Graphitic carbon nitride; Copper nanoparticles

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Visual Detection of Pentaerythritol tetranitrate (PETN) in Aqueous Solution Based on Aggregation of Gold Nanoparticles

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Background: Pentaerythritol tetranitrate (PETN) is an energetic material in plastic explosives and filling material in explosive caps, usable for military and civilian purposes. In spite of its high chemical stability, PETN is generally used in explosive mixtures with desensitizing additives because of its impact sensitivity [1, 2]. Ever-increasing needs for a secure society and green environment essentially require dramatic improvements in methods for the detection of PETN. Herein, we report a simple but sensitive method for the colorimetric visualization of PETN by using gold nanoparticles (AuNPs). The method is based on the color change of AuNPs induced by the donor–acceptor interaction between PETN and primary amines.

Methods: Citrate-capped AuNPs were synthesized according to the Turkevich method. Briefly, 50 mL of 1.0 mmol L^{-1} $HAuCl_4$ solution was heated to boil. Then, 5.0 mL of 38.8 mmol L^{-1} sodium citrate solution was added and the final solution was refluxed for 30 min. Different concentrations of PETN were added to the solution containing as-prepared AuNPs, NaCl, and the primary amine, respectively. After 10 min, the final solution (with a total volume of 1.0 mL) was transferred to a 1.0 cm cell to record the spectrum.

Results: The developed probe has been employed to measure the different concentration of PETN under optimum conditions. The calibration curve indicated that the absorbance ratio of A_{650}/A_{520} linearly depends on PETN concentrations in the range of 1.0 to 10.0 μmol L^{-1}. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated to be 0.169 μmol L^{-1} and 0.563 μmol L^{-1}, respectively.

Conclusion: A colorimetric strategy has been developed to detect PETN in aqueous solution. The proposed probe has shown no interruption from the co-exciting compounds and allowed for determination of PETN in soil and water samples. Compared to previous methods, our newly developed sensor possesses the advantages of simplicity, low cost, and providing the lowest reported LOD by a colorimetric probe.

Keywords: Pentaerythritol tetranitrate; Gold nanoparticles; Aggregation; Colorimetric detection

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Determination of acrylamide in heated foods using dispersive solid phase extraction using spectrophotometric method

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Background: Acrylamide (AA) is a toxic species for human health, and is a Maillard reaction product which forms spontaneously in heat treatment process of foods [1]. Therefore, a simple, fast and cost effective method was developed for the determination of acrylamide in processed foods.

Methods: In this research magnetic chitosan was successfully used as new dispersive solid phase extraction (dSPE) sorbent material for AA extraction in the determination of acrylamide in several foods using ultra violet-visible (UV-Vis) spectrophotometric method.

Results: This quantitative determination started with hydrolysing acrylamide in a strong basic condition to yield ammonia and acid salt. The optimum conditions of hydrolysis (concentration of the base used and time for hydrolysis) were also determined. From this study, the optimum conditions to hydrolyse acrylamide were achieved using 6.0 M of sodium hydroxide (NaOH) for 10 minutes. The hydrolysis process was characterised by monitoring the ammonia produced using Nessler's reagent through the formation of yellow colouration in the presence of ammonia [2]. In optimized conditions, the recovery ranged from 94.0% to 98.0% with the detection limit of 1.5 µg kg-1 with relative standard deviations (RSDs) of 1.2–4.1%.

Conclusion: A developed method was employed to determine acrylamide from heated foods.The effective parameters in UV-Vis determination of AA were optimized.magnetic chitosan had a high adsorption capacity.

Keywords: Acrylamide, Spectrophotometric determination, solid phase extraction, magnetic chitosan

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Silver nanoparticles capped with catechol and sulfanilic acid as a new Mo colorimetric sensor

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Background: In conventional synthesis of silver nanoparticles, glucose, sodium bromide hydride, and citrate ions have been used as reducing as well as dispersing agents [1-3]. in recent years, several colorimetric senses have been used to measure organic compounds such as amino acids, pharmaceutical compounds, and mineral cations such as Cu^{2+}, Mo^{6+}, Hg^{2+} in various samples. In this regard, one of the challenges in the application of silver nanoparticles is their lack of stability and, more importantly, the lack of selectivity. In the present work, we have used catechol and sulfanilic acid as appropriate organic reducer and stabilizer agents in synthesis of silver nanoparticles to develop a new sensitive and selective colorimetric sensor for detection of Mo in aqueous medium. By addition of Mo ions to silver nanoparticles solution, the absorbance of SPR band increases at around 400 nm and at around 500 nm absorbance decreases. The linear dynamic range of calibration curve and detection limit are 0.1 – 100 µM and 0.02 µM, respectively. The purposed method was successfully used for determination of Mo in Cement factory wastewater without significant interferences.

Methods: To prepare nanosilver-catechol sulfanilic acid, mix the 15 ml of the 0.01M caecule with 15 ml of 0.01M sulfanilic acid solution. Then place 10 ml of 0.01M silver solution on the prepared mixture and place at normal temperature for 24 hours and then centrifuge after 24 hours

Results: 2 ml of produced nanosilver indicate absorption in about 400 and 500 nm. As absorbance at about 400 nm exceeds 500 nm, gradually increasing by adding 0.001 M Sodium molybdate to the above nanosilver, the absorbance gradually increases at around 400 nm and at around 500 nm absorbance decreases.

Conclusion: The addition of molybdate enhances the SPR at about 400 nm and decreases it by about 500 nm and allows the measurement of molybden by colorimetry.

Keywords: Catechol; Silver nano-particles; Colorimetric methods; Heavy metals; Environmental samples; Reducing agent

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A Selective Fluorescent Nanoprobe Based on Graphene Quantum Dots and Hg^{2+} for Determination of Tetracycline

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Background: Recently, nano-materials have attracted intensive interest for determination a variety of inorganic and organic molecules. Graphene quantum dots (GQDs) as a new kind of zero-dimensional carbon nanomaterial, with oxygen-containing functional groups, can be significantly applied in florescent sensors [1, 2]. In addition, GQDs due to distinct advantages such as excellent biocompatibility, low toxicity, strong photoluminescence, and large surface area are promising alternative materials of the commonly QDs and carbon dots in sensing applications [3].

Method: For sensitive determination of tetracycline, 200 µL of **GQDs**, 100 µL of **Hg^{2+} solution, (1.0×10^{-3} mol L^{-1}),** 200 µL of phosphate buffer (pH = 8.0), and a proper volume of tetracycline solution **were added into** a 2 mL test tube. The solution was diluted to 1.5 mL with distilled water and incubated for 10 minutes. The Hg^{2+}-GQDs fluorescence intensity in the presence of tetracycline was measured at 463 nm (F). The fluorescence intensity of a blank solution was also measured at 463 nm (F_0). The relative fluorescence intensity ($F/F_0 - 1$) was used to calculate the fluorescence signal of the analyte.

Results: At optimized conditions, the linear relationship between the fluorescence signal and tetracycline concentration was obtained in the range of 3.0 to 44.0 nM. The limit of detection based on $3S_b/m$ (where S_b is the standard deviation of the blank solution and m is the slope of the calibration graph) was found to be 0.52 nM. The relative standard deviation at 20 nM concentration level of tetracycline was 1.9% (n = 6).

Conclusion: In summary, a rapid and cost-effective fluorescent nanoprobe based on GQDs and Hg^{2+} was developed for selective and sensitive determination of tetracycline. The proposed nanoprobe was successfully applied for the determination of tetracycline in urine and human serum samples.

Keywords: Tetracycline; Graphene quantum dots; Fluorescent nanoprobe; Hg^{2+} ions probe.

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SPMS – Quantitation Software For single particle- Inductively Coupled Plasma-Mass Spectrometry Data Processing Enabling Fast Access, Visualization and Analysis of Large Data Sets

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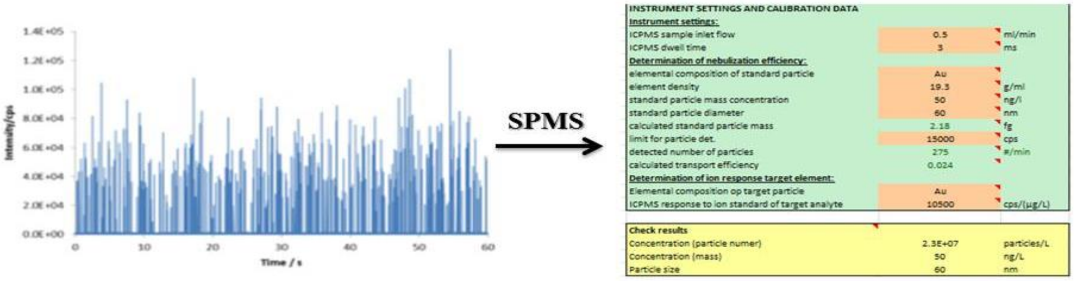
Background: Characterization of aqueous nanoparticle suspensions is now a robust field of science; however, application of available techniques to more complex, natural systems is hindered by numerous challenges including low nanoparticle number concentrations, polydispersity from aggregation, dissolution, and interference from other incidental particulates [1]. Single particle-inductively coupled plasma-mass spectrometry (sp-ICP-MS) as a novel emerging technology, has the potential to address many of analytical challenges when sizing inorganic nanoparticles in environmental matrices.

Methods: sp-ICP-MS measurements gathered in Time Resolve Analysis mode on the µs scale generates thousands of millions of data points, of which only a small percentage contains a nanoparticle event. The ICP-MS experts have developed their own algorithms and interfaces for data analysis. SPMS provides a user-friendly interface for processing raw data files in csv format from any ICP-MS instrument.

Results: SPMS provides some critical information about sp-ICP-MS measurements such as, plots, boxplots, calibration curve, histograms, critical value, limit of detection, transport efficiency by the particle size method and frequency method.(Fig. 1)



INSTRUMENT SETTINGS AND CALIBRATION DATA		
Instrument settings:		
ICPMS sample inlet flow	0.5	ml/min
ICPMS dwell time	3	ms
Determination of nebulization efficiency:		
elemental composition of standard particle	Au	
element density	19.3	g/ml
standard particle mass concentration	50	ng/l
standard particle diameter	60	nm
calculated standard particle mass	2.18	fg
limit for particle det.	15000	cps
detected number of particles	275	#/min
calculated transport efficiency	0.024	
Determination of ion response target element:		
Elemental composition op target particle	Au	
ICPMS response to ion standard of target analyte	10500	cps/(µg/L)

Check results		
Concentration (particle numer)	2.3E+07	particles/L
Concentration (mass)	50	ng/L
Particle size	60	nm

Fig1: Ag nanoparticles sp-ICP-MS signals and results processed by SPMS software by both particle size and frequency methods.

Conclusion: The program enables user into a quick, automated and streamlined method for accurate and simultaneous sp-ICP-MS data processing and provides key information about the nanoparticles. The implemented algorithm provides an excellent approach to avoid mild outliers and accurately estimate the size distribution and cover signals from nanoparticles for which the ionic component is not significant.

Keywords: sp-ICP-MS; Data processing; software development; Graphical user interface; Agilent Chemstation software; Size analysis.

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Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) For Protein Determination in real samples: Method Validation by LC-MS and 1D and 2D-NMR techniques

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Background: Determination of accurate protein concentration is a challenge for analytical chemists. Most protein quantification techniques like LC or CE, colorimetric assays and immunoassays cannot be considered as absolute because they also require a reference standard. ICP-MS is mainly used to analyze elements in environmental, geological, nuclear and pharmaceutical samples. However, it can also be used in biotechnology and proteomics [1].

Methods: Peppermint samples were collected from Mazandaran State. Leaves, roots and steams of plants were washed, air dried and then powdered (mesh 200). Crude extracts were extracted by an ultrasonic assisted hydro- alcoholic extraction at pH=3 for 24 h. Then the extracts were extracted by modified cellulose nanofiber sorbent. After the extraction Mn was eluted with HNO_3 1% and was analysed with Perkin Elmer Sciexe 9000 ICP-MS instrument in full spectrum mode.

Results: The effect of experimental parameters on the extraction performance including pH, volume and concentration of extraction solvent, pH and volume of elution solvent and amounts of sorbents were investigated. Under these extraction conditions, analytical figures of merits are: LDR= 0.1–3400.0 ng mL^{-1}, $R^2 \geq 0.9997$, LOD= 0.09 ng mL^{-1}, Recovery= 92.6%, RSD ≥1.5%, n = 10, and enrichment factor of 20. The proposed method was validated according to the ICH Q2 (R1) guideline [2]. This method was validated based on USFDA by cross experiments with LC-MS and 1D and 2D-NMR techniques.

Conclusion: In this work, low-cost cellulose nanofibers were applied to extraction of superoxide dismutase. This sorbent offers some advantages such as simplicity, low disposal costs, short time of extraction and rapid sample clean-up. The developed method can be applied in metabolomics studies.

Keywords: ICP-MS; Protein determination, Superoxide dismutase, Cellulose Nanofibers*; Peppermint, Method Validation.*

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Pre-concentration and speciation of chromium using a magnetic nano-composite based on nickel oxide/nickel ferrite/layered double hydroxide and flame atomic absorption spectrometry

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Background: Chromate ion is considered as one of the important environmental pollutants. Therefore, the development of an effective method for pre-concentration of chromate in environmental samples is important. Magnetic nano-composites are used to control and eliminate heavy metals from industrial effluents through the mechanisms of adsorption, ion exchange and electrostatic forces. This study is focus on the application of a magnetic nanocomposite (NC) based on nickel oxide/nickel ferrite/layered double hydroxide ($NiO/NiFe_2O_4$/LDH) as a sorbent for the solid-phase extraction and pre-concentration of chromate ion from industrial wastewater samples [1,2].

Methods: Ni-Fe LDH was performed using a facile hydrothermal method for 14 h at 140 °C. After being cooled to the room temperature, the product was washed several times with deionized water and absolute ethyl alcohol and dried in vacuum drying oven for 8 h at 60 °C. $3NiO$-$NiFe_2O_4$ NC was obtained after calcinating for 4 h at 500 °C. For preparation of $NiO/NiFe_2O_4$/LDH, appropriate amounts of Al and Ni nitrate salts was added into the solution containing $NiO/NiFe_2O_4$ and transferred final solution into the autoclave, which was heated at 140 °C for 6 h.

Results: The synthesized magnetic NC was demonstrated to be homogeneous, and having a magnetic property. The structure of magnetic adsorbent was investigated by XRD, SEM, TEM, FT-IR, and VSM techniques. Under the optimized experimental conditions (amount of adsorbent; 0.1 g, sample volume; 100 mL, 1 mL hydroxyl ammonium chloride 10% (w/v) as a suitable eluent, and adsorption and desorption times; 15 min), the calibration graph was linear in the concentration range of 0.2–100 ng mL^{-1}. The limit of detection and the pre-concentration factor were 0.06 ng mL^{-1} and 100, respectively.

Conclusion: Magnetite nanocomposite have high competency for solid-phase extraction of chromate from industrial wastewater, and extraction efficiency is reversely related to pH. The method was successfully applied for speciation of chromium in several real samples with relative recovery values between 94–104% for the spiked samples.

Keywords: Nickel oxide/nickel ferrite/layered double hydroxide; Magnetic nano-sorbent; Chromium; Speciation; Flame atomic absorption spectrometry; Wastewater samples

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5.Chromatography and separation methods

Synthesis and Preparation of a $Fe_3O_4@SiO_2@$Agarose Magnetic Nano-Adsorbent modified with Calmagite for the Extraction and Analysis of Biogenic Amines

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Background: Magnetic nanoparticles such as Fe_3O_4, have applications in many fields such as magnetic resonance imaging, immunoassay, medicine, biology, drug delivery and separation methods. The use of magnetic adsorbents in solid phase extraction (SPE), has been considered due to their separation from the solid phase by a foreign magnetic field [1-3].

Methods: In this work, agarose-coated Fe_3O_4/SiO_2 magnetic nanoparticles ($Fe_3O_4@SiO_2@$Agarose) modified with Calmagite were synthesized for the adsorption/desorption of biogenic amines such as Tryptamin using a magnetic solid phase extraction method. For this purpose, after synthesis of magnetic nanoparticles (MNPs) via a chemical precipitation method, the MNPs were homogeneously coated by a silica shell using a modified Stöber process. The particles were then activated by an epichlorohydrin method and functionalized with Calmagite. The prepared particles were then used for the extraction and UV-Vis. determination of the target analytes.

Results: The particles were successfully synthesized and characterized by field emission SEM, EDX and FT-IR. The effects of different parameters such as volume of sample, amount of adsorbent, pH of solution, and contact time were optimized by a central composite design (response surface) method and the effect of volume and type of eluent and desorption time were studied by a one-at-a-time procedure.

Conclusion: Magnetic solid phase extraction is fast, reliable, simple, sensitive and with a reasonable precision. The prepared $Fe_3O_4@SiO_2@$Agarose/calmagite nao-particles in this work could be successfully applied to the extraction and quantitation of biogenic amines.

Keywords: Calmagite, Biogenic amines, $Fe_3O_4@SiO_2@$Agarose, Magnetic solid phase extraction

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Electrospun polyurethane/graphene nanocomposite as a novel fiber coating

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Background: Solid-phase microextraction (SPME) was developed in early 1990s [1] as a solventless and simple technique to integrate extraction and pre-concentration of the compounds in one step. SPME procedure includes exposure of the SPME device to the headspace of sample or directly to the samples (liquid and solid). Herein, we developed polyurethane/graphene nanocomposite as a new SPME coating for extraction of volatile organic compounds (VOC) from water sample. Our goal is development of a sensitive technique using SPME fiber while providing a rapid and green technique. The nanocomposite was electrospun using a solution of polyurethane (PU) polymer containing dispersed graphene nanoparticles. The prepared coating showed good capability for extraction of trace amounts of PAHs along with acceptable precision and accuracy in real samples.

Methods: A manual home-made SPME holder containing the PU/G nanocomposite coating was used for headspace solid phase microextraction (HS-SPME) of VOC. In all experiments, 0.8 g sodium chloride was added to a 4 mL of water sample in a 10 mL vial containing magnetic PTFE coated stir bar. The extraction temperature was set at 45 ◦C by a circulating water bath. After 15 min, the SPME fiber was withdrawn into the holder and inserted into the GC injection port for thermal desorption and further separation and analysis.

Results: At the optimum conditions, the intra-day relative standard deviations for the determination of them in distilled water spiked at the levels of 50 ng L^{-1} were 2–5% (n = 3), the limit of detection is between 1 and 5 ng L^{-1}, and the calibration plots cover the 25 to 2500 ngL^{-1} range. The method was applied to the analysis of (spiked) water samples and relative recoveries were found to range from 99 to 104%.

Conclusion: Given the porous structure of the electrospun PU/G nanocomposite coating, high specific surface area with increased activated sites was achieved. The unique properties of the developed coating resulted in a short equilibrium time while providing the low ppt level of detection. The developed method based on the use of PU/G nanocomposite coating, is facile, simple, rapid and inexpensive to effectively apply for determination of CPs with sufficient sensitivity and reproducibility.

Keywords: Volatile organic compound; Gas chromatography/mass spectrometry, polyurethane /graphene Nanocomposite, Needle-trap extraction, Water samples

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Electrospun decyl-3-methylimidazolium mono bromate/ polyurethane nanofibers as solid-phase microextraction coating

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Background: Recently, the extraction of volatile organic compounds (VOC) from water sampling was widely performed by HS-SPME. The advantages of this approach compared with other conventional sampling methods are solventless, one step, rather rapid, sensitive, and economical [1]. The SPME technique was contained of the core part as substrate and a coating as a stationary phase. The main disadvantages of SPME core part based on fused silica is fragile its. To overcome this drawback, a number of home-made metal wire/tubing based SPME fibers were developed [2]. In addition, electrospun nanofibers with enhancing surface area have great analytical potential as an effective SPME coating. The morphology and construction of the electrospun nanofibers can be altered by changing the primary electrospinning process. In this work, we were investigated the effects of decyl-3-methylimidazolium mono bromated as well as other influencing factors on the structure and morphology of the electrospunnanofibers via the SPME coating for the pre-concentration of organic pollutants such as VOC from environmental water.

Methods: The SPME fiber containing IL/PU coating was first conditioned to eliminate contaminants in the GC inlet at 180 ^{o}C for 5 h. For this purpose, a manual SPME holder was manufactured for extraction/ desorption of organic compounds from water samples. Then, the SPME fiber was located in the sample headspace for 15 min. At this time, 4 mL of spiked aqueous sample in a7-mL vial containing 1.2 g of sodium chloride was stirred by a magnetic stir bar. After this time, the SPME fiber was retracted into the needle and immediately injected into the heated GC injection port for 3 min to desorb the trapped analytes.

Results: The limit of detections and limit of quantifications were obtained in the range of 0.5-0.9 and 2-5 ngL^{-1}, respectively, demonstrating high efficiency of the prepared nanofiber. The developed method also showed good repeatability, RSD 5–8% (n = 3), for the spiked aqueous solution at concentration level 50 ng L^{-1} of volatile organic compounds, and linearity, R= 0.997, in the range of 5- 1000 ngL^{-1}.

Conclusion: A decyl-3-methylimidazolium mono bromate/polyurethane was synthesized by electrospinning technique. The PU nanofibers at the presence of IL have thinner diameter and more porosity. The synthesized sorbent was applied for suitable isolation of VOC form various samples.

Keywords: Volatile organic compounds; Gas chromatography/mass spectrometry; Polyurethane/IL nanofiber; Ionic Liquid

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Electrospun polyethylene terephthalate / MWCNTs nanocomposite as a novel fiber coating

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Background: The fiber coatings of SPME have important roles at extraction efficiency, so developing new sorbent is great interest and significance [1]. The developments of fiber coatings are mostly focused on improving the mechanical, chemical and thermal stabilities, teaching diverse polarities and functionalities, and enhancing their extraction capacity [2]. One successful approach to prepare such nanocomposites is the electrodeposition of inorganic oxides in organic matrices via electrospinning. In this work, three novel polyethylene terephthalate/MWCNTs nanocomposites were individually electrospining on the surface of a stainless steel plunger and employed as the SPME fiber coatings. The nanofiber was developed as SPME coating for the pre-concentration of CBs pollutants. Also, the developed method was validated by gas chromatography /mass spectrometry (GC-MS).

Methods: The home-made SPME device containing PBT/MWCNTs fiber coating was first conditioned to eliminate contaminants in the GC inlet at 190 ^{o}C for 2 h. During the headspace extractions, the 4 mL of spiked aqueous sample containing 0.8 g of sodium chloride was continuously stirred by a magnetic stir bar at maximum stirring rate while the extraction temperature was controlled by a water bath. In the next stage, the SPME fiber was located in the sample headspace for 12 min at 45°C. Finally, the SPME fiber was retracted into the needle and immediately injected into the heated GC injection port for 3 min to desorb the trapped analytes.

Results: Under the optimal conditions, the detection limit results for double distilled water spiked with the selected CBs were 0.85–1 ng L^{-1} while quantification limit were found to be in the range of 3 - 5 ng L^{-1}, and the linear range was 5 to 2000 ng L^{-1} ($R > 0.9995$). The relative standard deviation (RSD) for five replicate extractions at a level of 50 ng L^{-1} ranged from 2 to 8%. The preparation reproducibility of three PBT/MWCNTs coating was good with the relative standard deviations (RSDs) ranging from 5 to 11% ($n = 3$) in the same condition. Finally, the PBT/MWCNTs coatings was applied for the extraction of CBs in Calan dam water and tap water at spiking trace-level of 50 g L^{-1} with relative recoveries ranging from 85 to 98%.

Conclusion: We developed a home-made SPME device based on a stainless steel wire substrate by the construction of MWCNTs into polybuthylene terephthalate (PBT) nanofibers structures as new coating, which is promising for the extraction of CBs from aquatic medium. The preparation of nanocomposite coating could be quickly accomplished in one step by electrospinning process. The electrospun PBT/MWCNTs nanocomposite coating due to non-smooth and porous structure, provides high specific surface area with increased activated sites.

Keywords: Electrospining, polybuthylene terephthalate/multiwalled carbon nanotubes; nanocomposite, Chlorobenzens; Gas chromatography/mass spectrometry; Aqueous samples

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Electrospun-based polyetherimide nanocomposite nanofibers coating for solid-phase microextraction

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Background: Solid-phase microextraction (SPME) integrates sampling and sample preparation in a single step, thus decreasing the analysis time, simplifying the analysis procedure, and offering the advantages of green chemistry. The applications of nanofiber as coating of SPME fiber are due to the need to improve the sorbent capacity and selectivity and to reduce the sorbent mass, while their tunable functionality and high filtration capacity are also of major concern [1, 2]. In this work, highly thermally stable PEI/silica nanocomposite was directly coated on a rotating stainless steel SPME needle and the extraction applicability of this new SPME coating was assessed by performing headspace solid-phase microextraction (HS-SPME) of some PAHs from aqueous samples using a homemade SPME device.

Methods: The fiber was conditioned daily prior to the extraction at 260 °C for 20 min. In all experiments, 1.2 g of NaCl was added to 4 mL of aqueous solution inside a 10 mL vial containing a magnetic stir bar and then the solution was spiked with the mixture of BTEX at 1 μg mL^{-1} for the optimization step. Afterward the vial was sealed with a PTFE-faced septum and an aluminum cap. The sample vials were heated in a circulating water bath while mixed by a magnetic stirrer. The headspace extraction was performed for 20 min at 45 °C. Then, the fiber coating was withdrawn from the vial and inserted into the GC injection port for thermal desorption at 250 °C for 3 min.

Results: The detection limits of the method under optimized conditions ranged from 5 to 10 ng L^{-1} using time-scheduled selected ion monitoring mode. The relative standard deviations of the method were between 3 and 6 %, at a concentration level of 100 ng L^{-1}. The calibration curves of selected analytes showed linearity in the range of 50– 1000 ng L^{-1}.

Conclusion: High thermal stability of PEI/silica nanocomposite up to 300 °C along with high surface area and highmechanical stability makes it an appropriate SPME coating. The fabricated SPME coating has good structural flexibility in spite of using a homemade SPME holder with poor alignment and the long lifetime of the coating was not limited by peeling off.

Keywords: Magnetic polyamide nanofibers, Fluorescence, Methamphetamine, Magnetic solid microextraction

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9-Undecylacridine modified silica as Stationary Phase of Liquid Chromatography with Reversed Phase, π-π and Anion Exchange Retention mechanisms

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Background: Mixed-mode chromatography is a type of chromatography in which at least two effective interactions exist among analytes and stationary phase [1]. The existing interaction type can be classified mixed-mode stationary phase into several groups [2].

Methods: The 9-undecylacridine was synthesized from Bernthsen's reaction [3]. The material was purified and characterized. In the making of the mixed-mode stationary phase, the 3-chloropropyltrimethoxysilane was reacted with silica. Finally, the product made of 9-undecylacridine is subjected to a reaction with a chlorinated reagent on silica. Mixed-mode the stationary phase has several effective groups as a conjugated ring, large hydrocarbon chain and anion exchange site. The extent several effective groups were created multiple interaction mechanisms (e.g. π-π, hydrophobic and ion exchange) among the analytes and the mixed-mode stationary phase.

Results: Stationary phase in the Silpr.9-UC.ec has a conjugative ring with π-π interaction property and hydrophobic hydrocarbon chain by creating an RP mode and which has an anion exchange site and can interact with the anion exchange. PAHs, Alkyl benzenes and inorganic anion were chromatographed to prove the mixed-mode property of the column.

Conclusion: The chromatographic parameters were calculated for PAHs, Alkyl benzenes and inorganic anions. The primacy of interactions in Silpr.9-UC.ec column was RP mode, π-π and anion exchange, respectively.

Keywords: 9-undecylacridine, Mixed-mode chromatography, π-π interaction, reversed phase, anion exchange

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Preparation and Characterization of a C_{18} Modified Column by 2-Methyl Indole as Mixed-Mode Stationary Phase in HPLC

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Background: The chromatographic performance of the stationary phase depends on its separation mechanism [1]. Mixed-mode chromatography combines both reversed-phase (RP) and ion-exchange (IEX) retention mechanisms [2].

Methods: C_{18} modified column contains an embedded the indole compound that combines the hydrophobicity chain-alkyl (C_{18}), Conjugative ring and anion exchange site (2-methyl indole). The specified amount of the indole compound was mounted on silica surface afterward C_{18} reagent used due to end-capping. The synthesized stationary phase was characterized by the elemental analysis, thermal analysis, and FTIR.

Results: The content of organic solvents in the mobile phase was optimized for all samples. Then, different analytes were chromatographed in optimal conditions. The chromatographic parameters are illustrated and compared in table 1.

Table 1. Chromatographic parameters obtained with the modified column in optimal condition.

Analyte PAHs	K	Rs	As	Analyte Alkyl benzene	K	Rs	As	Analyte Inorganic anions	K	Rs	As
Benzene	0.4	_	1.20	Benzene	0.3	_	1.06	Potassium Iodate (IO_3^-)	0.41	_	1.10
Naphthalene	0.8	2.14	0.84	Toluene	0.39	1	0.93	Potassium Bromate (BrO_3^-)	0.63	1.02	1.20
Acenaphthene	1.08	1.30	0.87	Ethyl benzene	0.52	1.17	1.00	Potassium Nitride (NO_2^-)	8.03	1.02	0.98
Fluorene	1.43	1.26	1.25	Propyl benzene	0.65	1.08	0.95	Lithium Nitrate (NO_3^-)	1.10	1.45	0.93
Anthracene	2.23	1.60	1.22	Butyl benzene	0.87	1.70	0.92	Potassium Iodide (I^-)	1.66	2.40	1.33

Conclusion: The stationary phase was designed to separation in addition non-polar compounds the inorganic anions and aromatic hydrocarbons.

Keywords: C_{18} modified column; 2-methyl indole; Mixed-Mode stationary phase; retention mechanisms;

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Potential of a Zn/Al layered double hydroxide nanosorbent for SPE-preconcentration followed by HPLC determination of naproxen in biological and wastewater samples

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Background: Naproxen (NAP) is a nonsteroidal anti-inflammatory drug and is used as a common pain reliever [1]. Nevertheless, water pollution by NAP affects human health and it is considered as an important menace of the environment, which must be monitored and controlled [2]. Solid-phase extraction (SPE) is one of the known methods in analytical chemistry used for the extraction and preconcentration of a target species. Different types of sorbents have been used is the SPE techniques, among them are layered double hydroxides (LDHs) with a variety of advantages [3]. In the presented study, the Zn/Al LDH was synthesized and characterized [4]. The prepared LDH was applied for the preconcentration of NAP.

Methods: Zn/Al LDH with carbonate interlayer anions was synthesized, based on a co-precipitation method, and it was characterized by FTIR, XRD, FESEM and BET methods. A univariate sequential optimization procedure was applied for optimization of the parameters affecting the adsorption of naproxen in aqueous samples. The analysis of NAP was performed by HPLC.

Results: The parameters affecting the preconcentration efficiency of NAP by the proposed method with their optimal values were: sample pH 7.0, Adsorbent dose 150 mg, eluent (NaOH) concentration 1.0 mol L^{-1}, Eluent volume 2 mL and sample volume 100 mL. Under the optimal experimental conditions, the calibration plots for the determination of NAP in hospital, pharmaceutical wastewater and human urine samples were linear in the ranges of 6-530 (R^2 = 0.999) and 9-440 (R^2 = 0.997) µg L^{-1}, respectively. The corresponding limits of detection were found to be as 0.35, 2.4 µg L^{-1}, and the evaluated preconcentration factor was 40 for all samples approximately.

Conclusion: A method for the determination of trace amounts of NAP on a batch solid phase extraction using a Zn/Al LDH followed by HPLC detection was developed. It was suggested that the adsorption is taken place via an anion exchange mechanism between the carbonate interlayer anions of the LDH and the anionic form of NAP. The proposed method showed an acceptable recovery values, good linearity, reasonable and repeatability, applicable for determination of NAP in the environmental and biological samples.

Keywords: Layered double hydroxide; Naproxen; Solid phase extraction; HPLC; Real samples.

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Determination of Fluoride in Water Samples After Preconcentration via Solid Phase Extraction Method and Investigation the Adsorption Isotherm

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Background: Fluoride ion in drinking water with the concentration 0.5-1 mg L^{-1} is useful for human health [1], but according to World Health Organization (WHO) guidelines maximum acceptable fluoride concentration in drinking water is 1.5 mg L^{-1}. Due to the relatively little difference between useful and harmful level of fluoride concentration in drinking water, exact determination of fluoride concentration in drinking water is really important.

Methods: Preparation and characterization of the adsorbent was performed according to procedures have been described in our previous work [2]. Fluoride ion was adsorbed by the adsorbent, then it was eluted with sodium hydroxide solution. After alkanity neutralization, Ca^{2+} ions were added to the elution, therefore in the elution containing fluoride ions, CaF_2 precipitate is formed. Absolutely, remained Ca^{2+} ions concentration in the elutions with different fluoride concentrations will be different. Calcium ion concentration of the elutions was determined by FAAS and it was related to fluoride concentration of the elutions. The effective parameters in SPE were investigated (fig. below). Also four isotherm models including Langmuir, Freundlich, Temkin and Dubinin- Radushkevich models were applied to find the best model which fitting the experimental data.

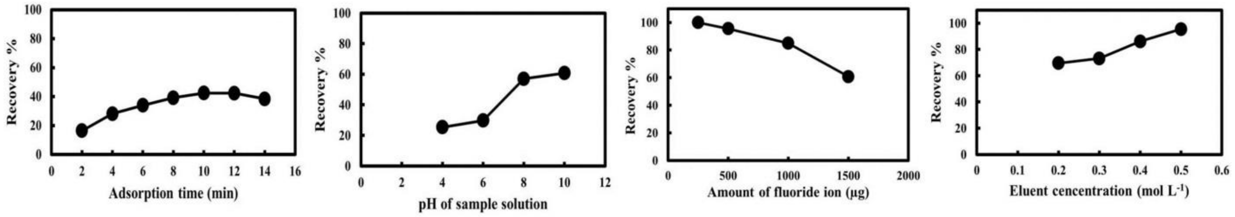

Fig. Optimization results.

Conclusion: Accuracy of the method was established via comparision between the results with those of ion selective electrode. The results were in agreement with those of ion selective electrode method. Fluoride concentration in some real water samples were determined by the proposed methods which were lower than the WHO guideline.

Keywords: Fluoride; SPE; FAAS; Adsorption Isotherm

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Preparation of carbon nitride reinforced polyamide nanocomposite as a thin film for ultrasound assisted microextraction of bisphenol A followed by gas chromatography

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Background: Recently, nanocomposites (NCs) due to their unique properties have received more attention in various fields of research [1]. Graphitic carbon nitride (g-C_3N_4) is a promising semiconductor nanomarial receiving more attention in various field due to its mechanical thermal, chemical and photochemical stability, because of its tri-s- triazine-based building blocks and strong covalent bond between carbon and nitrogen atoms [2]. g-C_3N_4 was applied as nanofiller in this work because of its high surface area, chemical and mechanical stability.

Methods: g-$C_3N_4$was synthesized by thermal condensation on urea in furnace. After successful synthesis of g-C_3N_4, it was used as nanofiller for preparation of g-C_3N_4 doped polyamide (g-C_3N_4/PA) nanocomposite through solvent blending method [3]. Then, the obtained films were used for ultrasound-assisted thin film microextraction (USA-TFME) [4] of bisphenol A (BPA) from mineral water samples followed by gas chromatography-flame ionization detector.

Results: The synthesized g-C_3N_4 was characterized by X-ray diffractometry, Fourier transform infra-red spectroscopy and the obtained results confirmed the successful synthesis of g-C_3N_4. The morphology and surface characteristics of the prepared thin film also was studied by scanning electron microscopy. The g-C_3N_4 doping level into NC was studied and the obtained results have revealed that 15 % g-C_3N_4 has led to the higher extraction efficiency. Other influencing parameters were studied and optimized. Based on the method validation, the linear dynamic ranges were in 0.6-500 ng $mL^{-1}$and the method precision (RSD %) with six replicates determinations was 6.5 %. The developed method was applied successfully to determine BPA in the mineral water samples; accordingly, the obtained high relative recoveries (RR %), indicating the negligible matrix effect and successful application of the developed method for determination of BPA in these real samples.

Conclusion: The incorporation of g-C_3N_4 into the bulk of PA can leads to higher extraction capability due to the increase of specific surface area and multi-functionality of NC. According to the obtained results, the g-C_3N_4 doping level of 15 % has been led to the best results. Furthermore, analytical data confirm that g-C_3N_4/PA-based sorbent is a suitable candidate as a TFME sorbent for extraction and determination of organic compounds with sufficient sensitivity and reproducibility.

Keywords: Ultrasound-assisted thin film microextraction, Carbon nitride, Polyamide, Bisphenol A.

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Head-space hollow fiber protected-liquid phase microextraction for the determination of alkylpyrazines in cocoa samples

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Background: Alkylpyrazines (APs) are a class of the principal cocoa aromatic compounds which are produced by non-enzymatic browning reactions between amino acids and reducing sugars via thermal treatment [1]. The pyrazinic ratio which is defined as the ratios between the concentration of some APs on the volatile fraction of chocolate and cocoa are considered as an important parameter for assessment of these products quality [2]. Therefore, it is required to determine APs in cocoa derived products applying a sensitive and selective analytical method.

Methods: Considering the high volatility of studied APs, the head space (HS) mode was selected for performing the proposed hollow fiber protected liquid phase microextractio (HFLPME) method [3]. First, 2 cm segments of hollow fiber membrane (HFM) was mounted on a stainless steel wire and was immersed in n-octanol as extracting media for a few seconds. Then, it was placed on the head space of sample solution for 20 min while the sample solution was agitated at **600 rpm. After performing the extraction, the desorption step was conducted by immersing hallow** fiber segment in 100 µL methanol and sonication for 5 min. Finally, 1 µL of it was introduced to the GC-FID injection port.

Results: Important parameters influencing the HS-HFLPME process including extraction time, extraction temperature, salt content and desorption solvent volume were optimized applying central composite design (CCD). Considering the method validation, developed method linear dynamic ranges were 1- 200 and 5-500 ng mL^{-1} for various analytes and the limits of detection (LODs) were in the range of 0.3 to 1 ng mL^{-1}. The method precision (RSD %) was evaluated by six replicate experiments and RSD % values were obtained in the range of 0.8 to 8.2 % for the distilled water (100 ng mL^{-1}). The developed method was used successfully for measurement of AP compounds in cocoa and chocolate-milk samples and the relative recovery percentages (RR%) in the range of 71.7 to 110.5% were obtained.

Conclusion: Analytical performance of the developed method has indicated that it has relatively low LODs, high repeatability and rather good linear dynamic range, showing the success of this method application for the determination of APs. Additionally, the relative recovery percentages indicate the relatively low matrix effect and the applicability of the developed HS-HFLPME-GC-FID method for the measurement of APs in the chocolate-milk and cocoa powder samples.

Keywords: Hollow fiber protected liquid phase microextraction; Head-space, Alkylpyrazines; Central composite design; Gas chromatography; Food samples.

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Determination of Guaifenesin in Biological Samples by Molecularly Imprinted Solid Phase Extraction Followed by UV-Vis Spectrophotometery

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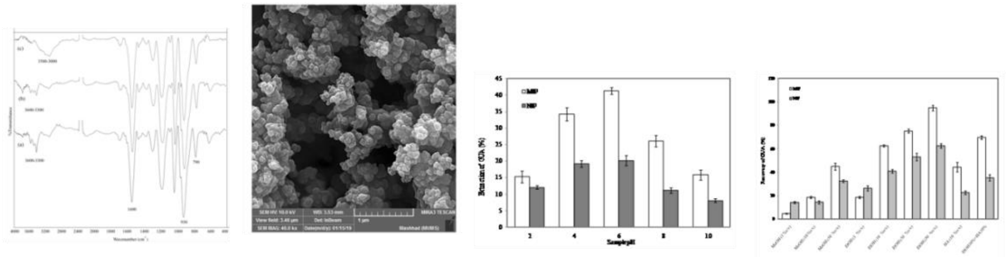
Background: Chromatography (HPLC, LC-MS, and GC) and electrochemical methods are used in determination of Guaifenesin (GUA). The identification can be made based on its characteristic UV absorbance but sample matrix produces significant challenge during development of an accurate assay. Generally, extraction and clean-up are crucial stages prior to instrumental analysis [1].

Methods: A molecularly imprinted polymer (MIP) was synthesized via chemical oxidation of pyrrole as monomer [2] and used as adsorbent in the molecularly imprinted solid-phase extraction (MISPE) followed by spectrophotometric determination of GUA.

Results: The prepared MIP was characterized through FT-IR and SEM analysis. GUA was quantitatively adsorbed on the MIP at pH 6.0 and eluted with an ethanol-water solution (50 %v/v) with an enrichment factor of 4 (Fig. 1). The recoveries of %87.0-95.0 were obtained and SPE columns can be sued for up to 6 consecutive elution-loading cycles.



(a) (b) (c) (d)

Fig. 1 (a) FT-IR and (b) SEM images of the prepared MIP and the effect of pH (c) and elution solvent (d) on the recovery of GUA

Conclusion: Under the optimized MISPE conditions, MIP can selectively extract and enrich GUA in different pharmaceutical formulations and biological samples. The method successfully detected trace GUA (3.0×10^{-6}-1.5×10^{-4} mol L^{-1}) with an LOD value of 1.4×10^{-6} mol L^{-1} and LOQ value of 4.5×10^{-6} mol L^{-1}. The results showed RSD values of 5.24% for runs between days and 3.21% for runs within the same day (n=3).

Keywords: Molecularly imprinted polymer; Guaifenesin; solid-phase extraction; pyrrole, UV-Vis spectroscopy

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Determination of clozapine and quetiapine in complicated matrices by membrane microextraction followed by high performance liquid chromatography

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Background: The atypical antipsychotic drugs such as Clozapine (CLZ) and quetiapine (QTP) are widely prescribed for treatment of schizophrenia and other psychotic syndromes, due to show less side-effect than the primary usual antipsychotics, they are prescribed more frequently. Determination of these drugs has a significant interest in forensic toxicology due to their abusive applications as intoxications and suicides [1, 2].

Methods: The method includes a simple extraction chamber and is a three-phase microextraction which according to it, the target analytes are extracted from sample solution (10 mL) into an aqueous acceptor solution (100 µL) through an organic solvent (1-octanol, 15 µL) which is supported by a membrane. The donor phase is circulated and agitated during the extraction process, at the end of the extraction, acceptor solution is transferred to the sample loop of the HPLC system for analysis of it.

Results: The method was evaluated under the optimal conditions, it showed remarkable limits of detection (0.3-1 ng mL^{-1}), good linearity range of 1.00-800 ng mL^{-1} and an excellent repeatability (RSD below 5%, n=5). The method provided a high efficiency for determination of understudied drugs in the human urine and plasma samples.

Conclusion: In this work, a selective continuous flow membrane microextraction coupled with high-performance liquid chromatography for the efficient determination of clozapine and quetiapine in biological fluid samples including urine and plasma samples. High sample clean-up, good preconcentration factor and suitable compatibility with the sensitive analytical instruments such HPLC were obtained by the method. The unique design of extraction chambers which provides a high mass transfer rate and reduction in mass transfer resistance causes the great ability of direct analysis of urine samples and also high viscous samples such as human plasma by only 10-fold dilution.

Keywords: Membrane microextraction; clozapine; quetiapine; HPLC.

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Isolation A Plant Toxic Protein from Milk by Affinity Chromatography and Identification Using Liquid Chromatography Tandem Mass Spectrometry

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Background: The aim of this work was isolation and analysis of a plant toxic protein (ricin) from milk using affinity chromatography. Because of low LD50 (5 to 10 μg/kg and 1 to 20 mg/kg through inhalation and ingestion), its toxicity and stability, ricin is considered as a potential bioterrorism agent especially in foods [1]. Ricin is a 60 kDa protein, originates from castor beans and has two chains. The B-chain has affinity to cell surface galactose receptors, binds to them and facilitates a transport of the A-chain across the cell membrane that halts protein synthesis and results death of cell [2]. This characteristic of the B-chain is used for isolation of ricin [3]. The most reliable technique for unequivocal identification, is detection of its specific peptides after enzymatic digestion, using LC-MS/MS technique and MRM method [4].

Methods: Casein in a contaminated milk, was precipitated at acidic pH. Lactose interference in whey part, was removed by washing, using 10 kDa centrifugal cutoff filter. The protein mixture was subjected to galactose affinity chromatography on acidic treated sepharose 4B. Bounded ricin was desorbed by elution with 0.1 M lactose in PBS. After enzymatic digestion (trypsin) and clean-up, 4 unique peptides specified for ricin, from A-chain and B-chain (T5A, T7A, TB14-ss-TB16, T24A-ss-TB1) were identified using LC-MS/MS technique and MRM method.

Results: The protein toxin ricin, unequivocally identified using LC-MS/MS and MRM method from a contaminated milk (25 ppm) after isolation and digestion. After tryptic digestion the concentration of digest peptides is typically in the ppb (from a ppm ricin solution) range.

Conclusion: A plant toxic protein was isolated from milk by galactose affinity column. Peptide analysis of digested protein was performed using LC-MS/MS and MRM method.

Keywords: Affinity chromatography; Protein; LC-MS/MS; MRM.

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Determination of triptans in complicated matrices by continuous flow three-phase microextraction coupled with high performance liquid chromatography

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Background: Migraine is a primary headache disorder, and the symptoms associated with it are nausea, anorexia, photophobia, and vomiting. Migraine affects about 15% of the world's population and usually begins in the childhood, puberty or early adult life. Triptans are a family of tryptamine-based medications applied as efficient drugs in the therapy of cluster headaches and migraines. The drugs of this class act as agonists for the serotonin 5-HT1D and 5-HT1B receptors at the nerve endings in the brain and blood vessels, and there are good evidences regarding their efficacy, tolerability, and safety. These drugs are widely used, and existence of reliable, accurate, and simple methods for the determination of them in the human biological samples is a necessity [1, 2].

Methods: This method is a liquid membrane-based microextraction one. An organic solvent (1-octanol, 15 µL) in a micro-porous polypropylene sheet separates the donor and acceptor chambers. The donor phase (10 mL, pH 13.0) is circulated in the donor chamber using a peristaltic pump. The basic target analytes are extracted from the donor phase into the organic mediator, and are subsequently, selectively back-extracted into the aqueous acceptor solution (75 µL, pH 2.0).

Results: Under the optimized conditions good limits of detection (1–1.5 ng mL^{-1}) and an excellent extraction repeatability (RSD < 4.7%, n = 5) were obtained. The developed method provides the preconcentration factors in the range of 44-48 and linearities in the range of 5–2000 ng mL^{-1} (R^2 above 0.997).

Conclusion: A sensitive and selective three-phase method coupled with high performance liquid chromatography for simple determination of the anti-migraine drugs rizatriptan and zolmitriptan in human plasma and urine samples was introduced. The ability for urine analysis without any sample dilution and the analysis of highly viscous human plasma with only 6-fold dilution are the exceptional features of the work.

Keywords: Three-phase microextraction; Rizatriptan; Zolmitriptan; Human biological samples.

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Determination of Methanol and Ethanol in Insulation Oils Transformers from Sarkhoon and Qeshm Gas Refinery Company after Headspace Single-Drop Microextraction by Gas Chromatography

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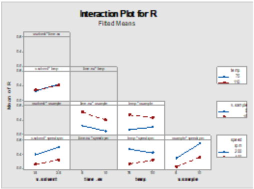
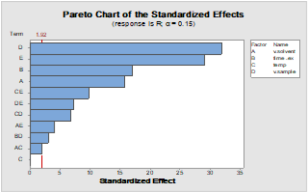
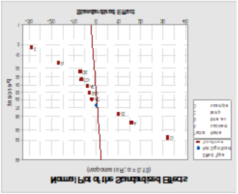
Background: Methanol and ethanol in transformer oils have been recently proposed as new markers of thermal and mechanical degradation of cellulose (the solid insulation in power transformers) [1]. The age of a transformer is evaluated by the health of its solid insulation. Indeed, the extent of insulation paper degradation is determinative of the remaining life of a solid insulation and subsequently a transformer. On the other hand, the advantages of using methanol and ethanol are the independency of the markers production from the type of the insulating paper, their early detection, and also stability of the markers over the transformer operating temperatures [2].

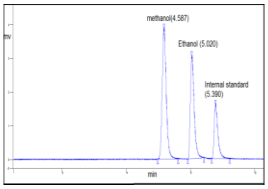
Methods: The headspace single-drop microextraction (HS-SDME) method coupled to gas chromatography with flame-ionization detection (GC-FID) was used for direct determination of methanol and ethanol in insulation oils transformers. The factors influencing the extraction process including extraction solvent, microdrop volume, extraction time, sample amount, stirring speed were studied. Screening and optimization of the microextraction system was carried out using design of experiment method (DOE) using Minitab software.

Results:10ml of oil sample was heating for 20 min at75°C prior to the extraction, then extraction was carried out with 2.5 µl of dimethyl sulfoxide (DMSO) as the microdrop for 5min and injected to the GC inlet, subsequently. For methanol and ethanol, the linear range and detection limits were respectively, 1 – 100 mg L^{-1} and 200 µg L^{-1}. A typical chromatogram of spiked oil sample and some of obtained curves for screening section of DOE method were shown as below.









Conclusion: HS-SDME is a useful technique for direct determination of methanol and ethanol in insulation oils transformers due to its sensitivity, low cost and low detection limits.

Keywords: Gas Chromatography; Insulation Oils; Headspace; Single-drop Microextraction; Design of Experiment

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Determination of Lamotrigine by Fluorescence Quenching of N-doped Graphene Quantum Dots after its Solid Phase Extraction using Magnetic Graphene Oxide

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Background: The selection of a suitable nanoprobe is important for the fabrication of a sensitive sensor. Graphene quantum dots (GQDs) have exhibited special abilities for the detection of different targets in sensing applications [1]. The fluorescence quantum yield of GQDs is often low. The fluorescence properties of GQDs can be improved through their heteroatom-doping [2]. A separation/preconcentration method including magnetic solid phase extraction is often required for determination of trace levels of a target molecule in complex matrices [3].

Methods: N-GQDs was synthesized according to the previously reported method [4]. Magnetic graphene oxide was applied as the sorbent for solid phase extraction of lamotrigine. For preconcentration and determination of lamotrigine, 30 mg of prepared sorbent was added to 200 mL of the sample solution containing not more than 3.0 µg of lamotrigine. The solution was stirred for 20 minutes and the sorbent was separated with the help of a magnet. Then, the sorbent was eluted with 500 µL of acetonitrile and the extracted analyte was determined by spectrofluorimetry at 440 nm.

Results: The calibration graph demonstrated linearity in the concentration range of 2.0-45.0 µg L^{-1} with a determination coefficient (r^2) of 0.9952. The limit of detection (LOD) based on $3S_b/m$ (where S_b is the standard deviation of the blank solution and m is the slope of the calibration graph) was 0.39 µg L^{-1}. The relative standard deviation (RSD) was found to be 2.4% (15 µg L^{-1} of lamotrigine, n = 6)

Conclusion: A novel effective analytical method was presented based on the combination of magnetic solid-phase extraction and fluorescence techniques for the preconcentration and determination of lamotrigine. N-GQDs are utilized as a fluorescent nanoprobe. The fluorescence nanoprobe shows a good selectivity and sensitivity for lamotrigine. The developed method was successfully applied for the determination of lamotrigine in urine and serum samples.

Keywords: Lamotrigine; Magnetic graphene oxide nanoparticles; Nitrogen-doped GQDs; Fluorescence nanoprobe

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Highly selective determination of amphetamine and methamphetamine in biological fluids by continuous flow three-phase microextraction followed by high performance liquid chromatography

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Background: Sample treatment has a key position in modern analytical chemistry. The tendency to measure low concentrations of analytes in complex matrices and the incompatibility of most samples with analytical instruments cause the sample treatment step to be an integral part of most analytical methods. In this work, an efficient microextraction device with a simple design was coupled to high performance liquid chromatography (HPLC) for the selective and sensitive determination of amphetamine and methamphetamine in complicated matrices [1, 2].

Methods: The sample solution was circulated into the extraction cell using a peristaltic pump. Amphetamine and methamphetamine, as the model compounds, were extracted from the donor phase (10 mL), adjusted to the basic condition through a supported liquid membrane (1-octanol), and finally, into an acidic acceptor solution (75 μL). The design of the cell causes to speed-up the extraction, introduces an excellent repeatability, and provides a distinguished efficiency in complicated matrices.

Results: The method provided a considerable repeatability (relative standard deviations below 2.9%), and it exhibited a wide linear range (5.0–2000 ng mL^{-1}). The detection limit obtained was equal to 1 ng mL^{-1}, and the enrichment factors were in the range of 54-65.

Conclusion: An efficient microextraction device was coupled to high performance liquid chromatography (HPLC) for the selective and sensitive determination of amphetamine and methamphetamine in biological fluids. This method simultaneously provides all of the sample treatment aims. It provides a very high sample clean-up and a good preconcentration. The extractant is an aqueous phase, and by prevention of the extraction of macromolecules through the membrane, the proposed method is totally compatible with HPLC as the final analyzer system.

Keywords: Three-phase microextraction; Amphetamine; Methamphetamine; Complicated matrices.

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Simple determination of lamotrigine in complicated matrices using drop-to-drop membrane based microextraction and high performance liquid chromatography

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Background: Despite the considerable advances in the analytical approaches and instruments, sample preparation is still a bottleneck in the modern analytical methodology, and this step is an integral part of most analytical methods. In this work, an efficient microextraction device was designed and coupled to HPLC for the selective determination of lamotrigine in biological matrices [1, 2].

Methods: The sample solution (100 μL) was injected into the donor chamber, lamotrigine was extracted from the donor phase (adjusted to the basic condition) through a supported liquid membrane (1-octanol) into an acidic acceptor solution (100 μL). The extraction process was followed by high performance liquid chromatography for final analysis.

Results: The method provided a wide linear range (5–500 mg L^{-1}), and it exhibited a good repeatability (RSDs$\leq$4.1%). The detection limit obtained was equal to 1 mg mL^{-1}. The method was successfully utilized for the simple determination of lamotrigine in human urine and plasma samples.

Conclusion: An efficient microextraction method namely drop-to-drop membrane based microextraction was coupled to high performance liquid chromatography (HPLC) for the selective determination of lamotrigine in biological fluids. The method provides a very high sample clean-up and the extractant is an aqueous phase that is totally compatible with HPLC as the final analyzer system.

Keywords: Lamotrigine: Three-phase microextraction; biological sample.

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Introducing of ultrasonic assisted dispersive liquid phase micro-extraction with magnetic dispersive solid phase extraction as a new simple sample preparation method

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Background: Rapid population growth of the world has led to an increase in demand for fuel and the advancement of chemical industry, fertilizers, pesticides, and medicine to maintain and improve living standards. Agriculture industry has become one of the most advanced industries of the world. The advancement in this industry has led to creation of new pesticides [1-4].

Methods: A tandem extraction method based on ultrasonic assisted liquid phase micro-extraction coupled to dispersive µ-solid phase extraction was utilized for determination of atrazine at µg L^{-1} concentration levels. In the first step a liquid phase micro-extraction based on dispersion of organic solvent was used for the fast extraction of atrazine from aqueous solution and in the next step the extraction organic solvent was effectively collected from the solution without any requirement to centrifuge step by using C-18-magnetic nanoparticles. After elution of the extracted targets from the magnetic nanoparticles, atrazine concentration was monitored by HPLC-UV at µgL^{-1} level.

Results: The influencing parameters in the pre-concentration step are: pH of solution, magnetic based sorbent amount (mg) and 1-octanol volume (µL). Selected data for factors that resulted by Box-Behnken design were: pH of sample: 9.0, solid phase amount: 22 mg and extraction solvent volume: 36 microliter. Relative standard deviation under optimized conditions by the hybrid extraction method was observed to be< 7 % and method detection limit for atrazine was 0.3µgL^{-1}.

Conclusion: In the current work an efficient hybrid extraction method based on ultrasonic assisted dispersive liquid phase micro-extraction tandem with dispersive µ-solid phase extraction assisted was prosperously used for trace monitoring of atrazine in environmental water samples.

Keywords: Hybrid extraction method; Dispersive liquid phase micro-extraction; Dispersive micro solid phase extraction; Box-Behnken design; Atrazine

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Combination of GEL-EME and SHS-HLLME: A tandem sample preparation method for analysis of antidepressants in biological fluids and wastewater

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Background: Recently, a new green membrane has been developed based on the gel configuration for the extraction which resulted in an improvement in the extraction efficiency. The first application of this gel membrane in EME was reported by Tabani et al. without using any additive reagents (GEL-EME) [1]. In homogeneous LPME, a new generation of solvents (called switchable hydrophilicity solvents (SHSs)) was introduced by Jessop et al. SHSs can reversibly switch between low ionic strength form to highly ionic one and create a monophasic solution. This allows the target analytes in a homogeneous phase to be transferred to extraction solvent without dispersive solvent [2]. In the present study, gel electromembrane extraction (GEL-EME) procedure was coupled with a switchable hydrophilicity solvent-based homogenous liquid-liquid microextraction (SHS-HLLME) process.

Methods: In this work, the analytes were extracted from 7 mL of the DP using an agarose gel membrane, to 500 μL of the AP under the optimized conditions. 500 μL of the acceptor solution collected from the first step was transferred into the extraction cell. Then, 50 μL of DPA was added to the cell, Afterward, 200 μL of HCl solution (6.0 M) was added and the cell was manually shaken for 10 s until reaching to a homogeneous phase. Finally, 200 μL of NaOH solution (10.0 M) was added to the cell which resulted in a cloudy solution. The complete separation of the organic and aqueous phases occurred after ~2 min of centrifugation at 2000 rpm. After centrifugation, the DPA, can be easily collected and injected to the GC-FID.

Results: The introduced technique exhibited good linearity with coefficients of $R^2 \geq 0.983$ and the acceptable linear range of 5.0-1000.0 ng/mL. Accordingly, the limit of detection (S/N = 3) for all the analytes was 1.5 ng/mL. The corresponding repeatability ranged from 4.0 to 8.7% (n = 3). The high enrichment factors were obtained in the range of 179-195.

Conclusion: This method brings noticeable sample clean-up and enrichment factor in the sample preparation procedure by inexpensive routes. Also, the problem of water injection to GC can be resolved by this technique.

Keywords: Agarose gel; Electromembrane extraction; Homogenous liquid-liquid microextraction; Switchable solvent; humane serum; breast milk; wastewater

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Slug-flow microextraction coupled with corona discharge ion mobility spectrometry for rapid analysis of complex samples

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Background: Nowadays, Drug abuse is an increasing societal and economic problem all over the world. Different types of analytical methods have been used for screening of drugs. Recently, established a new technique named slug-flow microextraction (SFME). SFME is an innovative method which target analytes are extracted rapidly from complex biological samples into a small amount of organic solvent[1,2]. In the present study, the combination of slug flow microextraction (SFME) and corona discharge ionization-ion mobility spectrometry (CD-IMS) was investigated in urine and breast milk for the first time as an efficient and effective coupled extraction method.

Methods: The urine and breast milk were used for SFME after diluting with pure water. A disposable glass capillary of 1.2mm I.D. was used for direct SFME of samples, through sequentially 10 microliters of samples and 10 micro of organic solvent (as extraction phase) into the glass capillary and two separate phase were formed, consequently. Afterward, thorough movement of capillary for several cycles, target analytes were transferred to organic phase. Finally, extraction solvent was collected by microsyringe, and 5 microliter injected into the CD-IMS.

Results: To evaluate the applicability of SFME-CD-IMS to the determination of illicit drugs, limit of detection (LOD), limit of quantification (LOQ), linearity were achieved, 30 ng/ml, 100 ng/ml, 100.0-2000.0 ng/ml, respectively. Acceptable correlation coefficients (R^2) were higher than 0.995 for purposed method. The intra-day and inter-day precision were calculated to be within the range of 8.2-9.5% and 5.1-9.3%, respectively, for spiked samples at 100 and 500 ng/ml concentrations of each illicit drugs.

Conclusion: Our developed SFME-CD-IMS technique have some advantages such as, high-efficient extraction, using a small volume of organic solvent, reducing the cost and analyzing time of method compared previous works by using the CD-IMS which presents an economic, fast, and sensitive instrument for drug analysis.

Keywords: slug flow microextraction; corona discharge ion mobility spectrometry; illicit drugs; urine; breast milk

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Extraction and determination of some polycyclic aromatic hydrocarbons (PAHs) by a coiled resistance alloy as a novel solid-phase microextraction fiber

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Background: Solid-phase microextraction (SPME) is a simple, efficient, sensitive, rapid and solvent-free sample preparation technique usually carries out on a coated fiber [1]. SPME commercial fibers offer a few drawbacks such as short lifetime, fragility of the fibers, bending of the needle, stripping of coatings, the poor reproducibility of the fibers and expensive cost [2]. Therefore developing stable, non-fragile and low-cost SPME fibers with easy preparation process and higher potential is necessary. In this work, a novel coiled-SPME fiber based on a stable, long life, low-cost and flexible resistance alloy is investigated for the first time. The quick-designed extraction fibers showed a unique ability to adsorption of PAHs analytes Soil and powerhouse and therefore were employed without any pre-treatment and special coatings.

Methods: A low-cost chromium based resistance metal alloy wire came in the form of a coil and was used as SPME fiber. Extraction of analytes was performed by direct immersion of fiber into the sample solutions includes phenanthrene, anthracene, fluoranthene, and pyrene. Then the fiber was placed in acetonitrile as desorption solvent. Finally, analysis of selected PAHs in samples was performed by HPLC-UV system.

Results: Under optimum conditions, linear ranges of 2.5–400 µg L^{-1}were obtained and the limit of detection (LOD) of method was ranged between 0.18 and 3.28 µg L^{-1}. Furthermore, the intra-day and inter-day relative standard deviations of prepared fiber were in the range of 3.23–8.43 and 4.55–9.69%, respectively. Enrichment factor (EF) was between 24 and 43. In addition, the proposed procedure was applied for determination of selected PAHs in real samples (soil, well water and black tea) and good recoveries (more than 70%) were achieved in all cases.

Conclusion: Fast preparation, low cost, no need for special coatings or any special materials, environmentally friendly, solvent stability, good extraction ability, simplicity of analysis process and high precision are some of the outstanding properties of the prepared fibers. Good analytical achievements and acceptable recoveries prove the suitability of the fiber for extraction and pre-concentration of target analytes especially at low concentration levels.

Keywords: Solid-phase microextraction; Coiled fiber; Polycyclic aromatic hydrocarbons; Adsorption properties

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A Green Dual-gel Electromembrane Extraction Combined with Colorimetric Paper-based Analytical Device for the Parallel Determination of Cr(III) and Cr(VI) Species in Water Samples

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Background: The microfluidic paper-based analytical devices (µPADs) are newly developed approaches which have been successfully applied to the qualitative and quantitative analysis in various research scopes [1]. Up to now, there is no combination between µPADs with electromembrane extraction (EME). In this regards, a green agarose-based dual-gel EME (DG-EME) was combined with µPADs (as a low-cost reader platform) for parallel extraction and quantification of Cr(III) and Cr(VI) in water samples.

Methods: By means of an electric potential of 65 V (during the extraction time lasting for 23 min), the positively charged Cr(III) and negatively charged Cr(VI), migrated selectively from a 12.0 mL aqueous sample (with pH 4.0, HCl) into the cathodic (pH 2.0, HCl) and anodic (pH 3.0, HCl) aqueous acceptor phases (with value of 200 µL each), respectively. After extraction, anodic acceptor phase with Cr(VI) was directly analyzed by µPAD (after adding diphenylcarbazide - DPC, as a selective colorimetric reagent onto the detection zone). Regarding cathodic acceptor phase with Cr(III), it was mixed with Ce(IV) to oxidize Cr(III) → Cr(VI). Cr(VI) ions were then analyzed again by µPAD based on adding DPC.

Results: The extraction recoveries (ERs, %) obtained under optimal conditions in the range of 58.8%-83.3%, referring to enrichment factors of 40-47. The limits of detection (LODs) and quantification (LOQs) were in the ranges of 2–3 ng mL^{-1} and 7.0–10.0 ng mL^{-1}, respectively. The developed method was successfully utilized for parallel determination of Cr(III) and Cr(VI) species in real water samples at trace of parts-per-billion (ppb) levels.

Conclusion: DG-EME configuration involves several benefits over classical up-to-date liquid-based extractions, namely: 1- The simple preparation of agarose gel membranes in various shapes and thicknesses is feasible. Due to this, both development and commercial laboratories could have utilized them for separation/purification purposes, in future. 2- Further, aspects of green analytical chemistry are highly maintained when such gel membrane is used, thus G-EME is strongly eco-friendly.

Keywords: Dual-gel electromembrane; Microfluidic paper-based analytical devices; Green extraction; Chromium speciation; Colorimetric analysis.

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Gel Electro-membrane Extraction: Investigation the Effect of Electroendosmosis on Extraction Efficiency in Different Types of Gel Membrane

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Background: Recently, gel electro-membrane extraction (G-EME) was introduced for extraction of some basic drugs [1]. Flux of analyte across the gel membrane is based on two driving force; one of them is electro-migration (like EME) and the another one is electroendosmosis (EEO) flow. EEO is a phenomenon that may occur during extraction. Here, anionic groups (e.g., sulfate) in the gel are affixed to the matrix and are thus incapable of motion, but dissociable cations can migrate toward the cathode by means of the electrical field. As a result, EEO (a motion of liquid through the gel) causes an increase and decrease in the volume of cathodic and anodic APs, respectively.

Methods: For investigation the effect of EEO on extraction efficiency, agarose with different concentration, types (low, medium and high EEO) and additive (Dextrin, Chitosan, and Xylan) were prepared and used as membrane in G-EME. Cr(III) and Cr(VI) were used as model cationic and anionic species, respectively. During the extraction, positively charged Cr(III) and negatively charged Cr(VI) migrated selectively from an aqueous sample into the cathodic and anodic aqueous acceptor phases (of 400 µL each), respectively.

Results: The intensity of EEO and extraction efficiency in G-EME depends on different parameters; such as, the type of agarose, the pH of AP, gel and DP, applied voltage, and also extraction time. In order to obtain the best result, these parameters were investigated. The optimal extraction was obtained at pH of the cathodic AP: 2.0 (HCl); pH of the anodic AP: 3.0 (HCl); pH of the cathodic gel membrane: 5.0; pH of the anodic gel membrane: pH of the DP: 4.0; voltage: 65 V; extraction time: 23 min. The results showed that the highest extraction efficiencies of cathodic and anodic gel membranes were obtained with agarose containing 5% dextrin.

Conclusion: By means of this work the mechanism flux of analyte across the gel membrane was found so that there are two main driving force. By electro-migration, analytes are transferred based on their charge. On the other hand, by EEO, the extraction of cationic compounds is accelerated while for anionic compounds, it acts as an inhibitor agent. In addition, the results showed with adding of dextrin in gel membrane, the amount of EEO decreased due to diminish of conductivity of the EME system. Also, via this setup, both cationic and anionic ions could be quantitatively extracted by using solely the gel-based membrane unit.

Keywords: Gel electromembrane; Electroendosmosis flow; Green extraction; Agarose.

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Online Solid Phase Extraction- Thermal Desorption- Gas Chromatography for extraction of Triazine herbicides from Aqeuous Media

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Background: Triazine herbicides are ascribed to triazole pesticides, which have been widely used as selective herbicides to control broadleaf and grassy weeds in many agricultural crops [1]. Because of excessive use of triazine herbicides in agricultural, the residues of these herbicides have been determined in soils, groundwater [2], surface water [3] and food [4, 5] in recent years. Among them prometon is used for total vegetation control on industrial sites, on noncrop areas on farms, in and under asphalt, and to a small extent by homeowners. Prometon has often been detected in surface water and groundwater in studies reported in the literature, but its presence is seldom discussed, partly because of its infrequent inclusion on lists of herbicides used in either agricultural or urban areas [6].

Methods: On-line SPE-GC achieved by using a retention gap or a programmed-temperature vaporizer (PTV). In addition, the performances of two Tenax sorbents (Tenax TA and GA 60-80 mesh) and a metal organic framework (MIL- 101(Cr)) were studied. For this purpose about 100-200 mg of desired sorbent was packed into the liner and the top and bottom of liner was blocked by glass wool. For the condition and treatment of the sorbent, the extraction unit, consisting of the liner and the sorbent, was placed onto the GC injector and heated to 250 ̊C for 2 hours. After that the about 900 µL of aqueous sample that was spiked by prometon standard was passed through the liner consist of sorbent. Then the injector was heated up to 270 ̊C for 30 min to evaporation of water and finally GC method was implemented.

Results: Several parameters that effect on extraction efficiency such as sorbent type, amount of sorbent, sample volume, sample pH and thermal desorption procedure were optimized. Linear range and detection limit for prometon was 0.5-1000 µg/L and 0.2 µg/L respectively.

Conclusion: The result showed that this method can be used for direct injection of large volume of aqueous sample into the GC inlet and applied successfully for direct injection and pre-concentration of triazine from aqueous media.

Keywords: on-line**;** SPE-TD; Triazine; Aqueous sample; Tenax; MOF.

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Development and application of solidification of floating organic drop microextraction for simultaneous extraction and preconcentration trace amounts of cobalt and nickel using deep eutectic solvents

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Background: The major source of nickel exposure is oral consumption, as nickel is essential to plants. Nickel and cobalt is found naturally in both food and water, and may be increased by human pollution. For example, nickel-plated faucets may contaminate water and soil; mining and smelting may dump nickel into waste-water; nickel–steel alloy cookware and nickel-pigmented dishes may release nickel into food. Humans may absorb nickel directly from tobacco smoke and skin contact with jewelry, shampoos, detergents, and coins [1] .In this study, dispersive liquid-liquid microextraction based on the solidification of floating organic drop method was developed and applied with deep eutectic solvents for separation, preconcentration, and determination nickel and cobalt in natural water samples with flame atomic absorption spectrometry (FAAS). Nickel and cobalt were complexed with 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol and extracted into a small volume of deep eutectic solvents (Decanoic acid and DL-menthol). Several variables that affect the extraction efficiencies, including pH, concentration of chelating agent, type and volume of the extraction solvent , extraction time and salt effect addition, were investigated and optimized [2,3].

Methods: 30 ml aqueous solution containing target analytes was introduced into the tube. Then, 100 µL of 0.1 mol L^{-1} Ligand added. Then, 100 µL DES as dispersive solvent was rapidly injected into the solution, then shaked for 30 s. The tube was closed and centrifuged for 10 min at 4000 rpm and then placed into ice for 15 min until the upper phase turn solidified. The bottom water phase was quickly poured out. Finally, the collected DES was diluted by 1 mL ethanol before FAAS analysis [2].

Results: After optimization of the complexation and extraction conditions the calibration curve was linear in the range of 3-266 µg L^{-1} and the limit of detection for nickel was 2.2 µg L^{-1} and for cobalt 2.5 µg L^{-1} . The relative standard deviation for nickel was 2.88 and for cobalt was 2.58. The proposed method was applied to the determination of nickel and cobalt in several natural water samples with satisfactory results.

Keywords: Deep eutectic solvents; Dispersive liquid–liquid microextraction; Solidification of floating organic droplet; Preconcentration; Cobalt; nickel; Water samples.

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Silica Aerogel Nanoporous Thin Film Microextraction Supported by Organic Solvent as a Sample Preparation Method Prior to Analysis by Ion Mobility Spectrometry

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Background: Among the various sample preparation methods, thin film microextraction (TFME) [1] and liquid phase microextraction (LPME) [2] are two relatively simple microextraction methods used for the analysis of analyte in the different matrices. Some advantages such as simplicity, low cost, low solvent consumption, and high absorption area may be considered in these methods, compared to other techniques based on the sorbent. However, some drawbacks, such as high extraction time in TFME and low enrichment factor in LPME method, limit the application of each method for sample preparation. Based on the advantages and potentials of both techniques, it would be useful to have the combination of both methods, as a new hyphenated method of TFME-LPME, whereas lessening their problems.

Methods: Silica aerogel nano-porous thin film microextraction coated by organic solvent, as a sample preparation method was followed by corona discharge-ion mobility spectrometry (CDIMS), as detection system, and used for the analysis of the herbicide molinate (as a model compound). Some parameters affecting the extraction efficiency such as organic solvent type, stirring rate, extraction temperature, sample pH, and extraction time were optimized by response surface method (RSM). Some real samples such as carrot, tomato, apple, river water, agricultural wastewater, well water, and drinking water were analyzed by the proposed method.

Results: Under the optimum conditions, the limit of quantification and limit of detection for herbicide molinate were 0.2 and 0.075 μg.L^{-1}, respectively. The linear dynamic range was obtained 0.2-7.0 μg.L^{-1} with correlation coefficient of 0.9997 for the model compound. The recovery values (%) of tomato, carrot, apple, well water, drinking water, river water, and agricultural wastewater samples were obtained 103±7, 92±4, 96±7, 97±6, 99±6,104±2, 105±5, respectively.

Conclusion: A hyphenated method of TFME-LPME was introduced as a sample preparation method. The silica aerogel nanostructure was placed into the polyacrilonitrile nanofibers and coated by organic solvent; bring higher contact area with sample solution for more absorption of the compound. The proposed method enhances of enrichment factor.

Keywords: Ion Mobility Spectrometry; Thin Film Microextraction; Organic Solvent; Sample Preparation Method

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Combination of hollow fiber supported solvent-stir bar micro extraction and fast electro membrane extraction for quantification of basic drugs in wastewater and biological fluids

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Background: In many analytical methods, extraction of analytes from complex matrices is an important issue because these matrixes contain disturbing factors that make it impossible to analyze analyte directly. For this reason, new analytical methods have been devised to solve these problem. In this study combination of two extraction methods, electro membrane extraction (EME) and hollow fiber supported solvent-stir bar micro extraction (HF-SS-SBME), was applied for the extraction of some basic drugs from wastewater, urine and plasma samples [1,2].

Methods: Frist, the porous hollow fiber (HF) was cut in length 3cm and then placed in the 1-octanol to fill the pores with organic solvent. Next, the HF was take evicted from solvent and rinsed inside and outside of it with water. In the next step, an iron bar was inserted in it and immersed into the sample solution and stirred. Then, the HF was removed from the sample solution and rinsed. The acidic acceptor solution was then introduced into the lumen of the HF and the end of HF was closed. A platinum electrode was placed into the HF and it was then inserted into the vial containing basic solution. The another electrode was placed into the basic solution. The extraction was then started by application of a constant voltage. After extraction, the acceptor solution was transferred to a vial for further analysis by HPLC.

Results: In this study, function of combination of HF-SS-SBME and EME for quantification of basic drugs (propranolol, diltiazem and lidocaine) in wastewater, urine and plasma samples was reviewed and effective parameters on the extraction were investigated and optimized. The LODs of the drugs were found to range within 0.6-1.6 ng mL^{-1}, while the corresponding repeatability ranged from 6.2 to 10.2% (n = 3).This method provided good linearity with the resulting determination coefficients ranging from 0.996 to 0.998 over a concentration range of 1.0-1000 ng mL^{-1}.

Conclusion: In the present study, combination of HF-SS-SBME and EME for quantification of trace amounts of three basic drugs in wastewater, urine and plasma samples was developed for the first time..The major advantages of this new method are high enrichments and good sensitivity ,reducing matrix effects and electrical current level in EME, decrease in extraction time and organic solvent consumption, simple operation and more effective sample clean-up.

Keywords: hollow fiber supported liquid membrane-stir bar micro extraction, fast electro membrane extraction, urine, plasma, wastewater.

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Determination of celecoxib in plasma sample by two phase hollow fiber based liquid phase microextraction and high performance liquid chromatography with the aid of chemometrics

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Background: The aim of this study was to use a very simple and sensitive technique to evaluate Celecoxib(CEL) in water and human plasma. The most reported techniques for the extraction and preconcentration of celecoxib are liquid-liquid extraction (LLE) methods [1-4] and solid phase extraction (SPE) [5,6]. To the best of our knowledge, there has been no paper on the use of liquid phase microextraction techniques for extraction of Celecoxib.

Methods: The extraction and preconcentration procedure was as follows: First, the hollow fibers were cut into 8 cm pieces. 25μL of 1-undecanol, acceptor phase, was withdrawn into the microsyringe, then the hollow fiber was attached to its needle and subsequently it was submerged in the organic solvent for a few seconds to impregnate with organic phase. Then 24 μL of the acceptor phase was flushed carefully with slow pushing of the microsyringe plunger into the fiber. At last, the end of the hollow fiber was sealed by a piece of aluminum. The prepared extraction device was introduced into 10 mL of the aqueous sample (100 μg L^{-1}, pH = 7.5, Salt% = 2) containing CEL that was poured into 12 mL sample vial having a 4 mm ×14 mm magnetic stirring bar, at a U-shape. After performing extraction at 1000 rpm for 62 min, the microsyringe containing the hollow fiber was removed from the sample vial and the sealed end of the hollow fiber was opened and the receiving phase was withdrawn into the microsyringe. Ultimately receiving phase was injected into the 20 μL HPLC loop for subsequent analysis.

Results: The different parameters that significantly affect on the extraction procedure optimized by central composite design (CCD), by using the Statgraphics Centurion XVII.II and also the interaction between them investigated. pH of acceptor phase, extraction time and Salt effect are three parameters that were studied. Under the optimized conditions the recoveriesy found 92% for CEL. Linearity was obtained in the range of 0.01–500 μg L^{-1} ($R^2 > 0.994$). The enrichment factor (EF) were 136 and LOD were 0.003 μg L^{-1} with RSD below 6%. The method proposed acceptable values to determine CEL in plasma samples sensitively and accurately.

Conclusion: The method provided good precision, wide DLR, high PF and a very low LOD comparing to the common methods. Regard to few microliters of organic solvent consumption, the extraction procedure can be considered as an environmentally friendly technique. Utilizing fresh acceptor phase and discarding the hollow fiber after each extraction has led to high reproducibility and repeatability of the method, thus the method can be successfully applied for analyzing the drugs in plasma.

Keywords: Celecoxib; Hollow fiber; Liquid phase microextraction; High performance liquid chromatography; Chemometrics**.**

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Development of organic gas steam-liquid extraction (OGS-LE) method for the extraction of chlorpyrifos and diazinon from aqueous samples and determination by GC-FID

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Background: Organophosphate pesticides (OPPs) such as chlorpyrifos and diazinon are widely used in agriculture to control pests and fruit and vegetable crops. Various methods have been developed by researchers to determine trace amount of OPPs [1-3]. In the present study, organic gas steam-liquid extraction method (OGS-LE) was applied as a fast, simple, efficient, economic, environment friendly and selective extraction of two types of OPPs. Then, the determination takes place by GC-FID.

Methods: the extraction cell consists of three columns: 1- First column named heated chamber that include an organic solvent (2 mL n-Heptane) tube. This column is warmed up by circulating thermostat a mixture of water and ethylene glycol to reach adequate temperature for the organic solvent tube. Organic solvent and N_2 gas inlet are on the top of this chamber while a liquid gas separator is in the bottom to prevent condensed liquid drops of the organic solvent entry into second column. 2- Second column is conical shape in the top and is equipped with a drain valve in the bottom that includes aqueous solution of analyte. 3- Third column is a narrow tube for addition of distilled water to enhance aqueous solution surface to easy collection of organic solvent including analyte from conical part in the second column.

Results: Parameters such as ionic strength, volume of aqueous sample, heating chamber temperature, time of extraction, flow rate of evaporating gas (N_2), type and volume of organic solvent were studied and using one variable at a time (OVAT) method optimized. Under optimum conditions, regression equations, correlation coefficient (r), Dynamic Linear Range (DLR), Limit of Detection (LOD) for both analyte were calculated. DLRs were in the range of 50–5000 µg L^{-1} with 0.999 for r. The practical suitability of the developed OGS-LE method was confirmed by the determination of analytes in real samples (well, river and spring water).

Keywords: Organic gas steam-liquid extraction; liquid-liquid extraction; organophosphorus pesticides

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Nano ball {Mo_{154}} Incorporated Polymer Monolith for Microextraction of Morphine in Undiluted Urine

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Background: Morphine determination in urine samples has been employed in forensic cases as an indicator of heroin usage and for the evaluation of drug consumption. Sample preparation is a main step for the analysis of drugs in biological samples. Microextraction techniques enhanced the sample preparation methods [1]. In the present study,{Mo_{154}} was synthesized as a new composite for selective and efficient Micro-extraction of morphine from biological samples. This method will be used in urine samples without the need for preparation.

Methods:In the first,{Mo_{154}} was synthesized according to the previous report [2]. The surface area and pore size distribution of products were characterized by a specific surface area and pore size distribution analyzer. The parameters effecting extraction efficiency such as pH, salt content, type and volume of desorption solutionwere optimized.

Results: In this research, microextraction based on {Mo_{154}} incorporated polymer monolith was investigated for the extraction of morphine from undiluted urine samples. The morphine analysis carried out by high-performance liquid chromatography-ultraviolet (HPLC-UV). Under the optimum experimental condition, the calibration curve was linear in the range 4–920 ng/mL with correlation coefficients (R^2) higher than 0.9940 and limits of detection (LODs) for the target morphine from 0.5 to 1.2 ng/mL. The recoveries percentage were achieved from 86.6% to 103.0% with precision (RSDs) of 0.38–10.2%.

Conclusion: The combination of new composite with HPLC makes it possible for the selective measurement of mrophine in humane urine samples. Compared with other studies, the results of this work show that it has good recoveries, lower LODs and wider linear of ranges. Taken together, the developed method presented a new strategy for the analysis of basic drugs in undiluted urine sample, which could be used for monitoring medicines in pharmacokinetic analysis.

Keywords: Polyoxomolybdate; Morphine, Microextraction; Urine Sample; Composite.

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Synthesis and use of a [Bmim][PF_6] as ionic liquid or green solvent in *in situ* solvent formation microextraction technique to concentration/determination of Ni(II)

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Background: A new mode of homogeneous liquid–liquid microextraction (HLLME) based on use ionic liquids termed in situ solvent formation microextraction (ISFME) were introduced. In this method aqueous phase contains of analyte ions were mixed by organic phase (miscible ionic liquid) and after of complete mass transfer, by adding of counter ion, an immiscible ionic liquid was formed and separation of phases was occurred. In this analytical technique, instead of toxic and hazardous organic solvents, ionic liquids that are environmentally friendly were used [1]. Ionic liquids are known as solvents consisting of entirely ionic species and do have melting points close to or below room temperature. Ionic liquids are becoming increasingly interesting from electrochemistry to energetic materials, and are also studied as potential solvents in separation processes. Properties, including low melting points, wide liquid ranges, and negligible vapor pressure, have encouraged re searchers to explore the uses of ILs to replace volatile organic solvents [2].

Methods: A five mL of the sample solution containing nickel ion, dithizone as complexing agent, and 1-Butyl-3-methylimidazolium chloride [Bmim][Cl] as ionic liquid (organic phase) that synthesized by our team was transferred to screw-cap conical-bottom glass centrifuge tube. After shaking, $NaPF_6$ as counter ion was added to cloudy solution and [Bmim][PF_6] was formed. Then, the mixture was centrifuged. As a result, aqueous phase was simply removed by inverting the tubes and IL-phase was dissolved in ethanol solution and was aspirated to the FAAS.

Results: The figures of merit were showed in table 1. Other analytical parameters such as pH of sample solution (5.0) (Fig. 1), amounts of ionic liquid (100 mg), counter ion (75 mg), dithizone concentration (0.02 M), centrifugation rate (5000 rpm) and time (4 min) were optimized.

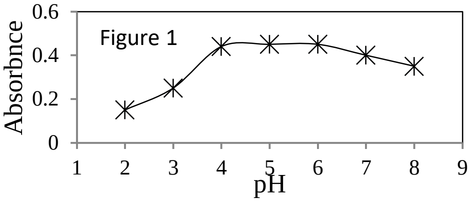

Table 1

Parameter	Value of optimized
Linear range (µg L^{-1})	10.0-7500.0
Limit of detection (LOD) (µg L^{-1})	0.1
R.S.D (%) (n=6)[b]	1.3
Enhancement factor[c]	70

Conclusion: [Bmim][PF_6] solvents/organic phase was chosen as a green organic phase and an alternative to the volatile organic solvents for this extraction system. The determination was carried out by flame atomic absorption spectrometry (FAAS). The in situ solvent formation microextraction (ISFME) technique was successfully used for the concentration of trace amount of nickel in saline samples. This method is fast, simple, safe and robust against very high content of salt (up to 30%). Therefore, ISFME is a powerful sample preparation technique for saline solutions and salt products that are used in food and pharmaceutical industries.

Keywords: *In situ* solvent formation microextraction, Ionic liquids, [Bmim][PF_6], Nickel determination

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Ultrasound-assisted matrix solid-phase dispersion coupled with reversed-phase dispersive liquid-liquid microextraction for determination of vitamin C in various matrices

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Background: Vitamin C (ascorbic acid) is a vital nutrient which plays an important role in body health including the production of collagen, L-carnitine, and some neurotransmitters. Several methods based on high-performance liquid chromatography (HPLC), ultraviolet (UV) spectroscopy and electrochemical have been reported in order to determine vitamin C content in beverages, foods and pharmaceuticals [1, 2].Vitamin C is a water-soluble vitamin that cannot be extracted into the organic solvents using conventional liquid-liquid microextraction (LLME). According to the above mentioned reasons, UA-MSPD as a modified MSPD was coupled with the RP-DLLME. The coupling has several advantages such as sample clean-up, increase of pre-concentration factor and reduces sample preparation steps.

Methods: Briefly, 0.04 g of sample was weighted and blended with 0.01 g of silica gel in an agate mortar for 1 min using an agate pestle to obtain a homogeneous mixture. The mixture was quantitatively transferred to a centrifuge tube and 0.5 mL methanol as elution solvent added to the mixture and subjected to ultrasonic probe for 10 s. Then, 110 µL of phosphate buffer (pH 6) and 1.5 mL of tetrachloride carbone (TCC) were injected into the tube. Finally, the mixture was centrifuged for 7 min at 5000 rpm and 20 µL of the aqueous phase which collected on the surface of mixture injected into the HPLC system.

Results: Efficiency of the proposed method for analyte pre-concentration was compared with the UA-MSPD. Under the optimized conditions, *Rosa canina* fruit powder was analyzed using the proposed method and UA-MSPD as reference method.The obtained chromatograms were shown in Fig. 1. As can be seen from these chromatograms, using the UA-MSPD-RP-DLLME method intensity of vitamin C peak was increased than UA-MSPD method.

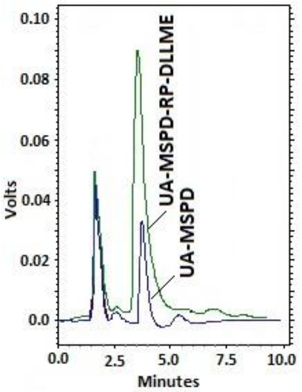

Fig. 1. Typical chromatograms of extracted vitamin C from *Rosa canina* fruits using the UA-MSPD and UA-MSPD-RP-DLLME methods.

Conclusion: Extraction of polar organic compounds is an important challenge in separation science. For the first time UA-MSPD procedure was coupled with the RP-DLLME method for the determination of vitamin C in solid and semi-solid samples.In the proposed method RP-DLLME procedure leads to clean-up and pre-concentration of target analyte. The UA-MSPD-RP-DLLME method was applied to the analysis of vitamin C content of several solid and semi-solid samples.

Keywords: ultrasound-assisted matrix solid-phase dispersion, reversed-phase dispersive liquid-liquid microextraction, vitamin C

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graphite carbon nitride with coral morphology as a new adsorbent for separation and preconcentration of Pb(II) and Cu(II) by using effervescent salt-assisted dispersive micro solid-phase extraction method

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Background: Due to the increased environmental pollution by heavy metals and their harmful effects on the human body, their separation is very important. Two types of common heavy metals are Cu and Pb. There are several methods to extraction these ions. The effervescent-assisted dispersive micro solid-phase extraction (EA-Dμ-SPE) is one of advanced methods for this purpose. Therefore, in the present work, graphitic carbon nitride with a coral structure was synthesized by a simple method and used for first time to determine the Pb(II) and Cu(II) using the EA-Dμ-SPE method [1].

Methods: To synthesis of adsorbent, melamine was homogeneous in ethylene glycol and acid solution, then sediments was washed and dried. Then powder was transferred to the furnace in 450 ^{o}C. To extraction method, first a tablet with specific length and thickness by mixing the sodium carbonate, citric acid and adsorbent was prepared. Then tablet was added to 10 mL of the solution (10 μg L^{-1} of Pb(II) and Cu(II)) and adsorbent was rapidly dispersed in it. Then adsorbent was separated and eluent were added to it and sonicated for 5 min. Finally the eluent was injected to flame atomic absorption spectroscopy.

Results: The synthesized adsorbent was characterized by the FT-IR, FE-SEM and XRD analysis. Also, optimum conditions were optimized as follows: pH: 7; adsorbent: 0.008 gr; eluent: HNO_3; concentration of eluent: 3 mol L^{-1}; volume of eluent: 300 μL and ultrasonic time: 5 min. The linear ranges were obtained between 3-800 μg L^{-1}, and 0.9-300 μg L^{-1} for the Pb(II) and Cu(II) ions, respectively. The LOD were obtained 0.9 and 0.27 μg L^{-1} for the Pb(II) and Cu(II) ions, respectively.

Conclusion: In this work the main advantages of this approach are: i) the extraction and pre-concentration of Cu(II) and Pb(II) were done in the shortest time by a small amount of adsorbent. The short time of extraction can be due to rapid and uniform dispersion of adsorbent in the sample solution and also the high absorption capacity of the adsorbent ii) in this technique was used very low volume of eluent (300 μL), which increases the preconcentration factor and iii) the results obtained were indicated that the separation method has a good precision.

Keywords: Coral; Graphite carbon nitride; EA-Dμ-SPE; ion metal.

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HP-TLC Bioautography of Five Iranian Antibacterial Plants; Detection of Active Compounds

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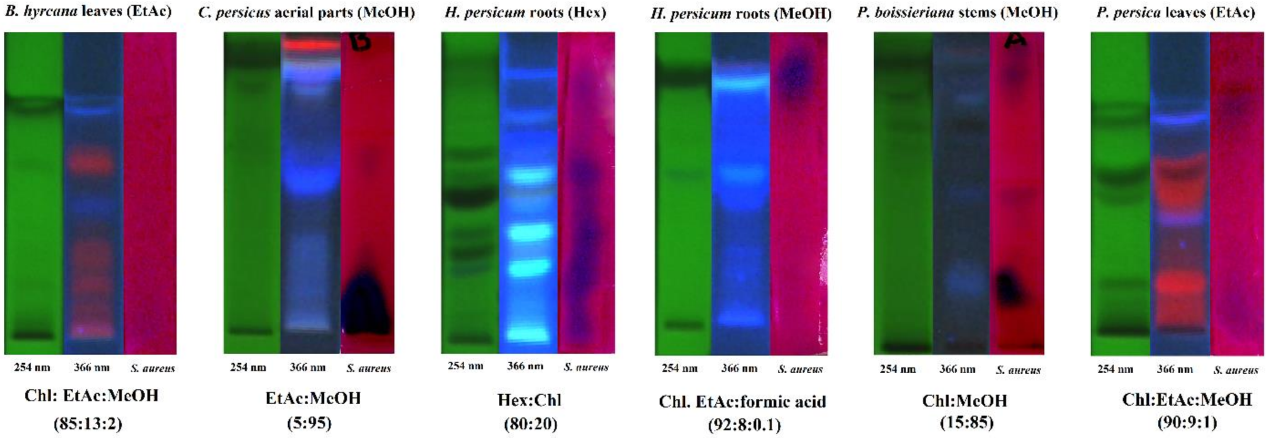
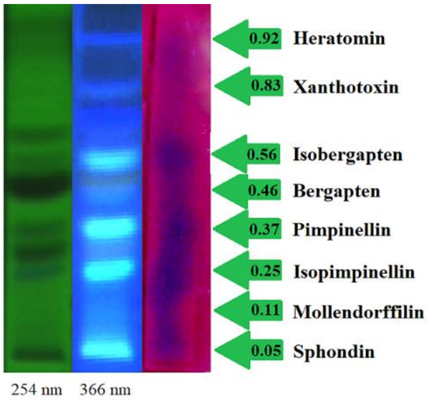
Background: In TLC bioautography, both separation and biological assays are carried out on a same TLC plate. This study aimed to determine the antibacterial compounds from some Iranian plants, Buxus hyrcana, Convolvulus persicus, Heracleum persicum, Pyrus boissieriana and Parrotia persica, by this method [1].

Methods: First, extract solutions were applied to TLC plates by use of a CAMAG sample applicator. After development, each TLC plate was examined under UV light at 254 and 366 nm, using CAMAG TLC scanner. Then, MHA medium and *Staphylococcus aureus* were poured into the surfaces of developed TLCs. Next, the TLCs are incubated at 37°C for 18 h. Subsequently, the plates were revealed with a solution of resazurin, as indicator of bacterial growth.

Results: As shown in the following figure, inhibition zones in TLCs (against *S. aureus*), where the antimicrobial compounds were existed, visualized as dark blue spots in a purple background.





The *n*-hexane extract of the roots of *H. persicum* was designated to identify its active components, comparing with standard compounds. As result, eight furanocoumarins were detected as heratomin, xanthotoxin, isobergapten, bergapten, pimpinellin, isopimpinellin, moellendorffilin and sphondin as potent antibacterial phytochemicals.

Keywords: HP-TLC; Bioautography; Antibacterial; Furanocoumarins

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Dispersive solid phase microextraction coupled with ion mobility spectrometry for simultaneous preconcentration and determination of bendiocarb, butachlor and diazinon in environmental samples

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Background: Among the microextraction methods, one of the most engaging sample preparation methods is the solid phase microextraction (SPME). SPME was originally based on the sorption of the target analytes from the headspace or the aqueous phase of a matrix on a fiber and the subsequent elution in the appropriate solvent [1]. Recently, dispersive solid phase microextraction (DSPME) was introduced in which instead of the fiber, a small amount of sorbent was dispersed in the sample solution. DSPME has brought about considerable attention for the separation and preconcentration of trace analytes in different samples because of its simplicity, rapidity, good recovery, low consumption of organic solvents, and the capability of combination with different detection techniques [2].

Methods: In this research, zinc sulfide/ reduced graphene oxide nanocomposites (ZnS/RGO) are successfully synthesized by a single step solvothermal method [3] and are used as sorbents for the extraction bendiocarb, butachlor and diazinon from real samples prior to their determination by ion mobility spectrometry. The effects of relevant experimental parameters such as desorption solvent type, pH, buffer type, buffer volume, sorption and desorption time, amount of adsorbent and desorption solvent on the method efficiency were investigated.

Results: Under the optimized conditions, linear range for bendiocarb 0.8-120 ng.ml^{-1}, for butachlor 1-140 ng.ml^{-1}and for diazinon 0.5-100 ng.ml^{-1}, ($R^2 > 0.999$) was obtained. The limits of detection were obtained <0.3 ng.mL^{-1}. The relative standard deviations of the method (n = 8) were obtained less than 3.8%. The proposed method was successfully applied for the preconcentration and determination of bendiocarb, butachlor and diazinon in environmental samples with 97.0-102.0% recoveries.

Conclusion: The ion mobility spectrometry was used as a sensitive, fast and cheap detection instrument. DSPME-IMS procedure offered some advantages such as low organic solvent consumption, low cost, low LOD, relatively wide linear range, and high sensitivity. As a good adsorbent, ZnS/RGO exhibited excellent extraction capability for bendiocarb, butachlor, diazinon with low detection limit and satisfactory recoveries in environmental samples.

Keywords: Diazinon; Bendiocarb; Butachlor; Solid phase microextraction; Simultaneous determination; Ion mobility spectrometry.

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Determination of quercetin using a molecularly imprinted polymer as solid-phase microextraction sorbent and high-performance liquid chromatography

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Background: Solid-phase microextraction (SPME) as a miniaturized technique can be used as an efficient method for the extraction and pre-concentration [1]. On the other hand, molecularly imprinted polymers (MIPs) are attractive artificial receptors which are able to specifically adsorb the target molecule. Combination of MIPs with SPME enhances the efficiency of the extraction process. The sol gel method in the preparation of MIP is used because of its simplicity and better physical, chemical properties of the polymer [2]. Quercetin is a polyphenol compound and the common methods used for its detection are HPLC, GC-MS, spectrophotometry.

Methods: MIPs synthesized through a sol-gel method on modified stainless steel wires using 3-aminopropyltriethoxysilane (APTES) as functional monomer and tetraethyl orthosilicate (TEOS) as cross link agent. The prepared fiber was characterized using FTIR, FESEM, EDX and TGA.

Results: Several parameters such as pH, desorption solvent, extraction and desorption time were investigated. The method was found to be linear from 0.05 to 100 µg mL^{-1} with R^2=0.9998. The limit of detection (LOD) was 9.94 ng mL^{-1}.

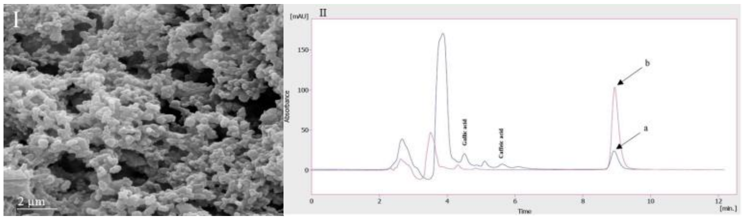

Fig. I) The FESEM images of quercetin MIP-coated SS fiber, II) Chromatograms of unspiked black tea sample (a) before, (b) after MIP-SPME.

Conclusion: A novel MIP-SPME fiber with great thermal and mechanical properties was successfully used for selective extraction of quercetin in beverage samples by HPLC-UV detection.

Keywords: Quercetin; Molecularly imprinted polymer; Solid-phase microextraction; HPLC-UV.

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Nanoporous silica aerogel as a new sorbent for the needle-trap extraction

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Background: Many new methods have been developed for the isolation of organic pollutant compounds from water samples. In the past few years, the needle trap extraction (NTE) technique has been developed as a solventless sample preparation approach and an alternative extraction method derived from solid phase microextraction (SPME) [1, 2]. In this work, an in-needle packed method using new synthesized modified nanoporous silica sorbent was employed for the extraction of polyaromatic hydrocarbon compounds (PAHs) from aqueous samples.

Methods: Working solutions (7 mL) of PAHs (1 mg L^{-1} in distilled water) were placed into a 10-mL volume glass vial containing 1.4 g NaCl. Sample vials were heated in a water bath and the solution was stirred with a magnetic stirrer while the NTD was maintained at an ambient temperature. The extraction was performed by exposing the sorbent to the HS of the sample for 20 min at 45 °C. Then, the NTD was inserted through the vial septum and placed in the HS of the sample. A 23-G needle was also inserted into the sample solution to purge the circulating HS into the sample. The NTD and the purging needle were connected to a peristaltic pump in such a way as to aspirate the HS sample through the NTD. The sampling flow rate was 2.5 mL min^{-1}. For thermal desorption of trapped analytes, the position of the needle was carefully adjusted so that the carrier gas was flowing through a small hole which was located 4 cm above the opening end, and analytes could directly be transferred into the capillary column. Three replicate determinations were performed per sample. Furthermore, prior to starting the set of experiments, a blank analysis was performed to verify that no extraneous compounds were desorbed from the needle.

Results: Under optimized conditions, the detection limit and quantification limit were obtained in the range of 0.5–1 and 2– 5 ngL^{-1}, respectively. The relative standard deviation values for water spiked with the PAHs at 50 ngL^{-1} under optimum conditions were 5–8%. The dynamic linear range of method was investigated in the range of 5–1000 ngL^{-1}. Finally, the current method for the analysis of real water samples containing spiked PAHs was applied and the relative recovery values were found to be in the range of 85–102%.

Conclusion: Analytical data along with relative recoveries confirm that modified nanoporous silica is an appropriate candidate as a new sorbent for extracting aromatic compounds. This sorbent, due to its non-smooth and porous structure provides high specific surface area with increased activated sites. Furthermore, synthesis of the modified nanoporous silica aerogels can be carried out conveniently as well as being inexpensive, simple, easy and highly durable.

Keywords: Modified silica aerogels; Gas chromatography/mass spectrometry; Needle-trap extraction; Water samples

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A New Electrospun Nanocomposite as Solid-Phase Microextraction Fiber Coating

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Background: Solid-phase microextraction (SPME) is one of the promising extraction techniques, which integrates extraction and enrichment in a single step using a small amount of solid phase to decrease reagent and time consumption [1,2]. Recently, for overcome SPME fiber coating drawbacks, many investigations for improving the thermal and chemical stability of coating and enhancing the fiber capacity were performed. In this work, electrospun polybutylene terephthalate/graphene oxide nanocomposites were synthesized as new SPME coatings for the preconcentration of organic pollutants such as chlorobenzens (CBs) from environmental water. Various parameters affecting the synthesized nanocomposite morphology and also the extraction–desorption steps were investigated and optimized. Finally, the proposed method was successfully applied to the analysis of trace CBs in environmental samples.

Methods: For extraction/desorption process, firstly, the synthesized fiber coatings was inserted in a manual home-made SPME holder. Then, the fiber was inserted into the sample bottle, and situated at about 1.5 cm above the surface of the aqueous phase. In all experiments, 1.2 g NaCl was added to 10 mL of aqueous sample, and then the solution was spiked with the mixture of CBs. Finally, the sample vial was sealed with a PTFE-faced septum and an aluminum cap. The sample vials were heated in a circulating water bath and agitated by maximum stirring rate for 10 min at 40 °C. Subsequently, for thermal desorption, the home-made SPME holder was immediately inserted into the GC injector port at 200 °C for 3 min.

Results: At the optimum conditions, the intra-day relative standard deviations for the determination of them in distilled water spiked at the levels of 150 ng L^{-1} were 3–6% (n = 3), the limit of detection is between 10 and 30 ng L^{-1}, and the calibration plots cover the 100 to 1000 ngL^{-1} range. Inter-day precision values obtained for three replicates measured on different days were in the range of 5–10% at concentration levels of 150 ng L^{-1}. The method was applied to the analysis of (spiked) water samples and relative recoveries were found to range from 98 to 102%.

Conclusion: The new composite coating containing PBT and GO as matrix and dopant was electrospining on a SPME metal rod. The morphology of the PBT/GO was more porous and provides high specific surface area along with increased activated sites. This sorbent, due to its non-smooth and porous structure provides high specific surface area with increased activated sites. The developed method based on PBT/GO nanocomposite coating is simple, rapid, facile and inexpensive.

Keywords: Chlorobenzene; Gas chromatography/mass spectrometry; Polybutylene terephthalate/graphene oxide Nanocomposite; Needle-trap extraction; Water samples.

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Butyl-3-methylimidazolium chloride/polybutylene terephthalate nanocomposite as a novel fiber coating

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Background: One approach to increase the efficiency of the SPME coating is application of a technique to prepare porous materials and nanocomposites such as electrospinning technique [1]. Also, ionic liquids (ILs) are used to improve the conductivity of the electrospun polymer solution to change the structure and properties of nanofibers [2]. Here, we developed butyl-3-methylimidazolium chloride-polybutylene terephthalate nanocomposite as new SPME coating for the extraction and analysis of chlorophenols representing the polar-oriented pollutants from aqueous samples. Our goal is development of a sensitive technique using SPME fiber while providing a rapid and green technique.

Methods: A manual home-made SPME holder containing the PBT/ILs nanocomposite coating was used for the headspace solid phase microextraction (HS-SPME) of cholorophenols. In all experiments, 0.8 g of sodium chloride was added to a 4 mL aqueous sample in a 10 mL vial containing a magnetic PTFE coated stir bar. The extraction temperature was set at 35 ◦C by a circulating water bath. After 15 min, the SPME fiber was withdrawn into the holder and inserted into the GC injection port for thermal desorption.

Results: The developed method is fast and sensitive providing sub and low ppt detecion limits, LOD of 0.75–5 ng L^{-1} and LOQ of 5- 15 ng L^{-1} with equilibrium time of 15 minutes. Wide linearity in the range of 15-2000 ng L^{-1} with $R^2 > 0.9993$ was also obtained. Repeatability of the method was accessed at 100 ng L^{-1} and RSD% of 6–12% was achieved. Finally, the developed method was applied to the analysis of real water samples and the relative recovery values were found to be in the range of 84–97%, showing no matrix effect.

Conclusion: The SEM images proved the lower diameter of the prepared nanofibers in the presence of ILs result-ing in the improved sensitivity of the SPME device. Relative recoveries along with other analytical data confirmed the suitability of the synthesized nanocomposite as an appropriate SPME fiber coating. Given the porous structure of the electrospun PBT/IL nanocomposite coating, high specific surface area with increased activated sites was achieved. The unique properties of the developed coating resulted in a short equilibrium time while providing the low ppt level of detection.

Keywords: Electrospining; butyl-3-methylimidazolium chloride-polybutylene terephthalate nanocomposite; Chlorophenols; Gas chromatography/mass spectrometry; Aqueous samples

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Electrospun magnetic polyamide nanofibers for magnetic solid microextraction

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Background: Magnetic solid microextraction is a novel separation procedure and is broadly used to remove certain classes of chemical pollutants from water. Magnetic nanocomposites, produced by functionalizing polymers with magnetic nanomaterials, are gaining more attentions. The incorporation of key features of magnetism and polymeric structure throughout the nanocomposite network have led to various applications [1,2]. In the present work, polyamide as a suitable polymer for electrospinning was used to prepare a nanofiber-based sorbent while its extraction efficiency was monitored at the presence of different amounts of Fe_3O_4 NPs. The most suitable polyamide nanofiber-based sorbent was eventually applied to the thin-film microextraction of methamphetamine.

Methods: The MSPE procedure is based on the following steps:
Step 1.—Add 10 mg of magnetic nanofibers to 50 mL water sample solution spiked with a concentration of 0.25 mgL^{-1} methamphetamine in a 70 mL beaker.
Step 2.—Stir the mixture at the maximum stirring rate (1000 rpm) for 5 min at room temperature and 0% salt to suspend the magnetic sorbent in solution and to completely trap the target analytes.
Step 3.—Place an external strong magnet (5 × 5 × 10 cm) at the beaker bottom to easily aggregate magnetic nanofibers from the solution. After about 1 min, separate away the solution supernatant.
Step 4.— In desorption step, the nanocomposites inserted in to a microtube containing 1.5 mL of ACN as desorbing solvent, then sonicated in ultrasonic bath for 4 min. Apply an external strong magnet to easily aggregate the magnetic nanoparticles at the beaker bottom.
Step 5.—Record the fluorescence spectrum of the desorbed solution using the spectrofluorometer.

Results: The limit of detections and limit of quantifications were obtained in the range of 25 and 75 ngmL^{-1}, respectively, demonstrating high efficiency of the prepared nanofiber. The developed method also showed good repeatability, RSD 4% ($n = 3$), for the spiked aqueous solution at concentration level 250 ng mL^{-1} of methamphetamine, and linearity, R= 0.998, in the range of 75 - 1000 ngmL^{-1}.

Conclusion: The simplification of the final solid–liquid separation by magnetic field can avoid the application of packed bed columns. In addition, a small amount of organic solvent (1.5 mL), a short analysis time (total analysis time of 10 min), and the use of small amounts of sorbent are clear advantages associated with this method.

Keywords: Magnetic polyamide nanofibers; Fluorescence; Methamphetamine; Magnetic solid microextraction

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Separation and preconcentration of trace amount of cobalt ion from water samples by application of ultrasound assisted deep eutectic solvent dispersive liquid-liquid microextraction

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Background: Trace amounts of cobalt (Co) can be found in air, soil, water, plants, and even our diets. Cobalt has low toxicity and has been regarded as an essential element. In small levels, Co is beneficial as it is one of the components of vitamin B_{12} [1]. However, Excessive concentrations of Co could result in several health-related problems including paralysis, diarrhea, hypotension, lung irritation, and bone defects [2]. Therefore, cobalt determination in various samples is necessary. This work presents a fast, feasible, and sensitive method for the preconcentration and separation of cobalt in various real samples through the use of ultrasound assisted deep eutectic solvent dispersive liquid-liquid microextraction (DES-DLLME).

Methods: At first, Choline chloride (1.39 g) and 4-bromophenol (3.46 g) were added to a 10 mL screw cap tube. It was then put inside a water bath at 75 ˚C for 10 min. Afterwards, it was vortexed for 5 min. The heating/vortexing cycle was repeated and a homogeneous liquid was achieved. For this extraction procedure, 25.0 mL of the solution which contained the analyte, 4.0×10^{-4} mol L^{-1} 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and 0.1 mol L^{-1} ammonia buffer (pH=10) was transferred to a glass tube. Afterwards, using a glass syringe, 0.5 mL of DES was injected into the aqueous solution as extraction solvents. Then the glass tube was placed in the ultrasonic bath for 5 min. Owing to the dispersion of small DES droplets, the solution turbidity increased. These droplets were precipitated by centrifugation at 3000 rpm for 3 min. The volume of DES precipitants was increased to 1.0 mL by addition of 1.0 mol L^{-1} ethanolic HNO_3. The obtained solution was manually injected into FAAS.

Results: Some effective factors that influence the microextraction efficiency were investigated and optimized such as volume of extraction solvent (0.5 mL), ligand concentration (4.0×10^{-4} mol L^{-1}), pH (10), centrifugation time (3 min) and speed (3000 rpm), ultrasound time (5 min). Under the optimized conditions, the relative standard deviation was 2%, the limit of detection and preconcentration factor were 1µg L^{-1} and 25, respectively. Calibration curve was linear in the range 4-200 µg L^{-1}. This method was applied for determination of cobalt in various water samples.

Conclusion: DLLME is a rapid, feasible, cost-effective, and sensitive technique which can lead to a low LOD, a high preconcentration factor along with extraction recovery in Co extraction and preconcentration from water samples. Moreover, unique properties of deep eutectic solvent including its low vapor pressure, low toxicity, non–flammability, and non–volatility have made DES-DLLME, a facile, vigorous, and environmentally friendly approach.

Keywords: Deep eutectic solvent, Dispersive liquid-liquid microextraction, Cobalt, Water samples.

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Application of deep eutectic dispersive liquid-liquid microextraction for separation and preconcentration of trace amount of cadmium ion from water samples

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Background: Cadmium is a well-known toxic and persistent pollutant that is naturally present at very low levels in common aquatic environments. Cadmium can be accumulated in several organs, producing carcinogenic effect [1]. According to WHO the upper permissible level of cadmium in drinking water is 3.0 μg L^{-1}[2]. For humans, the main sources of cadmium are from water and food. Therefore, sensitive, reproducible and accurate analytical methods are required for the determination of trace amount of cadmium in such samples.

Methods: At first, Choline chloride (1.39 g) and 4-bromophenol (3.46 g) were added to a 10 mL screw cap tube. It was then put inside a water bath at 75 ˚C for 10 min. Afterwards, it was vortexed for 5 min. The heating/vortexing cycle was repeated and a homogeneous liquid was achieved. For this extraction procedure, 25.0 mL of the solution which contained the analyte, 6.0×10^{-5} mol L^{-1} 1-(2-tiazole azo)-2-naphtole and 0.1 mol L^{-1} ammonia buffer (pH=10) was transferred to a glass tube. Afterwards, using a glass syringe, 0.5 mL of ethanol (disperser solvent) containing 0.5 mL DES (extraction solvent) was injected rapidly into the aqueous solution. Owing to the dispersion of small DES droplets, the solution turbidity increased. These droplets were precipitated by centrifugation at 4000 rpm for 10 min. The volume of DES precipitants was increased to 1.0 mL by addition of 1.0 mol L^{-1} ethanolic HNO_3. The obtained solution was manually injected into FAAS.

Results: Some effective factors that influence the microextraction efficiency were investigated and optimized such as type and volume of disperser solvent (ethanol, 0.5 mL), volume of extraction solvent (0.5 mL), ligand concentration (6.0×10^{-5} mol L^{-1}), pH (10), centrifugation time (10 min) and speed (4000 rpm). Under the optimized conditions, the relative standard deviation was 2%, the limit of detection and preconcentration factor were 1.5 μg L^{-1} and 25, respectively. Calibration curve was linear in the range 5-100 μg L^{-1}. This method was applied for determination of cadmium in various water samples.

Conclusion: DLLME is a rapid, feasible, cost-effective, and sensitive technique which can lead to a low LOD, a high preconcentration factor along with extraction recovery in Cd extraction and preconcentration from water samples. Moreover, unique properties of deep eutectic solvent including its low vapor pressure, low toxicity, non–flammability, and non–volatility have made DES-DLLME, a facile, vigorous, and environmentally friendly approach.

Keywords: Deep eutectic dispersive liquid-liquid microextraction, Preconcentration, Cadmium, Water samples.

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Magnetic solid phase extraction followed by HPLC for monitoring prokineticke drugs by a new graphene oxide/metal organic framework-74/Fe_3O_4/polytyramine nanoporous composite

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Background: Magnetic solid phase extraction as promising extractors considered for new and sustainable nanosorbents. In order to improve adsorption capacity, GO as an efficient nanomaterial functionalized with magnetic particles like Fe_3O_4. Polytyramine (Pty) significantly improves π-π stacking length, aromatic-aromatic interactions, steadiness of sorbent and extraction yield of compounds in various matrices and uses for modification of MOF-GO hybrid material [1, 2]. In this work, GO was functionalized with MOF-74 and then it was magnetized by Fe_3O_4 particles and then sorbent was polymerized by an oxidative polymerization of tyramine in the presence of Horseradish peroxidaze (HRP) enzyme. Two prokinetic drugs including domperidone (DOM) and itopride (ITP) were chosen for simultaneous extraction and enrichment prior to quantitation by HPLC-UV.

Methods: GO/MOF-74/Fe3O4/Polytyramine characterized by SEM and XRD. GO/MOF/ Fe_3O_4/Pty for extraction and preconcentration of target drugs was used in MDSPE-HPLC-UV.

Results: XRD patterns exhibited successful synthesis of GO and represented MOF-74 as a unique crystalline framework (fig 1). Analytical figures of merits involving linear dynamic range (LDR), limit of detection (LOD), limit of quantification (LOQ), for trace quantification of DOM and ITP by MDSPE-HPLC-UV were investigated (Table 1).

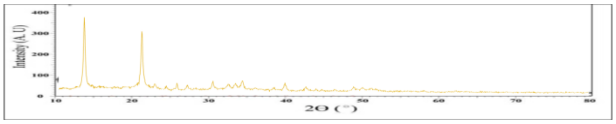

Fig.1: XRD pattern GO/MOF/Fe3O4/Pty

Table 1: Analytical figures of merits of the proposed MDSPE-HPLC-UV.

Analyte	LDR[a] (ng mL^{-1})	LOD[c] (ng mL^{-1})	LOQ[d] (ng mL^{-1})
DOM	1.50-1100.0	0.4	0.45
ITP	4.0-1750.0	1.1	1.19

Conclusion: A novelty hybrid material based on GO/MOF-74/Fe_3O_4/Pty was successfully fabricated and applied as a new sorbent for MDSPE. The newly designed nanosorbent revealed some other significant merits including simple magnetic separation without any special tools. Considerable accuracies and precisions were obtained through pharmacokinetic analysis by MDSPE was followed with HPLC-UV.

keywords: Magnetic dispersive micro-solid phase extraction, Metal organic framework, Graphene oxide,

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Magnetic graphitic carbon nitride nanoparticles modified with polyaniline for extraction of Pb(II) and Cd(II) using air-assisted dispersive solid–phase extraction prior to their quantitation by MS-FAAS

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Background: Among the preconcentration techniques, the air-assisted magnetic dispersive micro solid-phase extraction (AA-MD-µSPE) has received the most attention due to its simplicity. In this work, a novel magnetic nanoadsorbent graphitic carbon nitride (g-C_3N_4-$SnFe_2O_4$) modified with polyaniline was synthesized and applied for preconcentration and determination of Pb(II) and Cd(II) in water samples by the microsampling-flame atomic absorption spectrometry (MS-FAAS) technique [1]. The proposed method was used successfully for simple, rapid, and less hazardous for environment extraction and determination of metal ions from water samples.

Methods: The g-C_3N_4-$SnFe_2O_4$ was made according to reference [1]. Then nanoadsorbent (1.0g) was added to 1.5ml HCl (1 mol L^{-1}), then $(NH_4)_2S_2O_8$ (0.034g) was added and stirred at 1°C for 1h. The 0.01 ml aniline was added and stirred for 8h. The solid product filtered, washed and dried. To extraction method, the nanoadsorbent (8.0 mg) was added to 10.0ml of sample solution containing 10.0 µg L^{-1} of each analyte with a pH value of 7.0. Then the mixture was rapidly sucked and injected in to the tube (for 11 times) via syringe needle. In the next step, the nanoadsorbent was separated from the solution using magnetic field. 300.0µl of HNO_3 (2.0 mol L^{-1}) was added to the sample solution and sucked and injected for several times. Following desorption the ions were quantified via MS-FAAS.

Results: The (g-C_3N_4-$SnFe_2O_4$@ PANI) characterization was performed by the FT-IR, FE-SEM and XRD. Also, the following parameters were optimized: pH:7; amount of nanoadsorbent: 8 mg; type of eluent: HNO_3; concentration of eluent: 2 mol L^{-1}; volume of eluent: 300µl; numbers of extraction: 11 times. Under the optimized experimental condition the linear ranges and LOD were obtained. The nanoadsorbent can be reused up to 8 times with RSDs (n=3) and extraction recoveries of 1.88 and 3.46% and 90 and 100% for Cd(II) and Pb(II) respectively.

Conclusion: In this study a novel nanoadsorbent with a high capacity loading was synthesized and its application was checked out in AA-MD-µSPE as a sample preparation method. The metal ions were quantified by MS-FAAS and with the least amount of nanoadsorbent, high recoveries were obtained for the metal ions in a short time period. Also, a high preconcentration factor for trace amounts of the understudied ions due to the use of a low amount of eluent.

Keywords: Magnetic nanoadsorbent, Graphite carbon nitride, AA-MD-µSPE, Metal ions, FAAS.

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Preconcentration of copper and lead ions using air assisted dispersive liquid-liquid microextraction followed by flame atomic absorption spectroscopy

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Background: The determination of heavy metals such as copper and lead have a special importance. Different techniques such as flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), electro-thermal atomic absorption spectroscopy (ET-AAS) have been used for the determination of copper and lead in aqueous samples. The FAAS has been widely used in analysis of trace metals because of the low costs, operational facility and high sample throughput [1].The determination of heavy metal ions at trace level is possible due to the use of sample preparation and sensitive instrumental techniques. One of the popular sample preparation methods is liquid phase microextraction (LPME) and the dispersive liquid-liquid microextraction (DLLME) is one of the easy subclasses of LPME. The application of deep eutectic solvents has attracted a remarkable attention because of its environmental friendly and sustainability which is used in the liquid phase microextraction. These solvents are the newest sub-class of ionic liquids which have some attractive properties such as: simple, novel and green synthesis [2].

Methods: In this study, a new synthesized deep eutectic solvent based on choline chloride and alcoholic ingredient was used as the extraction solvent for determination of trace amounts of copper and lead by the air assisted dispersive liquid-liquid microextraction procedure followed by FAAS.

Results: The different parameters affecting the DLLME were optimized including: volume of the extraction solvent (350 µL), sample pH (6) and number of extraction cycles (5). The method was validated based on linearities ($R^2 > 0.971$), linear dynamic ranges (1.5-200.0 µg L^{-1}), limits of detection (0.1-1.0 µg L^{-1}), enrichment factors (45.5 and 38.5) and relative recoveries (80 and 94%) for lead and copper ions, respectively.

Conclusion: In this study, a LPME method based on a new deep eutectic solvent was proposed. This new solvent comprising choline chloride and alcoholic ingredient was simply and cheaply synthesized at room temperature and it successfully applied as extraction solvent for the analysis of low levels of copper and lead ions in aqueous samples.

Keywords: Deep eutectic; DLLME; FAAS; Heavy metals.

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Determination of benzene, toluene, ethylbenzene and xylene in water samples using organic gas steam-liquid extraction method

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Background: Benzene, toluene, ethylbenzene and xylene (BTEX) are among the important water pollutants [1-2]. Due to the toxicity of BTEX compounds, the development of the analytical techniques for efficient analysis of them is crucial [3-4]. The present paper intends to describe and apply a sensitive, economical, simple and fast analytical technique for analysis of BTEX compounds.

Methods: n-hexane was injected to the organic solvent tube, the heated chamber warmed up to certain temperature by circulating thermostated water. Aqueous saline sample solution was injected to the sample tube. Using gas stream flow rate at the bottom of the organic solvent tube, the gas steam of the organic solvent was transferred to the sample column and moved longitudinal from the bottom to the up. At the final stage, a small amount of double distilled water was added from the side tube to increase the level of aqueous phase up to the conical part, where the sample could be collected by using a microsyringe for the subsequent analysis by GC.

Results: The experimental response data were analyzed by a regression procedure based on the response surface methodology (RSM). The design was made of four factors at 3 levels with 6 center points. A total of 30 experiments were designed and performed. According to the obtained results, the effects of the main factors on the response were as the following orders: organic solvent volume > ionic strength > N_2 evaporating gas flow rate > heated chamber temperature. The practical suitability of the developed OGS-LE method was confirmed by the determination the BTEX in real samples that were obtained from two separated Qanats located in Alborz, Iran. The detection limit, precision, linearity of the method were obtained in the range of 10 µg L^{-1}, 5.3-8.7 % (RSD, n=4) and 50-5000 µg L^{-1}, respectively.

Keywords: BTEX,FCCD,Determination, organic gas steam-liquid extraction

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A novel Strategy based aptasensors and magnetic nanoparticles for selective indirect detection of mercury ions by graphite furnace atomic absorption spectrometry

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Background: Mercury is one of the toxic heavy metal, which can cause serious damage to the environmental safety and human health. Many instrumental techniques including cold vapor atomic absorption spectrometry [1], atomic fluorescence spectrometry [2] and high-performance liquid chromatography [3] have been developed for determination of mercury ion. These methods require complicated sample preparation, expensive equipment and time-consuming which limit their application mercury detection. Thymine (T)-thymine (T) is able to selectively bind to Hg^{2+} to form a stable T-Hg^{2+}-T complex, which is even more stable than the common A−T pair in DNA double strands. In this approach selectivity was guaranteed by the interaction of Hg^{2+} and aptamers and magnetic nanoparticles for simplification of the separation and Graphene-CdS for signal amplification.

Methods: A specific sequence of aptamer ssDNA (S_1) covalently bonded to the Fe_3O_4@SiO_2 magnetic nanoparticles (MNPs). On the other side, graphene-CdS was bonded to the secondary aptamer ssDNA (S_2). The mixture of this two-component generate the MN-dsDNA-Gr/CdS. Determination strategy is based on the capturing the generated complex and subsequently releasing the Gr/CdS in presence of Hg^{2+} ions due to strong and stable thymine-Hg^{2+}-thymine. Then the released Gr/CdS which dissolved digested by HNO_3 and the Cd^{2+} ions will be measured by graphite furnace atomic absorption spectrometry.

Results: Under the optimal conditions, the proposed aptasensor showed a wide linear range from 2.5 $amol.L^{-1}$ to 0.25 $nmol.L^{-1}$ with a detection limit of 7.6 $amol.L^{-1}$ (S/N = 3). The proposed aptasensor exhibited high selectivity for Hg^{2+}.

Conclusion: In this study, a new, easy to use and high efficient methodology is developed for mercury detection. The proposed method showed good precision, accuracy and large dynamic range for the determination of mercury.

Keywords: Aptasensor; Magnetic nanoparticles; Hg^{2+} detection; Graphite furnace atomic absorption spectrometry.

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Determination of Ethambutol in Biological Samples Using Dispersive Solid Phase Microextraction Followed by Ion Mobility Spectrometry

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Background: Solid phase microextraction (SPME) is a very successful and one of the most widely used technique for sample preparation and various modes of it have gained broad acceptance for separation and determination of target analytes in the complex matrixes [1]. Among them, dispersive solid phase microextraction (DSPME) as a fast and simple microextraction method is successfully applied for the quantification of various chemical compounds [2].

Methods: In DSPME, a very small amount of an absorbent is dispersed in a sample solution to trap the analytes. Then the adsorbed analytes are transferred to a smaller volume of a desorption solvent. In this work, preconcentration of trace amounts of Ethambutol was developed using graphene based dispersive solid phase microextraction prior to ion mobility spectroscopy determination (GO-DSPME–IMS). For this purpose, an appropriate amount of Ethambutol solution (pH=5) was mixed with an adequate graphene oxide suspension. Subsequently, the solution was centrifuged to isolate the GO. The supernatant was discarded, and the deposited GO nanosheets were redisposed in 150 µL acidified methanol to desorption the analyte. Finally, 5 µL of supernatant was injected into the IMS.

Results: The effects of relevant experimental parameters such as pH, time, amount of adsorbent, desorption solvent etc. on the method efficiency were investigated. Under the optimum conditions, the calibration curve was linear in the range of 1 to 120 ng mL^{-1} with the correlation coefficient of 0.9995. The limit of detection for proposed method (n=8) was 0.4 ng mL^{-1} and the relative standard deviations were obtained (n=8) 3.3% and 1.6% for 10 and 100 ng mL^{-1}, respectively. The proposed method was successfully applied for the preconcentration and determination of Ethambutol in milk and biological with 98.7-102.0% recoveries.

Conclusion: Here a GO-DSPME procedure was introduced for the preconcentration and determination of Ethambutol. The ion mobility spectrometry was used as a sensitive, fast and cheap detection instrument. The GO-DSPME-IMS procedure offers some advantages such as low organic solvent consumption, low cost, low LOD, relatively wide linear range, and high sensitivity. The proposed method was successfully applied for the determination of Ethambutol in the different samples such as human plasma, breast milk, saliva, and artificial tear.

Keywords: Ethambutol; Microextraction; Graphene oxide; Ion mobility spectrometry; Milk; Biological samples.

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Dispersive liquid–liquid microextraction based on solidification of floating organic drop coupled with gas chromatography-mass spectrometry for separation/preconcentration and determination of permethrine and deltamethrin in milk

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Background: Pyrethroids have been increasingly used to replace organophosphate pesticides which are widely banned due to their highly toxic and persistent nature [1]. Pyrethroid insecticides disrupt the sodium channel which leads to the death of a variety of insects. Permethrin and deltamethrin are two potent and common pyrethroids which are extremely toxic to aquatic life, bees, and wildlife. Therefore, separation/preconcentration of trace amount of permethrin and deltamethrin is essential. Solidification of floating organic drop liquid-phase microextraction (SFO-LPME) based on dispersive liquid–liquid microextraction (DLLME) is a facile and efficient method in which the extraction solvent is solidified near room temperature and can be easily separated without centrifugation [2].

Methods: In the present study, 5 mL aqueous sample of water free from pesticides was placed in a 10 mL falcon test tube and spiked with the target analytes 50 ng L^{-1}. Acetonitrile (0.5 mL) as disperser solvent and 30 µL 1-undecanol as extraction solvent was rapidly injected into the sample solution with a 1mL syringe. A cloudy solution, resulting from the dispersion of fine droplets in the aqueous solution, was formed in the test tube. After centrifugation for 5 min at 4000 rpm, the falcon tube was transferred into a beaker containing crushed ice; the organic solvent was solidified in 5 min. After 5 min, the solidified solvent was transferred to a conical vial; it melted quickly at room temperature and 1µL of 1-undecanol containing permethrin and delthametrin was injected to GC-MS.

Results: Dispersive liquid–liquid microextraction based on solidification of floating organic drop coupled with gas chromatography-mass spectrometry was applied for separation/preconcentration and determination of permethrine and deltamethrin. The detection limits of 5 ng L^{-1} and 3 ng L^{-1} for permethrin and delthametrin respectively, the linear ranges of 10-250 ng L^{-1} were achieved for both analytes. The precision of the method (RSD % for n=7) were 3.6 and 3.2 for permethrin and delthametrin respectively. The enrichment factors of 992.5 and 997.4 were achieved for permethrin and deltamethrin respectively. The accuracy of the method was considered in milk as a complicated matrix.

Conclusion: The proposed analytical method is facile, rapid, precise and with good linearity and high enrichment factor. The applied extraction solvent has lower toxicity and its separation from the media is really simple due to solidification. SOF-DLLME was successfully applied in milk as complex matrix.

Keywords: Dispersive liquid–liquid microextraction, Solidification of floating organic drop, Permethrine, Deltamethrin, Milk

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Determination of trace amount of thiabendazole residues in food and water samples by spectrofluorometry after preconecentration with micro solid phase extraction based on new modified magnetic nanoparticles

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Background: Benzimidazole pesticides are widely used before and after harvesting to prevent fungal deterioration and persist over long periods of time in crop production. Their application includes improving the yield of the product and also increasing the amount of fresh fruit and vegetables. However, the presence of pesticides residues in food has a negative effect on human health [1]. The maximum amount of Thaibendazole (TBZ) as a antifungal pesticide in fruits and vegetables is 0.05-15 mg/kg, depending on the product [2]. Therefore, sensitive and reliable methods are needed to monitor pesticide residues in water and food to ensure their safety. Several methods have been reported for the extraction and measurement of TBZ [3]. One of the most sensitive methods for measuring TBZ is fluorescence. However, a preconcentration method is needed prior to the determination of TBZ to eliminate the effects of complex matrix and increase the sample detection limit.
The aim of this work was to conduct a study on the micro solid phase extraction (µ-SPE) by employing a new adsorbent for preconcentration of trace levels of TBZ prior to the determination by spectrofluorometry. This method reduces the amount of adsorbent, minimize the cost, and decrease the amount of waste in the determination.

Methods: Micro solid phase extraction was carried out using functionalized Fe_3O_4 magnetic nanoparticles that were synthesized, purified and functionalized according to a previous work[4]. The adsorbent were characterized with FT-IR, SEM, EDX, and XRD. The absorbed analyte was then back-extracted into a small volume of a green solvent and was determined by spectrofluorometry. Different parameters affect the extraction and determinations of the analyte were optimized.

Results: The adsorbent could extract the TBZ from aqueous solution in five minutes and the analyte was back extracted into 2 mL solvent with high recovery. The calibration curve was linear in the concentration range of 1-200 µg mL^{-1} with the limit of quantification of 1 ng mL^{-1}. The present method was applied to the analysis of water and food samples with the relative standard deviations less than 7%.

Conclusion: The combination of µ-SPE and spectrofluorometry provided the selective determination of trace TBZ in complex matrices. Compared to other conventional sample preparation methods, the proposed method offers advantages, such as simplicity, ease of operation, relatively short analysis time, and lower consumption of organic solvents. The proposed method was applied to the analysis of TBZ in food samples with satisfactory results.

Keywords: Thiabendazole, Spectrofluorometry, Micro solid phase extraction, Magnetic nanoparticles

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Development of new nanocomposite based on Polyoxomolibdate nanoclusters/Graphene oxide as an efficient sorbent for solid-phase microextraction: Application in MDMA screening

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Background: The 3,4-Methylenedioxymethamphetamine (MDMA) is a commonly used recreational drug, which is frequently encountered in postmortem toxicology laboratories [1]. Drug abuse continue to be a remarkable public health concern worldwide [2], moreover the analysis of MDMA may be used in forensic toxicology as a representative of opiate abuse [3].

Methods: A nanocomposite structure of chitosan/ polyoxomolybdate /graphene oxide as a stationary phase coating of SPME was synthesized by a simple sol–gel process and then immobilized on stainless steel surface. The nanocomposite fiber successfully used in headspace SPME combined with ion mobility mass spectrometry for MDMA analysis in biological matrices. The SPME conditions such as temperature, pH, and concentration of NaCl and extraction time were optimized with the aid of central composite design through response surface methodology.

Results: The developed nanocomposite was characterized through FT-IR spectroscopy, and thermogravimetric (TG) analyses. A polynomial equation was fitted on the experimental data as a response surface methodology and the optimal values of variables were calculated. The limits of detections range from 0.12 ng mL^{-1}, and the calibration plots are linear within the 0.27–400 ng mL^{-1} concentration range. The method was successfully applied to the extraction and determination of MDMA in plasma, urine and hair samples. Under optimized conditions, the repeatability for one fiber (n=3), expressed as the relative standard deviation, is 5.2 %. The thermal stability of the fiber and the high relative recovery make this method superior to conventional methods of extraction.

Conclusion: The main advantages of this fiber are high porosity, high temperature, chemical and mechanical stability, reproducibility as well as low cost. The new nanocomposite coating offers good mechanical and thermal stability and high extraction efficiency due to its large specific surface. With relatively low LOD and good precisions, the established method had potential use for the screening of MDMA in real biological samples suspected of drug abuse.

Keywords: Ternary nanocomposite coating; Chitosan/ polyoxometalate /graphene oxide nanocomposite; Response surface methodology; Headspace solid-phase microextraction(HS-SPME); Ion mobility mass spectrometry

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Chromatographic Determination of the Flory-Huggins parameter of polyether sulfone

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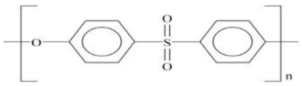
Background: The Inverse gas chromatography method (IGC) makes it possible to determine various parameters characterizing the thermodynamic properties of polymers such as the Flory-Huggins parameter χ_{12} which is an important parameter used for characterizing the interaction intensity between polymer and solvent [1]. In this work, PES and ten organic solvents were used. Polyether sulfone (PES) is an amorphous polymer and a high-temperature Engineering thermoplastic. Even though PES has high-temperature performance, it can be processed on conventional plastics processing equipment. As PES is amorphous, mold shrinkage is low, and is suitable for applications requiring close tolerances and little dimensional changeover a wide temperature range.



Methods: The main characteristic of IGC is that the interested species is the polymer material acting as stationary phase in IGC column. Probe solvent with known property is injected in the column and the retention time of the probe is measured at infinite dilution. The interaction between the probe solvent and the polymer is calculated from the retention time when the temperature was changed from 50°C to 80°C [2]. The principle of determining χ_{12} by IGC is as follows:

$$\chi_{12}^{\infty} = \ln\left[\frac{273.2 R \upsilon_2}{V_g^0 V_1 P_1^0}\right] - \frac{P_1^0 (B_{11} - V_1)}{RT} - 1$$

Results: The measured χ_{12} values from IGC for three solvent and PES in various temperatures are listed in table:

Name	50°C	60°C	70°C	80°C
Ethanol	1.867	1.820	1.782	1.739
pentanol	3.544	3.5	3.45	3.32
Ethyl acetate	3.388	2.991	2.65	2.48

Conclusion: For the PES and ten organic solvents, the χ_{12} measured by IGC technique which the results are acceptable. The results show that PES and organic solvents have weak interactions.

Keywords: Flory-Huggins parameter; polyether sulfone; IGC; solvent.

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ZIF-67 derived etched carbon/polymer membranes: Its application for the thin film microextraction of diclofenac in biological fluids

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Background: In the present work, we direct carbonization ZIF-67, by used zeolitic imidazolate framework (ZIF-67) as precursor to prepare porous carbon-ZIF-67. By applying a post-carbonization acidic etching treatment with hydrofluoric acid (HF), the initial surface area of the carbon-ZIF-67 sample increased. For applied applications, the porous carbon-ZIF-67-HF material was used to fabricate a carbon composite membrane using polyvinylidene difluoride (PVDF) membrane. The prepared membranes were applied as sorbent for thin film microextraction (TFME) of diclofenac sodium in biological fluids. After elution, diclofenac sodium was quantified by high performance liquid chromatography-ultraviolet detection (HPLC-UV).

Methods: According to the literature [1], ZIF-67 has been synthesized. Afterwards, ZIF-67 were carbonized in a tubular furnace under N_2 atmosphere at 1073 K for 3 h. A portion of the carbon-ZIF-67 samples was etched with 1.0 M HF aqueous solution at room temperature for 24 h, washed with water and dried under vacuum at 333 K for further use. Carbon-ZIF-67-HF membranes were prepared according to previously reported procedure [2].

Results: The high quality porous carbon- ZIF-67-HF membrane was prepared. Porous carbonized ZIF exhibited fast adsorption kinetics and an outstanding maximum adsorption capacity for the extract of diclofenac sodium. A Box-Behnken design (BBD) was used for the optimization of the experimental parameters. Under the optimum conditions, low limit of detection (LODs) were obtained. The method would afford an efficient tool for therapeutic drug monitoring and bioavailability studies of diclofenac sodium.

Conclusion: The high sensitivity, specific and cost-effective attained by the proposed TFME method allowed the determination of diclofenac sodium in biological fluids. Highly porous carbons have been prepared by carbonization of ZIF-67 in nitrogen atmosphere and etched with hydrofluoric acid to obtain additional porosity. MOF derived etched carbon/polymer membranes for the extraction of diclofenac sodium. The high quality etched-carbon/polymer membranes exhibited an excellent extract of diclofenac sodium. These carbon-ZIF-67-HF/PVDF membranes are very promising materials for extraction of diclofenac sodium.

Keywords: Nanoporous carbons, ZIF-67, Thin film microextraction, MOF, Biological fluids, Etching

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Preparation and characterization of nano liposomes of oleuropein in soybean phospholipids

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Background: Oleuropein is a main phenolic bitter compound found in green olives and olive leaves with remarkable pharmacological properties [1]. This study sought to prepare nano liposomes of oleoropein, obtained from olive leaves ethanolic extract, in unpurified soybean phospholipids in order to improve its solubility and permeability.

Methods: Oleuropein liposomes were prepared by a conventional film method [2], and were characterized for solubility and entrapment efficiency by UV/Vis. spectrophotometry, high performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

Results: HPLC, spectrophotometry and FTIR studies indicated the entrapment of oleoropein and interaction between soybean phospholipids and the olive leaves extract. Oleuropein liposomes were stable at pH 5.5 and 7.4, but showed reversible agglomeration at pH 1.6.

Conclusion: Enhanced solubility, absorption and antioxidant effect may improve the overall pharmacological effects and medicinal value of olive leaves ethanolic extract.

Keywords: Oleuropein, Soybean lecithin, Soybean phospholipids, Liposomal drug delivery system

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Air-assisted liquid–liquid microextraction of Azathioprine based on multivariate optimization and its trace determination in biological samples by high-performance liquid chromatography

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Background: Azathioprine is an immunosuppressant agent which has been clinically applied in the inhibition of organ rejection for the past thirty [1]. But it has a pancreatitis and hepatic toxicity and suppresses the bone marrow, which makes the patients sensitive to infection. Therefore, determination of Azathioprine concentration in urine and plasma is essential [2]. According to our knowledge, no usage of LLME for the extraction and preconcentration of Azathioprine in plasma and urine samples has been reported thus far. Optimizing the effective factors was done in two stages. First, the effective factors were identified by PBD, then the meaningful factors were optimized by BBD.

Methods: In order to do the extraction, initially, 9 mL of the aqueous solution sample with the concentration of 500 ng.µL^{-1} from each analyte was transferred to narrow-bore glass test tubes. Then 100 µL of extraction solvents were injected in the aqueous sample via syringe. The process of sucking out the mixture and rapidly injecting it back was done several times. In this stage, the extraction solvent was dispersed via air in the aqueous solution which contained Azathioprine. A cloudy solution was created and this compound was extracted. Then the solution was centrifuged at 5000 rpm for 10 min in order to separate the extraction phase. Then the extracted phase which has been accumulated on the tube was taken via a syringe and was put in the sample vial. After that 20 µL of sample was injected to the HPLC-UV system for the analysis.

Results: Under the optimized conditions, the extraction recoveries in urine and plasma samples were obtained 85 and 97, respectively. The detection limit of Azathioprine was 3 ng/mL in plasma and 3.2 ng/mL in urine. Also, this method makes it possible to measure this drug in urine and plasma in the linear range of 10-1000 ng/mL. RSDs for intra and inter day extraction of Azathioprine were less than 5.8% in three measurements.

Conclusion: This study indicated that the proposed AALLME technique coupled with UV-HPLC is appropriate for determination of Azathioprine in biological samples. The advantages of the proposed method are high recoveries, low detection limits, wide linearity range, simplicity of the extraction and rapid extraction. Therefore, the results showed that the presented method has great potential in preconcentration and trace determination of Azathioprine in biological samples.

Keywords: Azathioprine, Experimental design, Air-assisted liquid–liquid microextraction

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Utilization of air-assisted liquid–liquid microextraction followed by HPLC-UV based on multivariate optimization as a sensitive and efficient method for the extraction and determination of Morin and Quercetin in juice samples

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Background: Flavonoids are the major secondary plant metabolites with antioxidant activity. Because of its relative abundance in edibles including vegetables, especially onions, fruits, tea and wine [1], Morin and Quercetin are among the flavonoids attracting most attention. It has been reported to have biological properties that may play an important role in the prevention of human diseases, such as cancer, cardiovascular diseases, diabetes, ulcer, cataract and allergies [2]. Optimizing the effective factors was done in two stages. First, the effective factors were identified by PBD(Plackett Burman Design), then the meaningful factors were optimized by CCD(Central Composite Design) and the optimized conditions for AALLME were used for the analysis of Morin and Quercetin.

Methods: 9 mL of samples (200 ng/mL) were placed into a narrow-bore glass test tube. 100 μL of extraction solvent (1-undecanol) was rapidly injected in to the tube. Then, a portion of the mixture was sucked and injected into the sample tube using a 5-mL glass syringe. This procedure was repeated 15 times. The resulting cloudy solution was centrifuged for 8 min at a rate of 5000 rpm. Then the extracted phase transferred into another test tube with a HPLC syringe completely. After that 20 µL of sample was injected to the HPLC-UV system for the analysis.

Results: Under the optimized conditions, the extraction recovery of Morin and Quercetin were 94 and 97% and the detection limit of were 1.02 and 1.61 ng/mL ,respectively. A linear calibration curve was obtained from 3 to 5-1000 ng/mL with a determination coefficient of 0.9994. Also, RSDs for intra and inter day extraction were less than 3.8% in three measurements.

Conclusion: The advantages of the proposed method are high recoveries, low detection limits, wide linearity range, simplicity of the extraction and rapid extraction. Therefore, the results showed that the presented method has great potential in preconcentration and trace determination of Morin and Quercetin in juice samples.

Keywords: Morin; Quercetin; Experimental design; Air-assisted liquid–liquid microextraction

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Highly selective Liquid-Liquid micro-extraction of Diclofenac into synthesized nano-structured vesicles of Decanoic acid containing Molecularly Imprinted Polymer

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Background: Up to now, several methods have been used for separation of non-steroidal acidic anti-inflammatory drugs (NSAIDs) from matrix samples such as solid-phase extraction (SPE). But it suffers from its relatively low selectivity. To overcome this problem in SPE, molecularly imprinted polymers (MIPs) with higher selectivity are increasingly developed and applied to various samples [1]. In this research the application of a new kind of water immiscible solvent, supra molecular solvent (SUPRA), was investigated on the extraction of DCF from its aqueous solution into liquid SUPRA phase. Also for the first time, molecularly imprinted polymer (MIP) was completely dispersed into SUPRA phase and the new liquid phase, MIP- SUPRA phase, was used as an alternative and selective liquid phase for highly selective and quantitative separation of DCF from aqueous solutions.

Methods: The supra molecular solvent was prepared from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutyl ammonium ion (Bu_4N^+) [2] and diclofenac-molecularly imprinted polymer(DCF-MIP) was synthesized by precipitation polymerization method [3]. So, 533 µl of 5.63 g/L DFC-MIP in SUPRA, as the separation liquid phase, was added into 5 ml of 5 ppm aqueous DFC solution at pH=5 and 25°C and stirred about 75 min. Then the solution was centrifuged at 1500 rpm in 5 min and the concentration of remaining DCF in aqueous solution was determined.

Results: The results showed that in the presence of DFC-MIP in SUPRA phase, both efficiency and selectivity of DFC extraction into DFC-MIP-SUPRA phase were improved. Under optimal conditions, the analyte (DCF) was extracted into the separating liquid phase and its remained amount in the aqueous phase was determined. Therefore, the extraction percentage of DFC from natural drinking water into DFC-MIP-SUPRA phase was achieved 97.5% ± 0.067% (n=7).

Conclusion: It was concluded that besides of thoroughly dispersing of DFC-MIP into SUPRA phase, DFC-MIP-SUPRA phase can be used as an alternative selective and separating liquid phase to separate DFC from natural water samples. On the other hand, the separation process was so simple and fast and also very low volume of liquid separation phase (DFC-MIP-SUPRA phase) was used (533 µL).

Keywords: Diclofenac separation; Molecularly Imprinted Polymer; Supra Molecular Solvent (SUPRA); Liquid-Liquid micro extraction; Selective extraction.

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Simultaneous separation of silver (I) and lead (II) ions through two supported liquid membranes composed of selective crown ethers in supra molecular solvents

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Background: This research, for the first time, explores an innovative application of SLMs in the simultaneous selective transport of Ag^+ and Pb^{2+} ions and also the suitability of supra molecular solvents (SUPRAs) constructed of vesicles of decanoic acid as a proper solvent instead of organic solvents. In this work, two carriers Dibenzyl diaza 18 crown 6 (DBzDaza18C6) and Dicyclohexyl 18 crown 6 (DC18C6) were easily dissolved in SUPRA and imbedded in pores of two thin polypropylene films.

Methods: SUPRA was prepared from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutyl ammonium ion (Bu_4N^+) [1]. All transport experiments were carried out at ambient temperature and a two-membrane-three-compartments glass cell was used. The middle compartment with a volume of 500ml contained the source solution and the receiving solutions for silver (I) and lead (II) ions were located in the first and third compartments, respectively, with a volume of 100 ml. Two membranes with an area of 12.6 cm^2 could be fixed in between the three cell compartments. The source solution contained 1.85×10^{-4} mol L^{-1} picric acid, 2 ppm Ag^+ and 2 ppm Pb^{2+} ions, was placed in the middle compartment, one side of which comprised the DBzDA18C6 (8×10^{-3} mol L^{-1})-loaded SLM and the other side the DC18C6 (8×10^{-3} mol L^{-1})-loaded SLM. The first and third compartments contained the receiving solutions (100 ml each) 0.6 mol L^{-1} sodium thiosulfate at pH 6.4 for stripping of Ag^+ ion and 0.25 mol L^{-1} sodium pyrophosphate at pH 7 for stripping of Pb^{2+} ion, respectively. Each compartment was equipped with a Teflon coated magnetic stirrer for stirring the aqueous solutions and an inlet for filling and draining the source and receiving solutions.

Results: Under optimal conditions, silver and lead ions were transported into their receiving phases after 75 and 15 min, respectively, and a simultaneously quantitative separation of the cations was achieved in a relatively short time (i.e. 97.5% Ag^+ and 96.5% Pb^{2+}).

Conclusion: A novel application of supported liquid membranes (SLMs) to the selective and simultaneous separation of Ag^+ and Pb^{2+} ions from a dilute source by employing a two-membrane-three-compartment cell and two selective crown ethers dissolved in SUPRA solvent is introduced.

Keywords: simultaneous silver and lead ions transport; supported liquid membranes; selective crown ethers; supra molecular solvent (SUPRA).

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Spin-Column Micro-Solid Phase Extraction of Chlorophenols Using a Novel Metal-Organic Framework

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Background: Chlorophenols (CPs) have been considered as hazardous pollutants by different environmental protection agencies over the past decades [1,2]. Despite the hazardous effects of CPs, these compounds are still being utilized in many countries. Thus; the extraction, quantification, and determination of CPs in environmental samples is of analytical chemist's interest. Meanwhile, Metal-organic frameworks (MOFs) have been enormously used as the new generation of solid materials with favorable porosity and high surface area thanks to their unique structures. Owing to the facile and non-expensive synthesis of MOFs, these materials have attracted considerable attentions in the fields of chemistry, material science, and engineering.

Methods: In the present study, a novel MOF material named MFU-4l was successfully synthesized and applied as a sorbent in a Spin-Column Micro-Solid Phase Extraction **(**SC-µ-SPE) method. The usage of the sorbent led to the selective extraction and high preconcentration of the selected CPs (4-CP, 2,3-DCP, 2,4-DCP, and 2,4,6-TCP). It should also be noted that the quantification of the mentioned CPs were made using a gas chromatography-mass spectroscopy (GC-MS) instrument.

Results: The effect of influential parameters affecting on the extraction efficiency of the applied SC-µ-SPE method were assessed and optimized by a univariate method followed by the establishment of optimal extraction conditions. Under the optimal conditions, the calibration curves were plotted to calculate the figures of merit. Broad linear dynamic ranges of 0.5 – 400 and 1.0 – 400 µg Kg^{-1} and acceptable limits of detection of 0.10 and 0.50 µg Kg^{-1} were obtained for respective water and soil samples.

Conclusion: The applicability of the proposed method was investigated by quantitative analysis of the target analytes in soil and environmental water samples. Finally, it is concluded that the applied method represents a fast, sensitive, and reliable procedure which could be used for the ultra-trace analysis of the target analytes in various environmental samples.

Keywords: Metal-organic frameworks; Spin-column micro-solid phase extraction; Chlorophenols; Gas chromatography-mass spectrometry; Environmental samples.

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Polydopamine functionalized carbon nanotubes for pipette-tip micro-solid phase extraction of malathion and parathion in environmental samples

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Background: CNTs have been among the most developed materials with unique physicochemical and electrical features. Structurally, these nanomaterials are graphite sheets which are rolled up to form tube-shaped 3D structures. These tubes can be single-wall carbon nanotubes (SWCNT) or multi-wall carbon nanotubes (MWCNT). During the recent years, different types of SWCNT or MWCNT materials have been modified with different types of molecules and polymers to confer these nanotubes desirable properties for specific extraction procedures [1].

Method: In the present study, MWCNT were modified by polydopamine molecules and applied for pipette-tip micro solid phase extraction of two organophosphorous pesticides comprising malathion and parathion in environmental water samples. The extraction procedure was followed by gas chromatography instrument equipped with mass spectrometry detection system for separation and determination of the desired analytes.

Results: The applied method represents selective, fast, and efficient extraction of the analytes with favorable accuracy and high preconcentration factors. All the effective parameters comprising the effective parameters of the adsorption step as well as the effective parameters of the desorption step were identified and optimized using a one variable at-a-time protocol. Under the optimal conditions, calibration curves for the both analytes were plotted to obtain figures of merit. Broad calibration curves were obtained with the linearity in the range between 0.30-200 ng mL^{-1} for the both target analytes.

Conclusion: High preconcentration factors and favorable extraction efficiencies along with desirable relative standard deviations confirmed that the procedure was highly efficient and precise. Real samples analysis was carried out using the optimized technique for quantitative analysis of the target analytes in environmental water samples.

Keywords: Multi-wall carbon nanotubes; Pipette-tip micro solid phase extraction; Organophosphorous pesticides; Gas chromatography-mass spectrometry; Environmental samples.

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Developing novel hollow-fiber liquid phase microextraction for extraction of Metoprolol Succinate in aqueous and biological samples

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Background: One of the most important drug for controlling blood pressure and treatment of chronic chest angina is Metoprolol Succinate (MeSu) [1]. Nowadays, researchers focus on the hollow-fiber liquid phase microextraction (HF-LPME) as a preparation technique in environment and biological analysis combined with high-performance liquid chromatography (HPLC), gas chromatography (GC) and capillary electrophoresis (CE) for MeSu analysis [2]. The LPME can be classified in two groups of two-phase and three-phase [3]. If the target analytes are neutral compounds, it can perform the two-phase HF-LPME by using the organic solution as receiving phase. In this work, the novel three-phased HF-LPME was developed for extraction of MeSu.

Methods: The application of hollow fiber- liquid phase micro extraction in combined with high performance liquid chromatography and ultraviolet detector (HPLC-UV) for extracting Metoprolol Succinate in aqueous and biological samples investigated in three-phase method. For this purpose, 11mL of aqueous sample of drug (source phase, SP) inside an organic saturated phase within hollow fiber pores (the membrane phase, MP), extracted back into **24 µL** second aqueous solution (receiving phase, RP) that placed in a channel of hollow fiber. The effect of main parameters on extraction of MeSU was investigated and optimized.

Results: After extracting the Metoprolol Succinate drug under optimum condition (n-dodecane as organic solution type, the pH of source and receiving phase solutions of 11 and 5 respectively, the extraction time of 50 min and stirring speed of 800 rpm) 296 as a pre-concentration factor, the detection limit of 0.4 ppb, the relative standard deviation of 0.2495%, the linear calibration range of 1-100 ppb, the correlation coefficient higher than 0.997 and the extraction recovery of 64.7% were obtained for urine samples.

Conclusion: The results of extraction from real samples (urine samples) showed that this method has a high selectivity and separation ability. The recommended method has a favorite precision, selectivity and detection limit and it is noteworthy due to minimizing the organic solution consumption and therefore due to consistency with environment.

Keywords: Liquid phase microextraction; Hollow fiber; Metoprolol Succinate; HPLC

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Derivatization degradation products chemical nerve agents by method methylation and Analysis of their degradation products by gas and liquid chromatography-mass spectrometry

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Background: The effective methylation of phosphonic acids related to chemical warfare agents (CWAs) employing trimethyloxonium tetrafluoroborate (TMO.BF_4) for their qualitative detection and identification by gas and liquid chromatography-mass spectrometry (GC-MS&LC-MS) is presented. The method was demonstrated to successfully methylate a variety of Schedule 2 phosphonic acids, including their half esters, resulting in derivatives that were readily detected and identified using the instrument's spectral library. Most importantly, the method was shown to simultaneously methylate a mixture of the organophosphorus-based nerve agent hydrolysis products (at a 10 µg mL $^{-1}$ concentration each). In addition, the protocol was found to effectively methylate products arising from the oxidative degradation of the V-series agents VR and VX respectively. [1-2]

Methods: The methylation occurs in rapid fashion (3 hour) and can be conveniently carried out at temperature 50 ˚C and potassium carbonate catalyst.

Results: While methylation accomplished methodical described in refrences[1-3] has efficiency 40% but the optimized work described herein represents the use of TMO.BF_4 as a viable, stable and safe agent for the methylation of phosphonic acids and their half esters with yield 95% and detection limit 8 µg mL $^{-1}$, by use of potassium carbonate catalyst.

Conclusion: Derivatization methods for phosphonic acids, methylation has been a popular transformation due to the fact that it accomplishes what other methods such as silylations do but without the generation of interfering byproducts that complicate the analysis even further. For example, although diazomethane process is highly efficient and operationally easy to conduct; Diazomethane is highly reactive and will degrade on prolonged storage even if it involves an argon atmosphere coupled with careful refrigeration. An added problematic to the diazomethane method is also the explosive hazards associated with its preparation. For these reasons, the salt trimethyloxonium tetrafluoroborate has been introduced as a reliable derivatization agent for the methylation of analytes. Also the Defense chemical research laboratory (DCRL) identified all the spiked chemicals alkyl methyl phosphonic acid by this derivatization degradation products chemical nerve agents in Forty-Fourth Official OPCW Proficiency Test.

Keywords: methylation; phosphonic acid; trimethyloxonium tetrafluoroborate; GC-MS&LC-MS.

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Extraction and determination of dasatinib anticancer drug in urine sample using magnetic solid phase extraction technique based on modified cobalt ferrite/graphene oxide nanocomposite

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Background: Dasatinib is tyrosine kinase inhibitors (TKIs) used as first-line treatment of chronic myeloid leukemia. Therapeutic drug monitoring is important to achieve treatment efficacy and to control toxicity in the case of anticancer drug. New high-sensitivity sample preparation techniques to extract and monitor the drugs are needed. Thus, a simple method to determine plasma levels of dasatinib for application in clinical practice was important to develop.

Methods: A new and novel magnetic sorbent based on graphene oxide (GO) was synthesized and characterized [1, 2]. After conditioning of the proposed sorbet, the urine samples were loaded to extract and pre-concentrate the dasatinib. Then, a washing step was done to desorb unspecific interfering species to clean up. Finally, the elution process was performed followed for fluorescence detection.

Results: After preliminary experiments, the effective parameters in magnetic solid phase extraction (MSPE) procedure including the absorbent dose (mg mL^{-1}), the sample pH, and the extraction time were investigated and optimum conditions were obtained using experimental design methodology. In this regard, the central composite design (CCD) was used to define model for dasatinib MSPE procedures using modified magnetic GO. Under the defined optimum conditions, the method was linear in the range of 5.0-750 ng mL^{-1}, and the limit of detection and limit of quantification were 1.5 and 4.5 mg mL^{-1}, respectively. Finally, the proposed adsorbent was successfully applied for MSPE and determination of the dasatinib anticancer drug in urine samples.

Conclusion: The method enables rapid quantification of dasatinib and is being applied to therapeutic drug monitoring to adjust dose and to manage adverse reactions in clinical practice.

Keywords: Cobalt ferrite; Modified graphene oxide; Dasatinib; Magnetic solid phase extraction; Preconcentration; Fluorescence

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A new Co$_{0.7}$Mn$_{0.3}$Fe2O4@GO-EDA nano magnetic adsorbent for solid phase extraction and determination of dasatinib anticancer drug in urine and blood samples

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Background: Determination of anticancer drug is important to achieve treatment efficacy and to control their toxicity, but many of analytical techniques don't have efficient detection limit and precision. Therefore, new sample preparation techniques have proper high sensitivity and accuracy for extraction and determination of various analytes.

Methods: A novel magnetic solid-phase extraction (MSPE) technique coupled with high performance liquid chromatography has been utilized for the determination dasatinib in biological samples. The key point of this method was the application of a novel magnetic nanomaterial (Co$_{0.7}$Mn$_{0.3}$Fe2O4@GO-EDA) [1, 2]. The functional groups, morphology, and magnetic properties of this magnetic nanomaterial were investigated through fourier transformed infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM), respectively. After conditioning of the synthesized adsorbent, the urine/blood samples were loaded to extract and pre-concentrate the dasatinib. Then, a washing step was performed to desorb unspecific interfering species and finally, the elution process was performed using appropriate solvent.

Results: After the characterization of the new synthesized Co$_{0.7}$Mn$_{0.3}$Fe2O4@GO-EDA adsorbent, the main factors which could affect the drug extraction efficiency were optimized. Under the optimum conditions, the linearity of this method ranged from 250 to 750 ng mL^{-1} for dasatinib, with correlation coefficients of 0.9986. The enrichment factor, the relative standard deviation (RSD), and limit of detection were 20, 4.4%, and 75 ng mL^{-1}, respectively. In the final experiment, the developed method has been successfully applied to the determination of dasatinib in urine and blood samples, and the obtained recoveries were between 81.5% and 103.0%.

Conclusion: The new magnetic Co$_{0.7}$Mn$_{0.3}$Fe2O4@GO-EDA adsorbent enables rapid and accurate quantification of dasatinib and is being applied to therapeutic drug monitoring to adjust dose and to manage adverse reactions in clinical practice.

Keywords: Cobalt/Manganese ferrite; Ethylene diamine modified graphene oxide; Dasatinib; Magnetic solid phase extraction; Preconcentration; HPLC

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Synthesis of alumina nanoparticles with agarose coating for the preconcentration and measurement of pharmaceutical compounds

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Background: The main objective of this study is to synthesize alumina nanoparticles with agarose coatings as an adsorbent for preconcentration and measuring drug compounds. Coating with alumina nanoparticles with biocompatible polymers such as agarose can enhanced the contact surfaces and selectivities by modifying the biopolymer coating.

Methods: Alumina nanoparticles were synthesized by a sol-gel method [1]. The nanoparticles were coated with agarose by dropwise addition of a hot agarose solution. Agarose was activated in the outer shell with the aim of epichlorohydrine, which forms epoxy groups in the outer surface of the sorbent. The epoxy rings are unstable and highly reactive and can be covalently bound with the nucleophilic groups. Here, homocysteine was used as a ligand containing nucleophilic groups that was linked to the outer layer of agarose.

Results: Characterization of the adsorbent was performed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), Fig. 1. The results obtained confirm the agarose coating of the sorbent. The EDX analysis of the nano-absorbent elements also confirm the presence of aluminum, nitrogen, sulfur, and carbon elements. The adsorbent was then tested for the loading of drug compounds.

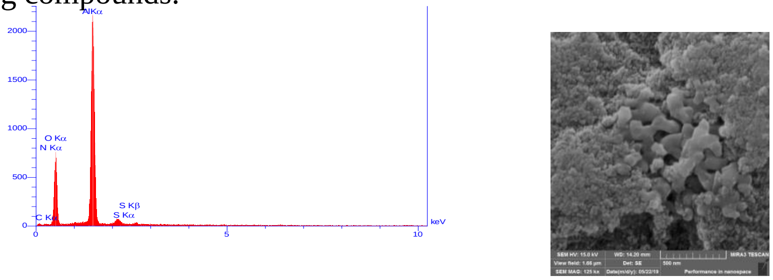

Fig. 1. SEM (right) image and EDX (left) spectrum of the prepared adsorbent

Conclusion: The use of alumina nanoparticles that provide a large contact surface, as well as their surface modification with a green bio-polymer, has been reported for the first time. The adsorbent have high efficiency for loading of drug compounds. The low cost and relatively simple synthesis are the other benefits of the prepared nano-absorbent.

Keywords: Nanoparticles, Alumina, Agarose coating, Homocysteine.

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Polyacrylonitrile / graphene oxide nanofibers for packed sorbent microextraction of drugs and their metabolites from human plasma samples

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Background: Microextraction by packed sorbent (MEPS) is a miniaturized form of SPE that was introduced in 2004 [1]. Graphene, a two-dimensional carbon based material, has attracted great interest in a wide range of applications including separation science due to its unique properties. Recently, polymeric materials have been widely used as sorbents for solid phase extraction. Adding graphene into polymers can improve their mechanical strength as well as the extraction capacity. This is the first study to use Polyacrylonitrile/Graphene Oxide (PAN/GO) nanofibers as an adsorbent in the MEPS technique in combination with Polystyrene (ENV+). The method was applied for the extraction of local anesthetics (lidocaine, prilocaine) and their metabolites from human plasma samples, and finally their analysis by LC-MS/MS.

Methods: PAN/GO nanofiber was synthesized using the electrospinning technique. Figure 1 shows the scanning electron microscope (SEM) of the nanofibers. MEPS tool was prepared as previously reported [1]. Two hundred microliter of plasma samples, spiked with lidocaine, prilocaine, 2,6-xylidine and o-Toluidine were diluted (1:5) with 1000 µ L of I.S solution (500 nmol/L). Then, 500 µ L of diluted samples were drawn slowly into the packed syringe five times (5 x 100 µ L). Afterward, the sorbent was washed with 2 x 100 µ L of 5% methanol in water. The analytes were finally eluted with 300 µ L of 1% formic acid in methanol and 25µ L of the eluates were injected directly into the LC-MS/MS system.

Results: The PAN/GO nanofibers showed higher extraction efficiency compared to silica, due to the higher surface area of the present nanofibers. The high surface area provides more active surface atoms to interact with the analytes resulting in better extraction efficiency. Additionally, the presence of hydroxylated copolymer ENV+ with high surface area improves the adsorption capacity considerably.

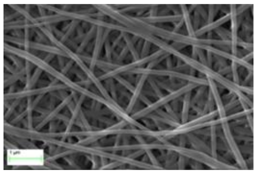

Fig1. SEM image of PAN/GO

Conclusion: PAN/GO in combination with polystyrene showed high extraction recoveries in comparison with conventional adsorbents which were used for the extraction of these drugs. The method accuracy, precision, carryover and matrix effect were in acceptance range based on FDA guidelines requirements.

Keywords: Nanofibers; Polyacrylonitrile/Graphene Oxide; Microextraction by Packed Sorbent; Human Plasma

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Novel Analytical Method to Avoid the Destruction of the Molecularly Imprinted Polymers Cavities by Water Molecules

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Background: Molecular imprinted polymers have the ability to identify selectively the interest template molecules based on the key and lock model [1,2]. However, application of MIPs is limited by many restrictions. One restriction is that, the selectivity of the MIPs mostly depends on the polarity of the extraction solvents and the extraction capability of it would decreases with polar solvents [3-5].

Methods: In this work, a novel and selective sample preparation technique was developed to overcome the problem of disturbance from water molecules when the molecularly imprinted polymers (MIPs) based sorbents were exposed directly to aqueous samples. This method was designed by combining ultrasound-assisted dispersive emulsification in-syringe microextraction (ultrasound-assisted DME) and ultrasound assisted dispersive magnetic solid phase microextraction based on molecularly imprinted polymers grafted magnetic graphene oxide (ultrasound promoted DMSPME-MIPs-MGO). The extraction steps are schematically shown in Fig. 1.

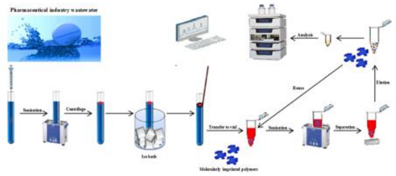

Fig. 1. Extraction stages schematically

Results: The relative standard deviation (RSD %) of the basic drugs are ranged from 3.15 to 4.59 and the detection limits are ranged from 0.3 to 0.6 ng ml^{-1}. To confirm the ability of the method to prevent the destruction of cavities by water molecules, reusability of MIPs-MGO sorbent in liquid–liquid–solid microextraction (LLSME) and DMSPME-MIPs-MGO techniques was compared.

Conclusion: The purpose of this study was to deal with the problem of water- compatibility in adsorbents based on the MIPs. This method combines many benefits, including high surface area of graphene oxide, selectivity and specifies of MIPs, easy separation of magnetic particles, and increased reusability of sorbent times.

Keywords: solidification, molecularly imprinted polymers, basic drugs, magnetic graphene oxide

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Alcohol-based Deep Eutectic Solvent as a Ferrofluid Carrier for the Development of Dispersive-Solid Phase Extraction: Application for the Preconcentration and Determination of Morin in food samples

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Background: In recent years, a new technique of magnetic dSPE method based on ferrofluids has been introduced to prevent the aggregation of magnetic nanoparticles (MNPs), and improve their dispersibility in the sample solution [1]. Ferrofluids are the stable and uniform suspensions of magnetic nanoparticles that suspends in a carrier liquid [2]. The aim of this study is develop the magnetic dSPE method based on a new ferrofluid for isolation and pre-concentration of Morin in food samples. In this work, a stable ferrofluid was formed by mixing ethylene glycol/tetramethylammonium chloride as deep eutectic solvent (DES) and SiO2@Fe3O4 without any stabilizer. DES increases the dispersibility of the sorbent, and decrease its consumption as well as the extraction time. These solvents as an excellent carrier for ferrofluids have exclusive features such as low-cost and toxicity, biodegradability, high purity, rapid, and simple synthesis process.

Methods: Firstly, 150µL of DES was added to the sorbent and sonicated. The prepared ferrofluid injected into the sample solution. Therefore, a dark cloudy suspension was formed immediately between MNPs and sample solution. Finally, the isolated analyte was desorbed using ethanol.

Results: Validation experiments in optimal conditions showed that the method had good linearity in the range 3-500 µg L^{-1} with the limit of detection of 0.9 µg L^{-1}. The extraction recovery of 97.7% and enrichment factor of 39.1, with a relative standard deviation of 3.8% (inter-day), were obtained through three replicated measurements on 30 µg L^{-1} of Morin standard solution.

Conclusion: In this method, the high sorbent capability of SiO2@Fe3O4 and DES mixture improved the extraction performance. Moreover, the possibility of fast injection of this mixture into the sample solution enlarged the contact surface between nanoparticles and analyte and helped in fast equilibration of the extraction in a few seconds.

Keywords: Ferrofluid; Deep eutectic solvent; Morin; High-performance liquid chromatography

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Determination of Buprenorphine in Biological Fluids after Dispersive Solid Phase Extraction Using Metal-Organic Frameworks as the Sorbent

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Background: Buprenorphine (BNP) is a semisynthetic opioid widely used in the treatment of chronic pain and also maintenance therapy for opioid addiction [1]. Quantitative determination of BNP in biological samples is a challenging issue since it needs advanced and expensive analytical systems [2-4]. Accordingly, a sample pretreatment method is vital prior to analysis while routine and available analytical systems such as ultra-performance liquid chromatography-ultraviolet detection (UPLC-UV) are employed. In this study, various MOFs, including MIL-53(Fe), MIL-101(Fe), MIL-101(Cr), Co-MOF-71, ZIF-8 and ZIF-67 were prepared and their ability as the sorbent was evaluated for the extraction of BNP. The highest extraction performance was observed by employing ZIF-67.

Methods: 10 mg ZIF-67 sorbent was added to 10 mL of the standard or sample solution (pH = 4.9) and the mixture was shaken for 5.0 min. Afterward, the sorbent was separated by centrifugation. The collected sorbent was eluted with 1.5 mL methanol and 10 µL of the eluate was injected into the UPLC-UV instrument for the analyte quantification .

Results: Under the optimized conditions, the calibration graph was linear in the range of 1-1000 µg L^{-1}. The limit of detection (LOD) was 0.15 µg L^{-1}. The relative standard deviation for five replicate determinations of BNP at 2 µg L^{-1} level was found to be 2.6%.

Conclusion: In this study, a metal-organic framework (ZIF-67) was applied as the sorbent for dispersive solid phase extraction of BNP prior to its determination with UPLC-UV. The sorbent showed high stability, reusability, and low toxicity. The method was successfully applied for the determination of BNP in urine and human plasma samples.

Keywords: Metal-Organic Frameworks; Buprenorphine, Dispersive solid phase extraction; Biological fluids.

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Development of an origami paper-based microfluidic device for separation also simultaneous quantification of color additives in food samples

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Background: Numerous analytical methods applied to determine mixtures of colorants in different matrices for monitoring the quality and safety of food products [1]. In many of these methods pre-treatment steps are required. Liquid-liquid extraction (LLE), solid-phase extraction (SPE), membrane filtration, cloud point extraction and other extraction [2]. Nowadays, studies focused mostly on the developing microfluidic paper-based devices (µPAD) technology due to several advantages as low-cost material that can be readily modified and patterned, power-free fluid transport via capillary action [3], and adaptability with a wide range of detection methods. Amongst, digital imaging devices are a simple, sensitive, and reliable alternative for the expensive analytical instruments for food colorant analysis [4].

Methods: In this work, after creating hydrophobic barriers on paper, 0.5 µl aliquot of the mixture was injected into the µPAD. Next, it was folded to origin an origami 3D µPAD. Then, the µPAD was fixed between two rectangular glass plates connected by bolts and nuts. A pore embedded in the center of the glass plates, therefrom the mobile phase was applied by micropipette. After completing the separation process each µPAD was scanned, ImageJ computer program was applied and the mean pixel value of each channel (R, G and B) were stored in Excel for subsequent calculations.

Results: The potentially effective parameters such as µPAD size, pH, solvent, and color space were studied. Following the optimization steps, analytical signals based on the color value were plotted for standard samples.

Conclusion: The proposed analytical method using the origami paper-based microfluidic device coupled with digital image analysis proved to be effective for the rapid separation and simultaneous quantification of the synthetic azo dyes. Linear ranges 0.01 g. L^{-1} - 20 g. L^{-1} (R2= 0.988) for E102 and a logarithmic relation was observed between 0.05 g. L^{-1} - 10 g. L^{-1} for E132 and limits of detection (3σ/slope) was between 0.07 and 0.09 g. L^{-1} respectively. This method was successfully applied in the separation and quantification of these dyes in jelly, candy, and three kinds of drinks samples with acceptable recoveries. Finally, the developed method presents advantages such as quickness, simplicity, environmentally friendly, economical, and ease of operation compared with other methods.

Keywords: Origami- microfluidic paper-based device; green separation method; scanner image analysis; Food colorants.

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Simple membrane microextraction coupled with high performance liquid chromatography for efficient determination of some beta-blockers in human urine and plasma samples

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Background: Propranolol and metoprolol are two usual beta (β)-blockers that are predominately used to manage cardiovascular diseases. Metoprolol is one of the β-adrenoceptor selective blocking drugs, which is applied for the treatment of hypertension, angina, myocardial infarction, and hyperthyroidism. Propranolol is commonly used in order to treat cardiovascular disorders such as hypertension and angina pectoris. Hence, determination of these two drugs in biological samples is very important. In this work, an efficient liquid membrane microextraction method was coupled with HPLC for the selective and sensitive determination of these drugs in complicated matrices [1-3].

Methods: According to the method, an aqueous source phase of analytes (donor phase, 10 mL) is circulated into the extraction cell, which is separated from an aqueous acceptor phase (100 µL) by a small piece of polypropylene membrane sheet whose pores are impregnated by an organic solvent (1-octanol, 15 µL). The target basic analytes are extracted from the donor phase into the organic solvent and then they are selectively back-extracted into the other side of the aqueous solution due to the pH gradient and distribution coefficient.

Results: The calibration curves were obtained with reasonable linearity ($r^2 = 0.999$) in the range of 3-1000 ng mL^{-1}. The limits of detection were 0.5 and 1.0 ng mL^{-1}, and excellent relative standard deviations between 3.2% and 4.0% were obtained.

Conclusion: In this work, a novel membrane microextraction method was coupled with HPLC to determine some beta-blockers in the human urine and plasma samples. This method is very convenient and environmentally friendly, provides a high sample clean-up, and all the sample preparation goals can be addressed by this new method.

Keywords: Membrane microextraction; Metoprolol; Propranolol; Biological fluid samples.

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Combination of dynamic single-interface hollow fiber liquid phase microextraction and fast electromembrane extraction for quantification of basic drugs in biological fluids and wastewater

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Background: Analysis of biological samples is a challenging field. Because this work really need a very hard and time consuming clean-up step. To overcome these problems new microextraction methods were developed. Hollow fiber liquid phase microextraction (HF-LPME) and electromembrane extraction (EME) are important two types of membrane-based microextraction techniques [1,2]. In this study combination of these methods was applied for extraction of some basic drugs in biological samples.

Methods: The porous hollow fiber (HF) was dipped in the 1-octanol to impregnate the pores. The excess organic solvent was gently wiped away with a medical wipe then the HF was sealed to the syringe needle. Using a syringe pump, sample solution (pH =12) was fed into the lumen of the HF by filling and emptying in continuous flow. After intended cycle of donor solution, HF removed from the syringe needle. After that the lumen of HF was washed with water and the lower end of the HF was closed. The acceptor solution (HCl, 100 mM) was then introduced into the lumen of the HF. The HF was then inserted, through a hole in the lid of the glass vial containing water (pH =12). Two platinum wires as electrodes were placed into the acceptor solution and water. The extraction was then started by application of a constant voltage. After extraction, the acceptor solution was transferred to a vial for further analysis by HPLC.

Results: In this study basic drugs (propranolol, diltiazem and lidocaine) were extracted from biological and wastewater samples. Effective parameters on the extraction were investigated and optimized. This method provided good linearity with the resulting correlation coefficients ranging from 0.992 to 0.996 over a concentration range of 2.5-1000 ng mL^{-1}. The LODs of the drugs were found to range within 0.8-2.0 ng mL^{-1}, while the corresponding repeatability ranged from 7.7 to 14.2% (n = 3).

Conclusion: In the present study, hyphenation between dynamic single-interface HF-LPME and fast EME was developed for the first time to analyze trace amounts of three basic drugs in wastewater, urine and plasma samples. By combination of these two extraction methods a high enrichments and good sensitivity observed while enabled efficient sample clean-up. Reducing real sample volume and matrix effects and also decrease in extraction time and electrical current level in EME are some important points of this new method.

Keywords: Dynamic single-interface; hollow fiber liquid-phase microextraction; fast electromembrane extraction, biological fluids, wastewater.

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Knitted Polystyrene as a New Sorbent for Extraction and Determination of Polycyclic Aromatic Hydrocarbons in water Samples by μ-SPE/GC/MS

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Background: One of the significant characteristics of a suitable sorbent is the high surface area. The porous materials such as metal organic frameworks (MOFs), covalent organic frameworks (COFs) and microporous organic polymers (MOPs), much considered due to their various applications in the separation science. Over the past few decades, the production of these materials, especially MOPs, has been developed because of its unique features, like high chemical stability, high surface area and low density. Knitted aromatic polymers (KAPs) are a new class of porous materials that are highly regarded for high chemical and thermal stability, easy preparation, low cost and high surface area [1]. In the present work, knitted polystyrene sorbent was synthesized and was used as a new sorbent in μ-SPE method for extraction of PAHs in water samples.

Methods: The knitted polymer was synthesized using a simple one-step Friedel-Crafts alkylation of disposable polystyrene cups (DPC) as source of polystyrene. In this approach, formaldehyde dimethyl acetal (FDA) was used as an external cross-linker. Certain amounts of cross-linker, catalyst ($FeCl_3$) were dissolved in 1,2-dichloroethane (DCE) and a piece of DPC was immersed in this solution. The mixture heated at 45°C for 5h to prepare the primary cross-linked network and aged at 80 °C for several hours, to complete the knitting process. The knitted polystyrene as sorbent were characterized by SEM, AFM, BET and FT-IR. For extraction, sorbent is added into the sample solution and the sample is stirred by using ultrasound. After sorption step, the sorbent is taken out from the sample solution and is transferred to small glass. Thereafter, the analytes are desorbed by adding a small volume of solvent and the extracted is then injected to GC-MS.

Results: Determination of analytes was performed by gas chromatography-mass spectrometry. To reach the optimum extraction efficiency, affecting parameters, including sorption and desorption time, amount of sorbent and volume of organic solvent were investigated by a central composite design. Under optimum conditions the calibration curves in the range of 0.01-1000 ng/mL for naphthalene and acenaphthene, 0.001-1000 ng/mL for acenaphthylene and 0.1-1000 ng/mL for anthracene. The limits of detection (LOD) and limits of qualification (LOQ) were 0.0003-0/01 ng/mL and 0.0008-0/03 ng/mL, respectively. The relative standard deviations (RSDs) for analytes at a concentration in 1 ng/mL were less than 11%. Recovery and enrichment factor were in 89-112 and 930-1120, respectively.

Conclusion: In this work, the knitted polystyrene was successfully synthesized characterized and applied as μ-SPE sorbent. By using GC–MS, the knitted sorbent exhibited a proper validation data for PAHs. Therefore, the new knitted polystyrene sorbent based on the disposable cups can be promising alternatives for monitoring of PAHs in water samples.

Keywords: Micro-Solid phase extraction; Polycyclic aromatic hydrocarbons; Knitted sorbent; Polystyrene

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Nicotine Determination in Aqueous Samples by HS-SPME/GC/MS Using a New Knitted Trimethoxyphenylsilane Coating

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Background: The most important compound in tobacco is nicotine, which is today the main cause of tobacco addiction and has been used as a pesticide in the past and is absorbed through the skin, nasal mucosa and mouth [1]. Due to the complexity of real sample matrix, the preparation stage is very important. In the present study, due to the high solubility of nicotine in aqueous media and the difficulty of isolating the environment, HS-SPME/GC/MS method was used for the extraction of nicotine.

Methods: To synthesize knitted trimethoxyphenylsilane coating by chemical bonding on silica fiber, material ratio were chosen based on previous work [2]. For coating preparation, the surface of the fibers was activated and for chemical binding monomers, the fibers were placed in trimethoxyphenylsilane and toluene solution for 24 h. Then, for knitting, the fibers were placed in formaldehyde dimethyl acetal and ferric chloride solution for 24 h. Synthetic coating was identified and examined with FT-IR, TGA, SEM, EDX and BET. Some of the benefits of this coating is simple synthesis, thermal and mechanical stability and high surface area. This coating was used to nicotine extraction from the aqueous samples using the HS-SMPE method. To extraction, 10 ml nicotine aqueous solution moved to extraction vial and the knitted fiber was placed to vial headspace. After extraction, the fiber was introduced to GC/MS. In order to achieve the best performance, the affecting parameters on the extraction process including, extraction time and temperature, pH and ionic strength were optimized using the central composite design (CCD).

Results: The special surface area of the coating was 155 m^{2}g^{-1} and was observed 7% weight loss at a temperature of 300℃. Linear range was obtained in two intervals of 0.1-1000 and 1000-5000 ng ml^{-1} with a correlation coefficient of 0.9955 and 0.9975. The repeatability and reproducibility of the method were obtained 5.7% and 10.1% respectively. The detection and determination limits were 0.02 ng ml^{-1} and 0.08 ng ml^{-1} respectively. The nicotine recovery in hookah water samples were obtained in the range 98-103%.

Conclusion: In this work for the first time, knitted trimethoxyphenylsilane on silica fiber used as a coating in SPME. The present work reveal wider linear range, better repeatability and reproducibility than the same work.

Keywords: Nicotine; Knitted polymer; SPME

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CO_2- effervescence assisted dispersive micro solid phase extraction based on a magnetic nanocomposite of layered double hydroxide/ modified conductive polymer for preconcentration of metal ions

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Background: The most important reason of environmental contamination by heavy metals is due to natural sources such as leaching of minerals and rocks and discharge of industrial pollutants from different industries such as mining operations, electroplating, dyeing, battery, glass, chemical manufacturing and etc. [1]. Sample preparation is one of the essential step in real sample analysis in the analytical chemistry, and extraction is one of the easiest and most appropriate sample preparation methods. DµSP aS asurface-dependent process is more efficient than the other techniques. The particle size and the surface area of the SPE sorbent affect its extraction efficiency. In the present work, effervescence-assisted dispersive micro-solid phase extraction based on layer double hydroxide (LDH)-coated magnetic nanoparticles coated with conductive polymer was used as a new sample pretreatment method for fast extraction/preconcentration of metal ions.

Methods: The synthesis of the Fe_3O_4/LDH- modified CP nanocomposite was done by the method reported by Rajabi et al [2]. After characterization and ensuring the successful synthesis of the adsorbent, the effervescence tablet was prepared using a combination of the synthetic adsorbent, CO_2 source, and proton donor agent. Finally, the prepared tablet was used to extract heavy metals (Pb, Ni, Cd, Co) from aqueous solutions and cosmetic sample including lipstick as follows: The prepared tablet was imported on the aqueous solution (pH=5, adjusted by 0.1 M phosphat buffer) containing nickel, lead, cadmium and cobalt metals at a concentration of 50 µg L^{-1}. In the next step, the magnetic field was used to separate the adsorbent from the aqueous phase. After separation of the phases, the sorbent was eluted by 450 µl of nitric acid, 3 M. Finally, in order to determination of analytes, the desorption phase was injected into a flame atomic absorption spectrophotometer.

Results: EDX and SEM were used for evaluation of synthesized adsorption. In order to maximize the efficiency of the extraction, some parameters such as pH, sorbent dosage and elution volume were studied and optimized. The linear range for nickel, lead, cobalt, and cadmium were about 3-750 µg/L. LOD of the method was calculated lower than 1.5 µg /L. The preconcentration factor was about 23. Finally, this method has been used successfully for extraction of analytes from cosmetic samples including two lipstick samples. The relative recovery percentages in all samples at two levels of concentration were more than 87%.

Conclusion: In the present work, CO_2- effervescence assisted dispersive micro solid phase extraction based on magnetic nanocomposite of layered double hydroxide/ modified conductive polymer was used for preconcentration of heavy metals from the aqueous solution and cosmetic samples. According to the results, it can be conclude that the proposed method is easy, rapid, with good linear dynamic range and with satisfactory accuracy and precision.

Keywords: dispersive micro SPE; layered double hydroxide/conductive polymer nanocomposite; heavy metals. Lipstick

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Synthesis of Dual-template Moleculary Imprinted Polymers for Extraction of Ciprofloxacin and Norfloxacin from Biological Samples

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Background: Fluoroquinolones (FQs) are a class of relatively new and entirely man-made, nonsteroidal antibiotics/antibacterials[1]. The FQ norfloxacin (NOR) is the first-choice drug for the treatment of diseases caused by Campylobacter, Escherichiacoli, Shigella, and Vibrio cholerae. NOR is used to treat gonorrhea, eye infection, and urinary tract infection [2]. The FQ ciprofloxacin (CIP) is used to treat systemic infections, including urinary tract, respiratory, gastrointestinal, and cutaneous infection. So determination and extraction of them seems important. Herein, a new dual-template malecuarly imprinted polymer based on quantum dots was prepared and employed for simultaneous selective extraction of ciprofloxacin and norfloxacin from biological samples.

Methods: In presented work, dispersive micro solid phase extraction (DMSPE) was applied. In DMSPE in order to extract target analytes, the defined amount of solid sorbent is dispersed in the aqueous sample solution by ultrasound energy, a manetic stirrer or a vortex device. In the following, for detection analytes high performance liquid chromatography (HPLC-UV) was used. The sorbent was characterized using fourier transform-infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Various parameters affecting the extraction efficiency such as pH, ionic strength of sample solution, amount of sorbent (mg), volume of eluent solvent (µl), adsorption and desorption time (min) were optimized.

Results: Under optimum conditions, calibration graphs of target analytes were found to be linear in the concentration of range of 0.5-300 $\mu g.l^{-1}$ with correlation coefficients (r^2) of more than 0.9990.

Conclusion: The developed sorbent offers the advantages of large specific surface area with more specific recognition sites, resulting high sorption capacity and selectivity and fast mass transfer rates of target analytes.

Keywords: Dual-template moleculary imprinted polymers; quantum dots(QD_S); extraction; HPLC-UV

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Application of Deep Eutectic Solvents and Magnetic Molecular Imprinted Polymers for Dispersive Micro-Solid Phase Extraction of Dipyridamole and Its Determination by HPLC-UV Detection in Biological Samples

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Background: Dipyridamole (DIP) is a well-known vasodilator drug that has been widely used for treatment of coronary heart diseases [1] and a classic platelet inhibitor which a key medicine in clinical therapy has been of thrombosis and cerebrovascular disease [2].

Method: In this work, Fe_3O_4 nanoparticles were synthesized as magnetic nanoparticeles, and then the synthesized nanoparticles was modified with amine groups using (3-aminopropyl) triethoxysilane (APTES). Finally by using ethylene glycol dimethylacrylate (EGDMA) as cross-linker and in the presence of dipyridamole as template, polymerization was carried out. The final product was used as a selective sorbent for dispersive-micro-solid phase extaction of DIP. Moreover, in desorption step an eco-friendly and non-toxic deep eutectic solvent (DES) was synthesized and used as extraction solvent to enhance the extraction efficiency. DES was synthesized by mixing choline chloride and urea. The mixture was then stirred in an oil-bath at a temperature of 80 ◦C until a clear liquid was formed. The optimized extraction solvent was 50 µL of phosphate buffer:DES (7:3 v/v) and was applied under ultrasonication to desorb the DIP from adsorbent.

Results: Response surface methodology (RSM) was applied to optimize the factors affecting the extraction of dipyridamole to increase the efficiency of extraction. The factors included in our design were sorbent dosage (w), the volume of eluent (v) and time of desorption time (t). HPLC-UV detection was used for analysis of drug after extraction. The highest adsorption capacity of synthesized MMIP for DIP was 2.82 mg g^{-1}. The linear range obtained for dipyridamole determination is 0.008-200 ng mL^{-1} and detection limit is 0.0087 ng mL^{-1}. The relative standard deviation was obtained less than 3.84% and the mean recoveries ranged from 95.0% to 101.0%.

Conclusion: The method was successfully applied to the determination of the analyte in spiked samples including pharmaceutical formulations and biological fluids such as, serum and plasma.

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Keywords: Dipyridamole**;** cyclic voltammetry; determination

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Verification of Nerve Agents Exposure by Identification of Free Metabolites and Protein Adduct Biomarkers in Human Urine and Plasma Samples Followed by GC & LC-MS/MS in the 4th Official OPCW Biomedical Proficiency Test

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Background: The purpose of this study was to analyse human plasma and urine samples for protein adducts and free metabolites with different analytical methods for the presences or absence of nerve agent exposure. Organophosphorus Nerve Agents (OPNAs) including tabun, sarin, soman, cyclosarin, and VX target the enzyme Butyrylcholinesterase (BuChE) and albumin to cause acute toxicity [1-2]. In this Biomedical Proficiency Test, plasma samples (4×5 mL vial with codes P451-P454) and urine samples (3×5 mL vial with codes U455-U457) receipted (23 February, 2019) from (OPCW) Laboratory (Rijiswijk, The Netherlands) analyzed for verification of human exposure to nerve agents. The spiking protocol was kept unknown for participating laboratories. The identification of each test chemical must be based on at least two different analytical methods giving consistent results base on identification criteria.

Methods: BuChE activity was measured spectrophotometrically using an Ellman assay as a preliminary test to diagnose exposure to OPNAs. Fluoride regeneration method and clean-up with HLB solid phase extraction applied to release the agents again. BuChE from plasma purified with Sepharose Q fast flow gel (anion exchange)-procainamide affinity gel chromatography and digested with pepsin, clean-up with C18 solid phase extraction identified the modified nonapeptide adducts by LC-MS/MS. Totally protein precipitation, digestion with enzyme of Pronase E, clean-up with 10KD MWCO identified the tyrosine adducts using LC-MS/MS. Clean up with LC-Si cartridge, derivatization with Pentafluorobenzyl bromide followed by GC-MS/MS analysis was applied to identify the free metabolites of nerve agents in urine samples.

Results: All reported chemicals were in accordance with preliminary report of the fourth Official OPCW Biomedical Proficiency Test. Cyclosarin was identified in plasma samples with code P451 and P454 with real concentration of 8 and 5 ng/mL respectively according to OPCW reports. Sarin with concentration of 20 ng/mL was identified in plasma sample with code P452. Isopropyl methylphosphonic acid (20 ng/mL) and Cyclohexyl methylphosphonic acid (5 ng/mL) were identified in urine samples with code U455 and U457 respectively. Reference chemicals (own synthesis) were used for the comparison to the data obtained with the test samples.

Conclusion: The samples with code P453 and U456 were blank samples. The Defense chemical research laboratory (DCRL) identified all the spiked chemicals in the concentration range of 5-20 µg L^{-1} in plasma and urine samples correctly with sufficient analytical data.

Keywords: Nerve Agents; Butyrylcholinesterase; Cyclosarin; Sarin

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Solvent bar microextraction based on eutectic solvent for the determination of flavonoid in apple sample

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Background: Flavonoids are a group of polyphenolic antioxidants that play an important role in the human diet [1]. Flavonoids have biological properties such as antioxidants, anti-carcinogenic, and anti-inflammatory [2]. The preconcentration and clean-up steps are necessary for the determination of analytes in food samples. Deep eutectic solvents (DESs) are new eco-friendly solvents. A DES (Tetramethylammonium chloride: ethylene glycol) is composed of parts, including the hydrogen bond acceptor and the hydrogen bond donor [3]. Tetramethylammonium chloride is available, and nontoxic salt. The aim of this study was to investigate the application of the DESs as acceptor phase in solvent bar microextraction for determine flavonoid of apple sample.

Methods: In this work, eutectic mixture was synthesized by stirring and heating the two components at 80 ⁰C. To prepare the solvent bar the hollow fiber was cut into a pieces. The acceptor solution (DES) was drawn into a syringe and its needle placed inside a fiber lumen. DES was introduced into the lumen of the hollow fiber. The solvent bar with two ends closed stirred. The acceptor solution injected to the HPLC-UV system for analysis.

Results: The optimized extraction conditions were as follows: pH=3, stirring speed= 1000 rpm, extraction time= 40 min. Under optimal conditions, the good recoveries obtained, precision (relative standard deviation) (n=3) below 3.6%.

Conclusion: In this investigation, solvent bar microextraction technique based on deep eutectic solvent was introduced as a suitable acceptor phase. The SBME method is inexpensive, eco-friendly, and simple. Also, the efficiency of DES was significantly better than conventional solvents in the SBME method.

Keywords: Deep eutectic solvent; Microextraction; Flavonoid; High performance liquid chromatography

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Selective Liquid membrane microextraction followed by high performance liquid chromatography for determination of tramadol in biological samples

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Background: One of the important analgesic centrally acting drugs used for treating moderate to severe pains is tramadol (TRA) [1]. Nowadays TRA is one of the most prescribed opioid in the world , and the selective activity at µ-opioid receptors make it an opiate agonist active material [2]. As TRA has a toxic nature, its overdose causes vomiting, nausea, and dizziness [1]. Hence, its determination in biological and pharmaceutical samples is of crucial importance. In most cases, there is no possibility for direct analysis of complex matrices without any sample preparation. Therefore, sample preparation is a bottle neck step of most chemical analysis in order to obtain suitable sample clean-up, preconcentration of analytes and instrumental compatibility.

Methods: In this work, a membrane based liquid phase microextraction (LPME) method was developed for the determination of TRA. A simple device was introduced which contains an extraction cell combined with a peristaltic pump for circulation of sample solution. The cell was comprised of donor and acceptor containers which are mediated by a supported liquid membrane (SLM). The target analyte is extracted from donor chamber and pre-concentrated into the acceptor one through membrane.

Results: For an efficient extraction of TRA, effective variables were investigated. The type of organic solvent, pH values of liquid phases, salt effect, acceptor volume, extraction time, circulation rate and stirring speed were studied. The relative standard deviation of 3.9%, limit of detection of 3 ng mL $^{-1}$, dynamic linear range of 10-1000 ng mL^{-1} and preconcentration factor of 52 were obtained.

Conclusion: A Liquid membrane microextraction followed by high performance liquid chromatography for determination of tramadol in biological samples. Low organic solvent consumption (15 µL), low relative standard deviation (RSD<3.9%), limit of detection of 3 ng mL $^{-1}$ and dynamic linear range of 10-1000 ng mL^{-1} are some of features of the method which propose it as an easy, fast and environmentally friendly method.

Keywords: Microextraction device; High sample clean-up; liquid phase micro-extraction; Tramadol.

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Simple determination of papaverine and codeine in biological samples by membrane microextraction followed by high performance liquid chromatography

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Background: Papaverine and codeine are two well-known opium alkaloids that are found naturally in large amounts in papaver somniferum (opium poppy). Papaverine is used to treat some diseases like renal or biliary colic and pulmonary embolism, and most varieties of opium contain papaverine in the range of 0.5-1%. Codeine or 3-methylmorphine is one of the main alkaloids present in opium poppy that has pharmacological activities. It is widely utilized to relieve moderate pains and also as a conventional cough suppressant. On the other hand, opium alkaloids have the potential of abuse and addiction, which make a lot of complicated physical and psychological problems. Therefor its qualification and quantification in different samples is very important [1, 2].

Methods: An extraction cell including the donor and acceptor chambers mediated by a liquid membrane (15 µL of 1-octanol) was used, and the target analytes were extracted from the sample solution into the membrane. Then by adjusting the pH value for the acceptor solution (100 µL, pH 1), the target analytes were selectively back-extracted into the acceptor solution.

Results: The effective variables in the extraction process were optimized, and under the optimal conditions, the method provided an excellent repeatability (RSDs below 3.7%) and a suitable linear range (5.0-700 ng mL^{-1}). The limits of detection were in the range of 1-3 ng mL^{-1}, and the range of 31-49 was obtained for the enrichment factor.

Conclusion: In the present work, the continuous flow membrane microextraction method has been coupled online with the HPLC system in order to determine papaverine and codeine in the biological fluid samples including urine and plasma. This method provides a high sample clean-up, a high preconcentration, and a low-cost determination of the understudied drugs.

Keywords: Membrane microextraction; High sample clean-up; Codeine; Papaverine.

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6-Chemometrics

Prediction of Surface Tension of Binary Mixtures Using Artificial Neural Networks

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Background: Surface tension is an important fluid property for the study of industrial applications. The removal of acid–gases from natural gas is performed under various conditions by some solvents such as alkanolamines in gas separation plants. Industrially important alkanolamines for this operation are monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). So to know the surface tension of these amine solutions is very important in gas refinery units [1]. Recently, more attention has been directed to artificial neural networks (ANNs) as an effective tool for prediction and correlation of thermo-physical properties [2].

Methods: For the modeling of surface tension of binary mixtures of alkanolamines/alcohols (methanol, ethanol, isopropanol), the feed forward artificial neural network (FFANN) toolbox is employed in this work. An artificial neural network contains of a series of neurons, which are accumulated in input, hidden, and output layers. The number of neurons in the hidden layer is determined through an optimization procedure. In the first step, the database (experimental data) is divided into three subdata sets including the “Training” set, the “Validation” set, and the “Test” set. For this purpose, about 70%, 15%, and 15% of the main data set are randomly selected for the “Training” set , the “Validation” set , and the “Test” set . Experimental data for the surface tension of binary mixtures were extracted from reference [3].

Results: After training and testing, calculated values of correlation coefficient (R^2) and absolute percentage deviation (%APD) of the designed FFANN has been compared with experimental data. The high correlation coefficient values ($R^2 \geq 0.999$.) and low %APD (less than 3.5%) reflect high accuracy and capability of the proposed FFANN for estimation of the surface tension.

Conclusion: An artificial neural network (FFANN) based prediction model, has been successfully developed to predict the surface tension of binary mixtures of alkanolamine/alcohol at 313.15 K with the absolute percentage deviations (%APD) less than 3.5% and $R^2 \geq 0.999$.

Keywords: Surface Tension, Prediction, artificial neural network, alkanolamine.

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Synthesis of novel adsorbent based on magnetic nanoparticles modified with L-lysine for efficient removal of Cr(VI) from aqueous solutions: central composite design and response surface methodology

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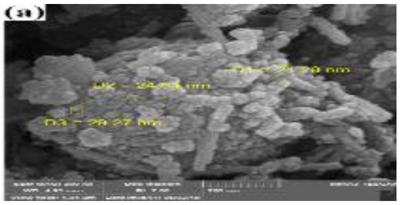
Background: Cr(VI) is considered to be a highly hazardous substance since it can cause critical health and environmental issues. Therefore, it is necessary to reduce the Cr(VI) concentration to an acceptable level in water or industrial wastewater. Adsorption method is one of the famous and efficient strategy in this purpose [1]. Here, novel adsorbent based on magnetic Nano-particle (MNPs) were synthesized and applies to remove Cr(VI) ions in water samples successfully.

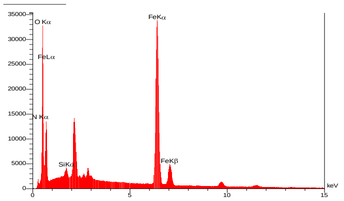
Methods: Magnetic nanoparticle was synthesized according to hydrothermal procedure [2]. Afterward, MNPs was modified with 3-glycidoxypropyltrimethoxysilane and lysine (MNPs-SiO_2-lysine).The removal processes were done at different experimental condition where the factors were the concentration of Cr, adsorbent dosage, pH and contact time. The procedure at optimal condition is as follows: 0.04 g of the adsorbent was added into 50 mL of Cr(VI) 5.8 ppm and the mixture was stirred for 24 minutes at 25 ^{0}C and pH 2.38. Finally, the adsorbent was simply collected by strong magnets the residual solution was measured by Atomic Absorption Spectrometer to find the residual Cr(VI) and then removal percentage was computed [3].

Results: The morphology and Characterization of MNPs-SiO2-lysine structure were illustrated in fig.1 and 2. This images shows new adsorbent was successfully synthesized and is made up of highly porous particles with an average diameter of 21-29 nm. The combination of central composite design (CCD) and response surface methodology (RSM) was used to achieve the optimal conditions. The Maximum adsorption capacity (88.954 mg/g) was obtained at 24 minute contact time, 0.04 g adsorbent dosage, 5.80 mg/l Cr(VI) and pH: 2.38.

1) FE-SEM



2) EDS



Conclusion: In the present study new adsorbent was synthesized as efficient and reusable adsorbent with excellent adsorption capacity, cost effective, selective, high surface area and fine size for efficiently removal of Cr(VI) in aqueous solution.

Keywords: Magnetic Nano particle, CCD, RSM

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A Genetic Algorithm Coupled with Supporting Vector Regression Model for Simultaneous Determination of Oxygenates in Gasoline by FTIR Spectroscopy

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Background: Precise and dependable calibration methods for oxygenate compounds in gasoline are needed in modern petroleum industry. An analytical approach such as FTIR spectroscopy which provides a lot of information, together with efficient regression tools, which have become available thanks to modern mathematical techniques, has made precise and efficient prediction of objects' properties feasible. Support vector machines (SVMs) can be employed in solving complex nonlinear classification and regression problems. Also, variable selection techniques yield favorable results in removing irrelevant and noisy variables and making a model less complex [1].

Methods: In the present study, a genetic algorithm-support vector regression (GA-SVR) coupled method has been suggested which can be a powerful model for simultaneous determination of oxygenates in gasoline by utilizing FTIR spectroscopy (Mid) in the fingerprint area (4000-600 cm^{-1}).

Results: The correlation coefficient between the measured and predicted values (R_p), root means square errors of prediction, and root means square errors of leave-one-out cross-validation were used to assess the models. According to the findings of this study, GA-SVR model is the better predictive factor of the two, having a higher R_p (0.981) and lower RMSEP (0.185) in comparison with PLS Model with R_p (0.960) and RMSEP (0.32).

Conclusion: the suggested approach can be deemed suitable for quantitative analysis as well as quality control of oxygenates found gasoline in petrochemical industries.

Keywords: Gasoline, Oxygenates; FTIR spectroscopy; Supporting vector machine regression (SVM-R) ; Partial least square regression (PLS-R)

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Application of PARAFAC algorithm for analysis of EEM fluorescence Data: A systematic way for discriminating honey samples from different sources

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Background: Fluorescence spectroscopy is a rapid, sensitive, and non-destructive analytical technique providing in a few seconds spectral signatures that can be used as fingerprints of the food products. Since fluorescence spectra are typically composed of broad overlapping bands containing chemical, physical, and structural information of all sample components, the analytical information contained in spectra is multivariate in nature and, therefore, non-selective [1]. For the analysis of the EEM data, an adequate multi way method to extract relevant information from the data is essential. The most commonly used multi way method is parallel factors analysis (PARAFAC) [2]. The PARAFAC model can identify the most dominant fluorophores in food as well as their relative concentrations in different samples. The results of the PARAFAC model provide the basis for further analyses of the food such as sample characterization, classification, and second-order calibration [3].

Methods: In recent years, the presence of fake honey in markets all over the world has become an increasing problem. Therefore, research has been focusing on finding fast and reliable methods for detection of adulterants in honey. In this work, a total of 70 honey samples were obtained and their EEM fluorescence spectra were recorded ranging 200nm to 800nm for excitation and 250nm to 750nm for emission channels.

Results: The recording of fluorescence spectra at various excitation and emission wavelengths was performed to study the differences between the seven honey groups. The emission patterns reflect the specificity of intrinsic fluorophores and their microenvironments in the honey. The main differences among the honey groups were evident in several spectral regions such as Em. 350-380 and Ex. 270-300, Em. 400-500 and Ex. 250-270, Em. 400-500and Ex. 350-400 and Em. 580-620 and Ex. 370-400. Finally, the PARAFAC scores were used as inputs for making discriminative models and the developed models could classify more than 90% of the samples, thoroughly.

Conclusion: The obtained results were encouraging and showed a promising potential of EEM fluorescence spectroscopy for detecting honey type. PARAFAC allows obtaining wide information about EEMs and the results suggest that the spectral information in data is originating from the honey.

Keywords: Honey, Multi way**,** Fluorescence, PARAFC

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External parameter orthogonalization combined with support vector machine as an efficient method for classification of NIR spectra of Saffron

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Background: Saffron, the dried red stigmas of the plant Crocus sativus L., is well known as one of the most important and expensive spices in the world. It is renowned as a culinary spice for its color and flavor, and also used as a medicinal herb. Under this perspective, there is an increasing interest by producers and consumers to have a high-quality product with clear geographical origin [1]. Various detection technologies are applied for food authenticity including spectroscopic, chromatographic and electrochemical techniques [2]. One promising technique in this context is near infrared (NIR) spectroscopy which is a rapid and non-destructive method. Additionally, similarity between the spectra of different sampels as well as scattering effects and instrumental and ambient noise make robust chemometric and machine learning methods crucial to extract the relevant information from the spectra [3]. In the present contribution, a new filter entitles external parameter orthogonalization (EPO) combined with support vector machine (SVM) was developed for quality control of saffron provided from different regions of Iran.

Methods: 100 saffron samples from different region of Iran were provided. Then, NIR spectra of the samples were recorded in reflectance mode. Before NIR spectroscopy, samples were grounded and passed through a sieve according to ISO/TS 3632-2. The spectrum of each sample was measured three times and the mean was used for multivariate analysis. The samples data matrix was then analyzed using principal component analysis (PCA), partial least squares-discriminant analysis (PLS-DA) and support vector machine (SVM) with quadratic kernel function.

Results: First, preliminary exploratory data analysis was carried out using PCA to visualize the sample distribution and investigate possible patterns of saffron. Evaluation of the PCA score plot (explaining 93.21% of variance for three PCs) show that saffron samples roughly belong to two clusters. In this regard, EPO was proposed as a new preprocessing technique which could cause clear discrimination. The rough results of PCA was used as input for supervised classification using PLS-DA. However, PLS-DA did not perform well. On this matter, quadratic SVM as a robust machine learning method showed a promising performance for saffron classification with good figures of merit of sensitivity (0.96), specificity (0.97) and accuracy (0.96).

Conclusion: Combing machine learning with rapid NIR analysis can be considered as a new insight to the analysis food quality control.

Keywords: Saffron; NIR spectroscopy; Chemometrics; Support vector machine.

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Effect of peeling and point of spectral recording on sucrose estimation in sugar beet root using infrared spectroscopy

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Background: Sugar beet is one of main sources of sucrose production with about 6.56 million tons' production in 2016 in Iran [1]. Sugar beet root consists of 23-24% dry matter of which 75% is sugar [2]. Selection of cultivars with high sucrose content is a major goal in breeding programs. The polarimetry method which is most commonly used for sucrose analysis is a destructive method not suitable for seed production. In recent years, near infrared spectroscopy (NIR) method has been greatly used for sucrose determination. The aim of this study was to evaluate the effect of root size, peeling, and points of spectral recording on sucrose estimation in sugar beet.

Methods: The experiment was conducted in a factorial (3×2×4) based on completely randomized design with 22 replications. Sixty-six sugar beet roots were weighted based on three sizes including small (<550g), medium (550-1000g), and large (>1000g) followed by longitudinal slicing into two parts. One half of the root was used for sucrose measurement by polarimetric method and the other half by spectra record (942-1576nm). Spectra recording was performed on two sides: peel and root tissue; samples were taken from four points including North West (NW), south west (SW), north east (NE), and the south east (SE), approximately one centimeter above and below the root neck where the root diameter is high. Totally, 528 specrta records were taken, 264 from each side, and 33 spectra mean from each side were selected for calibration and validation. Determination of the specific wavelength for sucrose estimation was done by partial least squares (PLS) regression considering minimum RMSEC and RMSEP and the maximum rc and rp. Statistical comparison in specific wavelength was performed using SAS software after correcting spectral data by Unscrambler software.

Results: Results showed that 1393 nm wavelength with a maximum of $r_c = 0.9999$ and $r_p = 0.9998$ and a minimum of RMSEC = 1.045 as well as RMSEP = 1.215 were suitable for sucrose estimation. Results of ANOVA showed no significant difference between root size and four points of Spectral recording at 1393 nm wavelength however a significant (*P* <0.01) difference was found between the root tissue spectrum and peel spectrum.

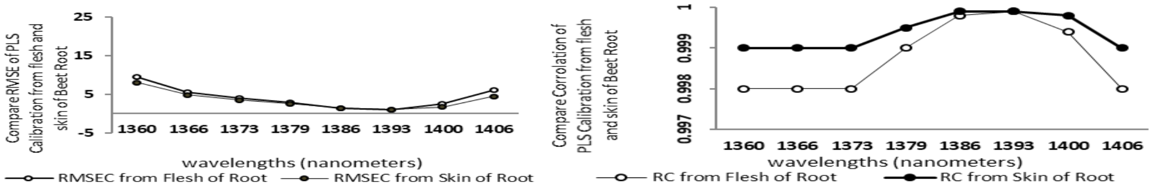

Fig. 1. Comparison of RMSE and rc between flesh and skin of sugar beet root

Conclusion: In general, results illustrated that near infrared spectroscopy at 1393 nm wavelength with RMSEC = 1.04 and rc=0.9999 can be used for sucrose estimation in sugar beet root tissue instead of the peel.

Keywords: calibration; near infrared spectroscopy; PLS; sugar beet.

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Liquid-phase microextraction of thiamine using supramolecular solvent as a carrier for ferrofluid

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Background: Thiamine is very important to the brain, particularly in terms of emotional health and well being, and also is useful for focus and concentration. Its absence is associated with serious diseases like Beriberi and Wernicke–Korsakoff syndrome. For all these reasons, the development of a sensitive method for the determination of thiamine is of much interest. This work reports, application a liquid-liquid microextraction based on supramolecular solvent (LLME-SUPSs) as a carrier for ferrofluid for the extraction and determination of thiamine [1].

Methods: A solution containing appropriate amount of thiamine, placed in 10 mL centrifuge tube. The pH of the sample solution was preserved at 11, then 1 mL of ferrofluid, 1.2 ml of potassium hexacyanoferrate (III) and 0.2 gr of salt were injected to the solution and the mixture was vigorously shaken using a shaker for 20 min. Subsequently, a strong magnet was placed next to the side of the centrifuge tube to collect the ferrofluid and the sample solution was discarded simply by decanting the glass tube. After that, appropriate amount of methanol was added to the vial in order to separate the extractant from magnetic particles (MPs).

Results: The effect of various variables (pH, ultrasonic mixing time, volume of ferrofluid and potassium hexacyanoferrate (III) and amount of salt) on the LLME - SUPSs was investigated and optimized by (RSM) and (CCD) [2-3]. Under the optimum experimental conditions, the calibration curves found to be linear in the range of 4–800 ng mL^{-1} with correlation coefficients 0.9921, the (LOD) and (RSD) were 0.95 ng m$L^{-1}$and %2, respectively (n=5). The mean extraction recovery was 96%.

Conclusion: In this study, a liquid–liquid microextraction technique based on the application of a nanostructured ferrofluid was developed. The proposed extraction technique lacks tedious steps of conventional microextraction methods. Moreover, this method offers significant advantages such as simplicity of the extraction, short extraction time and good precision and high accuracy.

Keywords: Supramolecular solvent microextraction, Separation, Response surface method, Thiamine, Ferrofluid

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Activity-based Analysis of Potentiometric pH Titrations

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Background: The discrepancy between concentrations and activities is a predicament well known to the analytical chemist. Because of the difficulty of determining activity coefficients, the standard technique for quantitative equilibrium studies is to work under a particular 'constant ionic strength' by adding an excess of an inert salt [1]. Throughout the numerical analysis of the titration data, activity coefficients for all individual species are approximated by well-known equations based on the work of Debye-Hückel.

Methods: The mV signal was used directly in the analysis of the potentiometric titration data. For each acid several different titrations were undertaken, they mainly differ in the total concentrations of the acid. The titrations were analysed by the ReactLab pH software [2].

Results: The claim of this contribution is that a single and simple titration at minimal ionic strength delivers good estimates for the thermodynamic equilibrium constants. The standard deviations for activity-based analyses are considerably smaller than those for the classical concentration-based analysis. During any titration the ionic strength will always change and consequently each concentration based, classical analysis is expected to be inferior and this should be reflected in a larger sum of squares.

Conclusion: The analysis of potentiometric pH titrations based on activities rather than concentrations serves several purposes. (a) The law of mass action is based on activities and thus the suggested analysis are close to theoretically correct. Classical concentration-based analysis rely on constant ionic strength during the titration which is never completely achieved. (b) The results of the analysis include a set of thermodynamically correct equilibrium constants. These are otherwise only accessible via analysis of extended ionic strength dependences. (c) In classical analysis, inert salts need to be added to the titration solutions; inert salts are never perfectly inert, being of ionic nature they will always interfere with other ions in the solutions. Avoiding inert salts can only be advantageous.

Keywords: Activity coefficients; Potentiometric titration; pH titration; Law of mass action

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Calibration Augmented Inverse Least Squares (CAILS) Using Tikhonov Regularization, A New Modified ILS Calibration For Unmodeled Interferents

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Background: Multivariate calibrations are divided into two directions, Classical (CLS) and Inverse Least-Squares (ILS) [1]. Inverse methods are more popular than CLS because ILS methods allow one to study multicomponent samples where only one or few analytes are of interest, but the concentration, spectra, and chemical identities of other components in calibration samples are unknown. There is a so important restriction for both ILS and CLS that the structure of calibration and prediction samples must be unify, otherwise recalibration is necessary. Estimated model coefficients for ILS methods depends on two main important factors; direction and vector size. Direction is known as the orthogonality of desired analyte spectrum to interfering's spectral space and vector size must be as short as possible to increase the sensitivity of the method [2]. By changing the structure of the prediction samples, there is no longer the orthogonally of regression coefficient on spectral space and, moreover, the length of the vector is not in optimal value.

Methods: Suggested modified CAILS method corrects the model coefficients in calibration step by augmenting the pure spectrum or spectral shape of unmodeled components to calibration data set. Model coefficient according to Tikhonov Regularization (TR) [3] must fulfilled three condition in calibration step: $\begin{pmatrix} y \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} X \\ \tau I \\ S \end{pmatrix} b$. This process is defined by the minimization of: min ($\|Xb-y\|^2+\tau^2\|b\|^2+\|bS\|^2$). Model coefficient can be estimate by solution: $\hat{b}= (X^TX+\tau^2I+S^TS)^{-1}(X^Ty)$. Where y is the vector of concentration of interest analyte, X is calibration data set, s is pure spectra of unmodeled component(S), τ is ridge parameter and b is model coefficients.

Results: Since regression coefficients for desired analyte is Net Analyte Signal (NAS) [4], so including the pure spectra of known interferents in calibration step corrects the direction of model coefficient for analyte of interest.

Conclusion: In this contribution a new procedure is proposed based on (TR) which properly solves the problem of presence of un-modeled known interferent(s) that left out the calibration.

Keywords: Multivariate Calibration; Tikhonov Regularization; Modified ILS; Net Analyte Signal

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Inspection of Affecting Factors on Synthesized CdS Color Using Smartphone Based Diffuse Reflectance Spectrometer and Experimental Design

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Background: Cadmium Sulfide (CdS) is an important semiconductor material, which under various synthesis conditions gives different crystal structures and colors. Diffuse reflectance spectroscopy (DRS) has been widely used for the characterization of pigments [1]. Using a grating containing accessory, and the camera of the smartphone a simple smartDRS instrument, with resolution of 5 nm, was manufactured in our lab [2]. The design of experiment capabilities improve the processes by screening the factors [3]. The aim of this study is using smartphone-based diffuse reflectance spectroscopy (DRS) and experimental design to investigate the effects of different parameters on CdS precipitate color.

Methods: The diffuse reflectance spectra of CdS precipitates were taken by homemade smartphone-based diffuse reflectance spectrometer. Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS) methods were used to resolve the data matrix of diffuse reflectance spectra [4]. Additionally, the effects of different parameters on CdS precipitate color is assessed using a 2^4 full factorial experimental design.

Results: Using MCR-ALS, smartDRS spectral data from CdS samples were resolved into two spectral profiles and two concentration profiles, with explained variance value of %83.2. Estimated concentration profiles illustrated the ratio of contributions of the two crystal forms in each of the 16 synthesized CdS samples. The proper condition for the synthesis of CdS with yellow-white color is pH=3, Cd:S molar ratio of 1:2, 5 day time for the drying of CdS precipitate and without using furnace.

Conclusions: This study shows the successful application of MCR-ALS analysis of spectral data from smartDRS assisted with a proper experimental design for quantitatively investigation of affecting factors on synthesized CdS color.

Keywords: Diffuse reflectance spectroscopy; Smartphone; CdS; Experimental design.

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Colorimetric sensor arrays as Simple and Low-Cost Method for Detection of Different Adulterations in Saffron

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Background: Saffron is the most expensive spice in the world that is often used as a coloring and flavoring agent. It is also used in traditional medicine and its antioxidant properties are proved in recent medicinal studies. It is applied for preservation and prevention of cancer and for many other health problems (e.g. insulin resistance). Due to its demanding market, finite production and high price, saffron has been extremely susceptible to be adulterated through mixing with similar cheaper ingredients. Many widespread works (e.g. various LC methods, FT-IR, UV-Vis, NMR, GC, E-nose) have been reported for authentication of saffron. ISO 3632 inspects the authenticity and quality of saffron based on spectrophotometric and chromatographic techniques. But it is so defective when saffron is adulterated by a substance with a highly similar color and morphology (e.g. safflower) [1]. Colorimetric sensor array (CSA) as a fast, visual field-test, simple and low-cost method has been used recently for detection various analytes with similar structures that cannot be investigated by routine analytical methods [2].

Methods: The CSAs were fabricated according to a procedure has been described in the literature [3]. The before image of the CSA was acquired using a scanner. The CSA was stuck on the inner surface of a lid of a chamber containing the sample and was exposed to the analyte at a certain temperature for a specific time period. The after image was recorded. The RGB color values of the images were measured by an image processing program. Subtraction of the two before and after RGB datasets provides a difference vector of 3N dimensions where N is the total number of the array spots. The datasets were analyzed by principal component analysis (PCA) and linear discriminant analysis (LDA) methods.

Results: Discrimination between pure saffron and adulterated mixtures with 100% accuracy achieved by PCA and LDA in liquid phase, 96% and 100% by PCA and LDA respectively, in solid phase. The LDA model could predict unknown samples with 100% and 83% validation accuracy for liquid and solid phases, respectively. Classification of saffron samples based on grade category with 100% and 87% accuracy obtained for liquid and solid phase by both PCA and LDA methods, respectively.

Conclusion: The proposed CSA successfully discriminated between pure saffron samples and artificial mixtures containing even 5% of adulterants by chemometric methods. It also could classify saffron samples based on grade category.

Keywords: Sensor array; Saffron; Adulteration; Discrimination; Classification; Chemometrics.

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Reduced graphene oxide as an extremely effective and recyclable oil-absorbent in oil contaminated sea water: A combined chromatography and chemometrics approach

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Background: Oil pollution is an ever-present threat in the marine environment with large numbers of spills being recorded every year. In this respect, burning, oil dispersants and oil skimmer are frequently used in oil spill accidents. Additionally, a variety of absorbent materials such as graphene-based absorbents have been developed to remove oils [1]. Very often, graphene oxide (GO) as a hydrophilic absorbent, has been reduced to rGO to change the material from hydrophilic to hydrophobic which is more suitable for oil removal [2]. The purpose of this study was development of a rGO absorbent using two different synthesis methods and its application for separation and monitoring of oil pollutants in remaining water.

Methods: rGO synthesized by modified Hummer and shear exfoliation methods [2] were characterized using SEM, TEM and Raman spectroscopy. After separating the oil from the water using rGO, the amount of residual oil pollution dissolved in water was determined using rGO. For this purpose, mixture of seven polycyclic aromatic hydrocarbons (PAHs) was used as model compounds for optimizing absorption and desorption processes. Consequently, a monitoring method based on the micro solid phase extraction (μ-SPE) was developed and was analyzed using gas chromatography (GC). The six extraction factors of sorbent amount, sorbent volume, sample volume, extraction volume, extraction time and salt concentration were designed using central composite design (CCD) and were optimized by scores of principal component analysis (PCA) as a novel response factor for multi-response optimization. Finally, partial least squares regression (PLSR) as a multivariate calibration was used for quantification of seven target PAHs.

Results: After characterization of rGO and comparing the performance of two methods, μ-SPE factors were optimized. On this matter, 54 runs of experimental design resulted in a matrix of responses having 7 columns (the areas of the 7 peaks of analyte). The scores of the first PC on which all the variables had positive loadings and which was explaining a very high percentage of the total variance (i.e., 92.2%), was used as a response vector for optimizing the extraction factors [3]. Therefore, a significant model with $R^2=0.75$ and S/N=17.2 which was optimum for seven PAHs was obtained. Then, PLSR was used for quantitation of 7 target PAHs in the presence of uncalibrated interferences. In this regard, calibration set for external calibration strategy was randomly designed in concentration range 0.1-100 ngmL^{-1}. Then, multivariate analytical figures of merit (AFOM) including sensitivity (SEN), selectivity (SEL) and limit of detection (LOD) were calculated [4]. In all cases, the AFOMs were in acceptable ranges.

Conclusion: It is concluded that the present multi-stage analytical strategy using rGO as an effective absorbent in combination with chromatography and chemometrics in order to remove oil spills from water and investigate the residual oil pollution in water.

Keywords: Oil spill; rGO; μ-SPE; GC-FID; Chemometrics.

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Simultaneous monitoring of adsorption process of two food dyes, amine functionalized metal organic framework as an adsorbent.

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Background: Dyes are widely used in foodstuff to improve the quality and good-looking of the products. During the process of production, a significant amount of dyes are likely wasted and eventually they cause to pollutant the environment [1]. Amaranth (AM) and Sunset yellow (SU) are extensively used in the food industry and therefore those dyes can be presented in the wastewaters [2]. Due to the overlap of absorption peaks of these two dyes, it is impossible to measure and simultaneous monitoring adsorption process. The principal component regression (PCR) was assisted to overcome this problem.

Methods: In this work, to be constructed calibration set, 24 mixtures of dyes were planned and utilized for PCR modeling. Standard solutions were prepared in 5 mL volumetric flasks by adding appropriate amounts of each stock solution and diluted by deionized water to the mark. The UV-Vis spectra of all solutions were recorded with a spectral range of 350-600 nm. Results of this experiment were used for analyzing of PCR model.

Results: After the performance of calibration/training, the final PCR model is applied for prediction the unknown concentration of the samples. For this purpose, 7 samples were prepared and the corresponding absorption of the samples was applied to prediction the PCR model. Results show that the PCR model has significant predictive abilities for both dyes, with R^2 values higher than 0.995. Furthermore, the excellent values of Relative Error of Prediction (3.047) and root mean square error of prediction (0.241) can be achieved by this method. Isotherm studies were also performed, results revealed that the adsorption of both dyes was an agreement with the Langmuir isotherm. The maximum adsorption capacities of 131 and 116 mg. g^{-1} was obtained for AM and SU, respectively.

Conclusion: The amino-functionalized Fe-MIL-101 was synthesized and used for simultaneous adsorption of amaranth and sunset yellow dyes. The PCR was assisted for the simultaneous determination of dyes. The PCR model was also examined by using real sample and the predicted values were remarkably close to the actual values. The data of isotherm studies were well fitted by the Langmuir model and the adsorption capacity was 133 and 116 mg. g^{-1} for AM and SU dyes.

Keywords: Amaranth; Sunset yellow; principal component regression; Box-Behnken design.

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Employing artificial neural network for predication of removal of sarafloxacin from aqueous solution by the magnetized metal-organic framework

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Background: Antibiotics are one the pollutants that their existence in the environment which causes series problems, hence their removal from the environment is a vital task [1]. Sarafloxacin **(**SRF) is a fluoroquinolone antibiotic which is commonly used in curing pigs, cows, sheep, chickens, and fish [2]. In this study, the removal of sarafloxacin has performed using magnetized metal organic-framework (Fe_3O_4/MIL-101(Fe)). Artificial neural network (ANN) was applied for building up a predictive model and predication of the SRF removal efficiency from aqueous solution.

Methods: At first, the initial standard solution of SRF was prepared with a concentration of 500 ppm and the other standard solutions (5-50 ppm) were made with the stock solution. To find the optimization condition of the SRF removal efficiency, the response surface methodology was applied. For this propose 4 independent variables (i.e., initial concentration of SRF, pH of the solution, the dosage of adsorbent and contact time) were studied. Finally, the removal percentage of SRF and adsorbent capacity was calculated. The inputs for the neural network are as follow; the initial concentration of SRF, pH of the solution, adsorbent dosage and the contact time. The output refers to the removal efficiency of SRF.

Results: The optimized removal efficiency of SRF was obtained under following conditions: the SRF initial concentration 10 ppm, pH value of 7.0, the adsorbent dosage of 20 mg and the contact time of 40 min. Moreover, in the modeling section, the values of R^2 (R^2=0.9995, 0.9951) and MSE (MSE=3.98e-05, 0.0023) were for training and testing data set, respectively. Results showed that a good agreement between experimental and predicted data was obtained by the ANN model as a powerful tool for prediction removal percentage of SRF (R^2_{pred}= 0.9861).

Conclusion: A three-layer feed-forward of neural network with Levenberg Marquardt training algorithm was implemented for predicting the removal efficiency of sarafloxacin. The maximum removal efficiency estimated by model (93.57%) was obtained close to the experimental result (93.15%). Results showed that the experimental data were fairly compromised with the Langmuir isotherm and the second-order kinetic. The maximum adsorption capacity for the adsorption of SRF with the Fe3O4/ MIL-101 (Fe) nanocomposite was obtained 81.31 mg/g.

Keywords: Sarafloxacin; Response surface methodology; Artificial neural network; Levenberg–Marquardt

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Molecular dynamic simulation study of Triton X-100 self-aggregation in aqueous and non-aqueous solutions

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Background: Understanding the behavior of surfactant systems at different conditions by the investigation of the interaction mechanism and aggregation form is indispensable for describing solution properties and subsequent applications. The surfactants possess extensive applications in analytical and industrial fields as detergents, coatings, pharmaceuticals, and tertiary oil recovery as well [1,2]. In recent years, molecular dynamic simulations (MDs) have attracted much attention in resolving the intricate structure of spherical micelles and their interactions with solvent. In this study the molecular dynamic simulation is employed to simulate the dynamic self-assembly process of aggregates of Triton X-100 as a model of a non-ionic surfactant.

Methods: The molecular dynamics simulations were performed at different concentrations of Triton X-100. Moreover, the effects of other variables like temperature; solvent and salt addition have also investigated. The MD simulations were performed using the GROMACS 4.5.3 package. The polarity changes with the concentration of organic solute, temperature, solvent type and amount of salt in the solution. The simulation time for all the simulated runs was 20 ns.

Results: The aggregation of Triton X-100 showed different forms by changing of the conditions. The change of the solvent accessible surface area (SAS) for Triton X-100 over the time, the decrease of total energy and the partial density of Triton X-100 across the box length were computed and used to justify the derived results. The end-to-end distances of Triton X-100 molecules as a good indicator of hydrophilic forces in the solution were investigated. The Triton X-100 molecules exhibit diverse forms of aggregation depending on the polarity and other conditions in the solution.

Conclusion: The aggregation of Triton X-100 surfactant was investigated by considering the effects of some variables. Molecular dynamic simulation as a powerful tool was employed to provide solution media. The concentration of surfactant molecules determines the forms of aggregation (tubular, spherical, or semi spherical). It has inferred that the aggregate of Triton X-100 at cyclohexane is less dense than what is in water environment. The simulation results were in high agreement with the experimental data.

Keywords: Molecular dynamics simulations; Triton X-100; Aggregation, Surfactant; Molecular modeling.

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Ligand and structure-based virtual screening to the identification of novel compounds as non-nucleoside HIV-1 reverse transcriptase inhibitors

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Background: In this work, a multistep virtual screening protocol, merging ligand-based screening with structure-based methods was adopted to identify powerful and potent HIV-1 RT inhibitors in the NCI and Specs databases [1].

Methods: Ligand-based virtual screening (LBVS) of compounds was performed with the using LigandScout 4.09.3 [2]. Structure-based virtual screening (SBVS) has favorably been applied to design novel drug-like molecules [3]. Shortlisted of NCI and Specs compounds were docked into the active site of target HIV-1 RT molecule through AutoDock Vina [4] to arrive an optimal supplementarity of steric and physiochemical properties.

Results: We performed ligand-based pharmacophore modeling for the data set using the software LigandScout 4.09.3 to identify the chemical properties or necessary structural specifications of the data collection which they must possess to bind to their targets [2]. Through LBVS of NCI (265,242) and Specs (213,354) database, 178 and 247 hits were enriched, respectively.

SBVS was used, to identify the fit binding mode and affinity of ligands within the active site of non-nucleoside HIV-1 RT. In the state, by AutoDock Vina docking (score of $\leq$ -10 kcal/mol) of 178 and 247 compounds, 54 and 146 hits were obtained, respectively.

Conclusion: From LBVS and SBVS methods were used to evaluate and identify new potent compounds from NCI and Specs databases that may act as good hits against HIV-1 RT. Structural interactions between antagonists and amino acid residues present in HIV-1 RT.

Keywords: Virtual screening; LBVS; SBVS; HIV-1 RT.

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Isotope Ratio Mass Spectrometry Combined with Chemometrics as New Fingerprinting Method for Saffron Quality Control

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Background: Chemical Fingerprint is an analytical signal related to the composition of food which can mainly use for characterization and authentication of food [1]. Isotope ratio mass spectrometry (IRMS) of food bio-elements has been reported as an alternative tool for food quality control. Among different food, saffron as a spice produced from the red stigmas of Crocus sativus L., has attracted great attention in recent years due to its coloring, flavoring and biological properties [2]. However, determining saffron quality is challenging because of the effects of geographical origins and processing methods of its quality. The objective of this work was to propose elemental analysis (EA)-IRMS and gas chromatography (GC)-IRMS fingerprinting combined with chemometrics for authentication of saffron provided from main regions of Iran.

Methods: Sixty-two saffron samples were provided from Khorasan province. For EA-IRMS, the samples were powdered and then analyzed for measuring bulk carbon and nitrogen isotope ratios. In other words, saffron metabolites were extracted using ultrasonic-assisted extraction-dispersive liquid-liquid microextraction (UAE-DLLME) before GC-IRMS. The optimum extraction factors were obtained using response surface methodology (RSM). Principal component analysis (PCA) as an unsupervised classification method and partial least squares-discriminant analysis (PLS-DA) as a supervised classification method were used for data exploration and interpretation [3].

Results: First of all, EA-IRMS data of C and N for 62 samples were analyzed using PCA. The scores plot showed a good discrimination of samples which was related to N delta values according to PCA loadings plot. These results were related to the bulk analysis of samples, to have a detailed picture of the contribution of individual metabolites on these discrimination, GC-IRMS analysis was mandatory. For GC-IRMS data, first, baseline was corrected using asymmetric least squares (AsLS) and elution time shifts were corrected using interval correlation optimized shifting (icoShift) and correlation optimized warping (COW). Then, delta values for ten major peaks were calculated and data matrix (62×10) was submitted to PCA. The PCA results were used as class labels for PLS-DA which could correctly assign samples to two groups. The figures of merit were reasonable and always higher than 0.90.

Conclusion: It is concluded that EA- and GC-IRMS coupled with chemometrics can open a new window for authentication of complex food samples such as saffron.

Keywords: Chemical Fingerprint; IRMS; Saffron Quality; Chemometrics; Food Authentication

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Combined chemometrics and NMR spectroscopy for evaluation of the effects of parabens and pharmaceuticals in recycled water on metabolic pathways of lettuce

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Background: Plant metabolomics aims to study the plant system at the molecular level to provide a non-biased characterization of the metabolome of a plant's tissue in response to its environment. Contaminants of emerging concern (CECs), such as pharmaceuticals and personal care products, have been increasingly detected in agricultural irrigation waters [1]. The occurrence of CECs in irrigated crops and the linkage between plant morphological changes and plant metabolomic response have been investigated in the previous study [2]. In this study, a non-targeted metabolomic analysis was performed on lettuce exposed to nine CECs by irrigation and the subsequent changes have been traced by NMR spectroscopy and chemometrics.

Methods: The experiments were conducted inside the laboratory with the average temperature of 19 °C. Experimental units consisted of 4.5 L cylindrical amber glass pots filled with autoclaved soil. Lettuce seedling was planted in pots and watered with Hoagland nutrient solution. The plants were watered with different CECs for 30 days under controlled conditions. Then, metabolites of the lettuce were extracted using solid-liquid extraction. The extracts were then centrifuged in order to separate the aqueous and lipid phases. Finally, the aqueous phase containing metabolites was transferred to a glass vial. The extracts were freeze-dried and stored at −80 °C until NMR analysis. The resulting raw data were then analyzed using principal component analysis (PCA) and partial least squares-discriminant analysis (PLS-DA) [3].

Results: The NMR data of control and exposed samples were arranged in a data matrix. The shifts in NMR spectra were first corrected using interval correlation optimized shifting (iCOShift). Afterwards, the corrected data matrix was analyzed using PCA. However, the scores of PCA did not show a clear difference between control and exposed samples using different preprocessing methods. Then, PLS-DA models were built using full spectra and variable selected spectra using variable importance in projection (VIP). The values of sensitivity and specificity of PLS-DA model were higher than 0.90 and the selected variables were reasonable.

Conclusion: The metabolic response indicated that the CEC exposure produces large plant metabolic alterations (carbohydrate metabolism, TCA cycle, pentose phosphate pathway and glutathione pathway) at environmental relevant CEC concentrations (0.05 µg L^{-1}).

Keywords: Metabolomics; NMR; CEC; Chemometrics; PLS-DA.

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Examination of the relation between the quantity of hydrogen ulfide and other parameters of condensate with the help of partial least squares method in chemometrics

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Background: Determining the exact and rapid parameters of various types of petroleum products for refineries, customs and the standard office is an important and necessary issue. Current analysis methods require a lot of time and cost. The required analyzes are mercaptan, hydrogen sulfide, Reid vapor pressure, distillation, density, water content and color, All of them need time, cost, specialized equipment and expert experts

Methods: 50 sampling periods from gas wells of Sorkhoon and Qeshm gas refineries were performed, all of the mentioned parameters were measured using the national and international standard method and then analyzed by pairwise hydrogen sulfide And none of the correlations had any meaning And then from 50 samples of absorption spectra IR. And sufficient correlation between the results of the absorption spectrum IR and the amount of hydrogen sulfide.

Results:The hydrogen sulfide parameter is a dependent variable in the project And the best independent test variable is the FT-IR absorption spectrum. the predicted values are consistent with experimental values and the measurement error between predicted and experimental values is negligible. the proposed method can be an appropriate replacement for the sarkhon and gheshm gas refinery and without the need for different physical and chemical parameters can be effective only with FT-IR absorption spectrum in predicting the hydrogen sulphide amount and economically reducing the costs of the analysis [1,2].

Conclusion: The project, using multivariate calibration and IR spectroscopy, has been able to predict the amount of hydrogen sulfide in samples of gas liquids in Sarkhon and Qeshm refinery companies and a new method for measuring the hydrogen sulfide parameter was introduced . without the need for physical and chemical parameters, it was only by IR spectrum that was effective in predicting the amount of hydrogen sulfide.

Keywords: chemometrics , Hydrogen Sulfide , Condensate, partial least squares

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Exploring the effects of Lx-norm penalty terms in multivariate curve resolution methods for resolving LC/GC-MS data

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Background: There are different problems for resolution of complex LC/GC-MS data, such as the existence of embedded chromatographic peaks, continuum background and overlapping in mass channels for different components. These problems usually cause rotational ambiguity in recovered profiles and bring uncertainties in the final solutions found using the multivariate curve resolution (MCR) methods. Since mass spectra are sparse in nature, the sparsity constraint has been proposed recently as a constraint in MCR methods for analyzing LC/GC-MS data. There are different ways for implementation of the sparsity constraint, and the majority of methods rely on imposing a penalty term based on the L0-, L1- and L2-norms of recovered mass spectra. Ridge regression and least absolute shrinkage and selection operator (Lasso) can be used for implementation of L2- and L1-norm penalties in MCR, respectively. However, the main question is which Lx-norm penalty method is more worthwhile for implementation of the sparsity constraint in MCR methods. In order to address this question, two and three component LC/GC-MS data were simulated and used for the case study in this work.

Methods: The areas of feasible solutions (AFS) were calculated using the grid search strategy and fminsearch algorithm. Moreover, the magnitude of the L0, L1- and L2-norms of all mass spectra in AFSs were calculated and visualized as contour plots. The results revealed that the gradient of optimization surface for minimization of L1-norm is much more than those seen for minimization of L2-norm. Therefore, minimization of L1-norm would be a more reliable and practical way for confining AFS and reducing rotational ambiguity for these simulated LC/GC-MS data. Calculating Lx-norms in AFS for $0 \leq x \leq 2$ revealed that the gradient of optimization surface increased from $x=2$ to x values near zero. However, for $x=0$, the optimization surface was similar to a plateau, which increased the risk of sticking in local minima.

Results: The results in this work, recommend the use of L1-norm penalty methods like Lasso for implementation of the sparsity constraint in the MCR-ALS algorithm for finding more sparse solutions and reducing the extent of rotational ambiguity.

Keywords: Multivariate curve resolution; Sparsity constraint; Rotational ambiguity; Norm penalty; GC-MS.

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Determination of °API gravity in petroleum by ATR-FTIR spectroscopy and multivariate calibration

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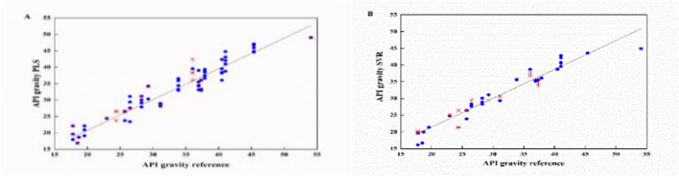
Background: Determination of physicochemical properties of crude oils is one of the most important trends in oil industries. Most of the methods have been reported under standard condition established by the American Society for Testing and Materials (ASTM), and the American Petroleum Institute (°API). However, most of the standard test methods are time consuming, environmental non friendly, expensive. Spectroscopy is an alternative method that shows some advantages over ASTM and °API methods[1]. In this work Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), in association with multivariable calibration based on partial least squares regression (PLS-R) and support vector machine regression (SVM-R) was used for determination of °API gravity of crude oil samples.

Methods: The 100 crude oil samples were analyzed with °API gravities values corresponding to the light, medium, and heavy crude oils. In order to evaluate the proposed calibration methods for °API gravity, the samples were analyzed by FTIR spectroscopy and chemometrics methods.

Results: Multivariate methods including PLS-R and SVM-R were applied using absorption spectra. After constructing the calibration models by PLS-R and SVM-R algorithms, the °API gravity of the prediction set samples were predicted by the models (Fig. 1). Also, R^2, RMSEC, and RMSEP statistical parameters were calculated and presented in Table. 1.



Model	PLS-R	SVM-R
$R^2_{\text{Cal.}}$	0.937	0.958
R^2_{Pre}	0.929	0.939
RMSEC	2.208	2.006
RMSEP	2.993	2.452

Fig. 1, Predicted °API gravity values versus reference °API gravity values by (A) PLS and (B) SVR (○) Calibration samples and (*) prediction samples. Table 1. Statistical outputs of PLS-R and SVM-R method

Conclusion: The ATR-FTIR associated with multivariate calibration methodologies was efficient technique for determination of the °API gravity in crude oil samples. This study indicated that the SVM-R as a nonlinear model was more accurate than PLS-R as a linear model for prediction of °API gravity in crude oil samples.

Keywords: ATR-FTIR, Crude oil, Classification, PLS-R, SVM-R, PLS-DA, SVM-C

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Partial least square discriminant analysis for classification of crude oils by gas chromatography and ATR-FTIR spectroscopy

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Background: Petroleum is a naturally mixture of hydrocarbons, and even the non-hydrocarbon that are generally present as components of complex molecules. With the increase in sea transportation and the expansion of offshore crude oil exploitation, oil spills often occur, which are not quickly identified. So, it will be classified as “no source”. Therefore, finding the true source of crude oil is a crucial step in the oil spill investigation [1]. This paper deals with developing a method for rapid classification of light and heavy crude oil samples based on their hydrocarbon percent by using ATR-FTIR spectroscopy combined with chemometrics method.

Methods: A total of 65 crude oil samples were obtained from different Iranian petroleum fields. Samples were distributed based gas chromatography results. In this regard, classes number of 1 and 2 were applied for heavy and light crude oil of Iran, respectively. The partial least squares linear discrimination (PLS-DA) classification approaches was performed on the whole data set.

Results: The PLS-DA algorithms was used to correlate between ATR-FTIR spectra and the class number of the samples according to gas chromatography as reference analysis. The confusion matrix and the model efficiency parameters were calculated or calibration and validation samples.

Real/Prediction	Method	Class 1	Class 2
Class 1	Calibration	12	0
Class 2		0	35
Class 1	Validation	6	0
Class 2		0	10

Method	Class	Spec	Sens	Prec	ER	NER	Acc
Calibration	1	1.00	1.00	1.00	0	1.00	1.00
		1.00	1.00	1.00			
Validation	2	1.00	1.00	1.00	0	1.00	1.00
		1.00	1.00	1.00			

Table 1and 2,The confusion matrix and efficiency parameters of PLS-DA model for calibration and validation samples

Conclusion: The crude oil samples was successfully analyzed according to their gas chromatography analysis using ATR-FTIR spectra by applying PLS-DA classification algorithms. Zero error rate and 100 % accuracy in classification for PLS-DA algorithms was obtained. However SIMCA classification algorithm showed results by providing 4% misclassification and 98 % accuracy which was lower than PLS-DA algorithms.

Keywords: Crude oil; Chemometrics ; Classification ; FTIR; PLS-DA

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Discrimination of almond oils using gas chromatography-mass spectrometry and chemometrics techniques: A need for an automated and standard strategy

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Background: Chromatographic fingerprinting is a common method for classification, authentication and quality control of natural complex samples such as plant extracts [1]. In this regard, gas chromatography –mass spectrometry (GC-MS) is one of the best options for fingerprinting and identification of chemicals in such samples [2]. On the other hand, due to the complexity of natural sample matrices and lack of selectivity in analytical instruments, multivariate chemometrics methods have been largely applied to extract maximum useful information from chromatographic data [1, 3]. In the present contribution, a chemometrics-based strategy is proposed for GC-MS fingerprint analysis of almond oils for source identification and quality control.

Methods: Soxhlet approach was used to extract oil of almond samples from seven different geographic areas in Fars province. Almond powder was placed in an extraction thimbles, and the oil was extracted by hexane and ethanol solvent with an equal ratio, at 70 °C for one hour. This action was repeated several times to provide enough oil to fulfill experiments. The extra solvent was separated from the oil by a vacuum evaporator, and the resulting solution was allowed to cool, and then centrifuged for 15 minutes at 3500 rpm. The Soxhlet extracts underwent trans-esterification with high efficiency. The esterification procedure was performed as follows: 1 mL of extract solution with 10 mL methanol and 2 mL H_2SO_4 was heated under reflux for 60 min at 65◦C. After cooling to room temperature, 10 mL hexane and 10 mL distilled water were added; the contents were shaken vigorously to mixed well and allowed to phase separated. The top hexane layer was transferred into a 10-mL vial. 1 L of the organic phase which was dried with anhydrous Na_2SO_4 was purred into a sample vial fitted with a septum for GC–MS analysis.

Results: Gas chromatography –mass spectrometry (GC-MS) coupled with chemometrics was used to develop a fast method for discriminating almonds (amygdalus). The GC-MS signals were recorded by taking three scans per sample. GC-MS together with pattern-recognition methods such as principal component analysis (PCA), linear discriminant analysis (LDA) and counter propagation artificial neural network (CP-ANN) were developed to discriminate each types of almonds. The results showed excellent discrimination between the almond groups and obtaining high levels of sensitivity and specificity for each class.

Conclusion: The obtained results were encouraging and showed a promising potential of GC-MS and chemometrics methodes for detecting almond type. the proposed approach in this work could classify more than 85% of the samples correctly, in each group.

Keywords: almonds, Classification, GC-MS, PCA, LDA, CP-ANN

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Colorimetric sensor arrays based on mixing of quantum dots and organic reagents for aldehydes and ketones recognition

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Background: The colorimetric sensor array (CSA) represents a fundamental new approach to array-based chemical sensing. Colorimetric detection is a fairly simple technique, and the advent of universal digital imaging has given it new and exciting possibilities. colorimetric sensor array provides a facile, rapid, portable, visualized tool for the identification of various chemical compounds [1]. CSAs are facing new opportunities and challenge by nanomaterials boom. Gold nanoparticles (GNPs), organic modified silicates (ormosils, e.g., sol-gel silica), molybdenum disulphide quantum dots (MoS_2 QDs) and graphene oxide (GO) monolayer is used in design of CSAs to improve sensitivity and specificity of receptors [2]. The development of a low-cost, sensitive colorimetric sensor array for the detection and identification of different aldehydes and ketones based on MoS_2 QDs is reported.

Methods: To design sensors different dyes are mixed with MoS_2 solution and then 0.5 µL of each solution is spotted on the TLC paper (1.5×1.5 cm). Then, these sensors exposed to the different aldehydes and ketones compounds (8 different compounds, 24 samples). Before exposure of analyte, a picture of the array was imaged with scanner and served as "before-exposure image". After exposure, the "after-exposure image" was collected. A difference map was easily generated through digitally subtracting red, green, and blue (RGB) values of the before-exposure image from the after-exposure image.

Results: Previous studies revealed that MoS_2 has rich sulfur vacancies which show specific and higher molecular affinity to oxygen-functionalized VOCs (e.g., aldehydes, ketones) and that numerous sulfur atoms facilitate the formation of hydrogen-bond interactions.
For the high dimensional data from the array, a statistical analysis that could fully utilize the total dimensionality is very necessary. In this study, hierarchical cluster analysis (HCA) and principal component analysis (PCA) was used to condense the high dimensionalities of original data. Both HCA and PCA (the first two PCs captured 75% of variance) revealed a good classification with the accuracy of 0.96.

Conclusion: In this work, a simple and portable colorimetric sensor was applied for the aldehydes and ketones recognition based on the use of MoS_2 QDs and the use of the scanner as a capturing digital image. This CSA will be used for the determination of these compounds in different environmental, food, water and etc. samples.

Keywords: colorimetric sensor array, aldehydes, ketones, image analysis

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Multivariate Statistical Assessment of Ground-Water Quality. A case study in Zanjan-Iran

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Background: Water pollution has been considered as a serious threat for human beings and natural ecosystems in recent decades. Anthropogenic processes as well as natural processes degrade waters and impair their use for drinking, industrial, agricultural, recreation, or other purposes [1]. Groundwater quality is a function of physical and chemical properties, which is also strongly influenced by the geological and geochemical structure, surface water quality, and human activities in the studied area [2].

Methods: In this study, 12 water quality parameters were selected and collected in 15 years at 5 sampling stations (Zanjan, Goltape, Gheydar, Abhar and Sujas) in Zanjan province- Iran. Water quality index (WQI) was assessed for all stations [3]. Multivariate statistical techniques such as principal component analysis (PCA) and multivariate curve resolution-alternative least squares (MCR-ALS) and Geostatistical technique as powerful tools used to data analysis [4-5].

Results: WQI at five sampling stations were equivalent to 28.6, 24.9, 28.3, 38.9 and 44.3 respectively. A Similar pattern is seen in PCA and MCR-AlS results of Zanjan, Abhar and Sujas. Gheydar and Goltape also show similar patterns. This similarity is maybe because of the similar geochemical and the agricultural pattern in these stations. PC1 explains 49.3%, PC2 explains 38.3% and PC3 explains 8.0% of the total data variance of ground water dataset. The Geostatistical and mapping analysis confirm that geochemistry, and anthropogenic sources affected water quality in studied area.

Conclusion: As a conclusion, multivariate data analysis confirms WQI results. PCA and MCR-ALS results allowed for a deeper and summarized interpretation of the water quality dataset in different stations. Simultaneous use of multivariate statistical techniques and geostatistical analysis is very suitable for detecting the causes of water quality changes.

Keywords: Water quality; WQI; PCA; MCR-ALS

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Investigating Photo-degradation Processes of Some Textile Dyes with Novel Synthesized Nano-photo-catalyst $CoO@SiO_2@TiO_2$

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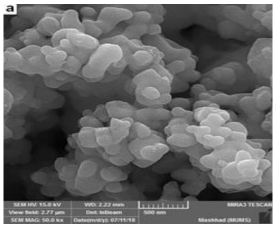
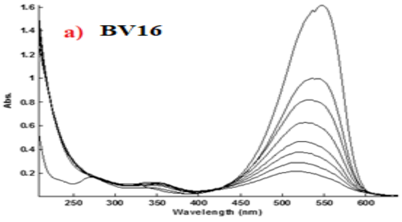
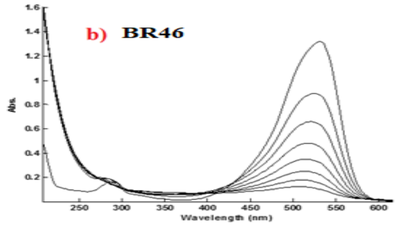
Background: Reduction and removal of dyes is important because to the effect on the quality of drinking water, reduces photosynthetic activity, low biological degradation potential. Azo dyes such as Basic Red46 and Basic Violet16, Due to high usage of these dyes, large volumes of colored wastewater are discharged into environmental water sources. The release of them is of concern due to their toxic, mutagenic and carcinogenic characteristics of the dyes [1]. In this work, advanced oxidation process based on nano-photo-catalyst was used for degradation BV16 and BR46.

Methods: Core-shell nanoparticles was synthesized according to procedure has been describe in [2,3]. Photo-degradation of dyes was done by the visible light source of 400 W cathodic lamp. First, 100 mL of standard solution of BV16 or BR46 was prepared and transferred to a Pyrex glass vessel and 3mg $CoO@SiO_2@TiO_2$, 1.3ml H_2O_2 were added to vessel, then the mixture was stirred throughout the reaction. Temperature was controlled in photo-reactor by cooling waters circulation around vessel. For each sample were taken every 10 min until no significant changes observed in the signals.

Results: The morphology of nano-photo-catalyst was illustrated in Fig a. Time-spectral data of standard solution of 15mg/l of BV16and 30mg/l of BR46 were collected. Each data was converted to variation matrix [4]and then analyzed by singular value decomposition method (SVD). SVD analysis showed one significant component for each data set. Therefore, the kinetic profile of the degradation product was estimated from the first score vector. Finally, the score vector was fitted to a first order kinetic reaction and the rate constant of each reaction was calculated. The Kinetic rate constants were 0.042 min $^{-1}$ and 0.027 min $^{-1}$ for BR46 and BV16, respectively.







Conclusion: High kinetic rate constant of the photo-degradation of the dyes indicated the synthetic nano-photo-catalyst has high efficiency in dyes destruction; nearly during one hour 15mg/l of BV16and 30mg/l of BR46 were completely degraded.

Keywords: photo-degradation, $CoO@SiO_2@TiO_2$ nano-photo-catalyst, Azo dyes

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A novel and efficient nanozero-valent iron based nanocatalyst immobilized on graphene oxide for dyes reduction

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Background: Nanozero-valent iron (nZVI) based catalysts, because of their large surface area, high reactivity, strong reductive capacity, and cost-effective, have been used as reducing composite. NZVI is a potential reductive composite because of its sufficient mobility and low toxicity. It can instantaneously adsorb and reduced anionic dyes on its surface. Though, the aggregation tendency of nZVI refers to intrinsic magnetic interactions and high surface energy. This limits its dispersibility. Also, in aqueous media, reductive property of nZVI decrease significantly due to quick formation of a Fe oxide and hydroxide layer on its surface. Supporting nZVI on graphene oxide (GO) results efficient dispersion of nZVI which prevents its aggregation causing greater reduction performance.

Methods: In this study, nanozero-valent iron (nZVI) based trimetallic nanoparticle supported on GO was synthesized [1, 2]. The reduction of tartrazine and sunset yellow by the proposed nanocatalyst was examined using the batch experiments technique and all involved parameters affecting the reduction efficiency such as: dose of nanocomposite, sample pH and contact time were modeled and optimized by response surface methodology.

Results: The synthesized GO@Fe-Cu-Ag trimetallic particles were characterized by TEM, FT-IR, XRD, SEM, EDS and BET. The results showed that the nZVI trimetallic was successfully synthesized and immobilized on GO. The optimum conditions for reduced sunset yellow and tatrazine dyes are respectively: pH= 5.5 and 3, dose of nanocomposite= 4 and 4 mg mL^{-1}, time= 30 and 26 min, initial dyes concentration= 100 and 100 ppm , the kinetic data for nanocatalyst were fitted well with the pseudo-second order model.

Conclusion: The experimental results of the present research indicated that the presence of GO as support could decrease the aggregation of nZVI and increase it's adsorption and reactivity. Furthermore, high reactivity of Fe^0-based trimetals was mainly attributed to the plating order of transition metals (i.e., Cu and Ag). Theory is that the trimetallic structure of Fe-Cu-Ag could improve the electron transport and create active sites with high electron density at the surface (Ag layer) that could enhance the generation of surface-bonded atomic hydrogen ($[H]_{abs}$) or the direct reduction of pollutant. GO@Fe-Cu-Ag trimetallic system would be a promising process for the removal of the dyes from food industrial wastewater.

Keywords: Nanocatalyst; Nanozero-valent iron; Graphene oxide; Sunset yellow; Tartrazine; Optimization

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Synthesis and characterization of novel zero-valent iron based trimetallic supported on bentonite nanocatalyst and its application in dye reduction

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Background: Tartrazine (Ta) and sunset yellow (SY) are synthetic food colors used most extensively as food additives, to improve the appearance, color, and texture of foods. When added in excess, however, these synthetic food colors can be pathogenic. Therefore, it is important to develop effective methods for removing these synthetic colors from aqueous media. Different methods were applied for this purpose, and among these methods, chemical reduction by a cheap and eco-friendly nanocatalyst is the most efficient and simplest method.

Methods: Nanozero-valent iron (nZVI) based trimetallic nanoparticle supported on bentonite clay as a new low-cost and eco-friendly nanocatalyst was synthesized [1, 2], characterized and then applied for the reduction of sunset yellow and tartrazine as model dyes from aqueous solutions. The reduction of the model dyes by this new nanocatalyst was examined using batch technique and all parameters influencing the reduction procedure were considered.

Results: Central composite design (CCD) was used to model and optimized the reduction procedure. Both coefficients of determination (R^2) and adjusted-R^2 obtained from the analysis of variance (ANOVA) were above 0.9, ensuring a satisfactory adjustment of the model with experimental results. The optimum conditions for reduced sunset yellow and tartrazine dye are respectively: time= 26.7 and 27 min, pH= 3 and 3, dose of nanocatalyst 3.6 and 4 mg mL^{-1}, initial dyes concentration= 100 and 100 ppm. The interaction effects of significant parameters were also considered and the results showed that there is no interaction between the parameters in the case of SY while there are interactions between pH-concentration and dose-concentration. Under the defined optimum conditions, the kinetic models parameters were investigated and the results showed the pseudo-second order model has good agreement with the procedure. Finally, under the defined optimum condition, the proposed nanocatalyst was successfully applied for dyes reduction from food industrial wastewaters.

Conclusion: The nanocatalyst for Ta and SY dyes reduction simultaneously from aqueous solution are reported. The results suggest that the bentonite could effectively lighten the aggregation of nZVI trimetallic nanoparticles and enhance their reactivity towards dyes.

Keywords: Nanocatalyst; Nanozero-valent iron; Bentonite clay; Sunset yellow; Tartrazine; Optimization

References

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7-Nanochemistry

A Smartphone-Based Microfluidic Wearable Patch for Optical Multisensing of Sweat Biomarkers

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Background: Recent developments in wearable sensors aim to overcome time consuming traditional medical diagnostic methods by giving individuals an immense perspective about their own physiology [1]. The burgeoning advances in chemical sensors, advanced materials and microfluidics enabled scientists to design novel wearable sensors to analyze bio-fluids. Herein, we utilized photoluminescent probes to measure glucose, chloride, pH and sweat volume in a wearable, microfluidic nanopaper/thread-based sensing platform coupled with a smartphone [2].

Methods: Laser printing technology was used to create hydrophobic barriers on dried nanopaper. A glucose oxidase (GOx) /carbon dot (CD) was used for glucose assay. Mixture of CDs with Ag^+ ions resulted chloride assay. Dilute fluorescein and CDs solutions yielded pH and volume assays respectively. The assays were drop-casted in the test zones and dried at ambient condition. A 3D-printed smartphone-based sensing setup was used to measure the photoluminescence (PL) intensity of the fabricated sensors. Cotton threads were also used as microfluidic channels to harvest sweat and introduce it to the developed sensing bioplatform. The wearable device could attach to skin for analyzing sweat chemicals generated by exercise.

Results: PL intensity changes in each test zone correlated with the concentration of each analyte. Glucose oxidized by GOx to generate H_2O_2. In the presence of Fe^{2+}, based on Fenton reaction hydroxyl radicals achieved and caused the PL quenching of CDs. (Dynamic range (DR): 0.1-2 mM). Ag^+ ions cause PL quenching of CDs but in the presence of chloride ions it recovered due to AgCl formation (DR: 5-70 mM). Fluorescein has pH dependent PL intensity behavior which increases in pH ranges from 4 to 9. A physical phenomenon known as coffee-ring effect was utilized to measure sweat volume using diluted CDs (DR: 1.0- 8.0 μl).

Conclusion: Emergence of new optical materials, bioplatforms and cheap microfluidic systems made it possible to fabricate a wearable patch coupled with a smartphone for non-invasive analysis of sweat biomarkers. It has great potentials to investigate sport performance, cystic fibrosis diagnosis and non-invasive diabetes management.

Keywords: Wearable sweat sensor; Smartphone; Nanopaper; Cotton thread.

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Naked Eye detection and Colorimetric and Fluorescence Sensing Approach for Sensitive and Selective Determination of Fe^{3+} ions and Histidine Based on Carbon Dots in Food Samples

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Background: Fe^{3+} as a vital element in human body required in a number of diverse cellular functions and biological processes, for instance, cellular metabolism, enzyme catalysis, and electron-transfer processes [1], responsible for carrying the oxygen in heme. Histidine contains varied functions in living systems such as a neuromodulator or neuromodulator in the muscular and nervous systems [2], human growth and repair of tissues [3]. A colorimetric and fluorescent dual mode sensing was developed for the sensitive and selective determination of Fe^{3+} and histidine.

Method: N,S-CDs were synthesized with pyrrolidine-1-dithiocarboxylic acid using the hydrothermal method. The fluorescence intensity of the N,S-CDs at 420 nm or its absorbance at 520 nm gradually decreased by an increasing the concentration of Fe^{3+} ions, while the fluorescence or absorbance intensity recovered by the subsequent addition of histidine.

Results: The developed method is the first report of dual modality for assessing Fe^{3+} ions and histidine based on the CDs formation of a nonfluorescent complex in the ground state. The limits of detection were 1.9 μM and 0.03 μM for Fe^{3+} and histidine by fluorometric, respectively and 5.0 μM and 4.2 μM for Fe^{3+} and histidine by colorimetric, respectively.

Conclusion: The proposed nanosensor showed good biocompatibility, high selectivity, low cytotoxicity and is a candidate for the determination of Fe^{3+} in food samples and histidine in human serum and urine samples.

Keywords: Carbon dots; Colorimetric determination; Fe^{3+}; Histidine; Fluorimetric determination.

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Modification of Carbon Dots with Mixed Hemimicelles of Ionic Liquid-Based Surfactants for Removal of Aniline Blue from Wastewater Samples

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Background: Aniline blue (AB), a water-soluble triphenylmethane dye, is used in many textile industrial branches such as dying of nylon, polyacrylonitrile, wool, silk, cotton and food, leather and cosmetics industries [1]. Due to its stability, it has a long residence time in wastewater [2]. The presence of aniline blue at low concentration in water reduces its transparency. It can lead to decreased photosynthetic activity and causes oxygen deficiency [3].

Method: In this study, mixed hemimicelles of ionic liquid-based surfactants loaded on carbon dots (CDs@MHILs) was applied for the aniline blue removal from wastewaters. Modification of carbon dots (CDs) was performed through electrostatic self-assembly technique which is very simple, facile and mild. The assembly of (1-hexadecyl-3-methylimidazolium bromide) onto carbon dots was performed.

Results: The results indicate that the mechanism of the adsorption process followed the pseudo-second-order kinetic. Adsorption isotherm was also studied with Freundlich, Langmuir and Temkin models. Aniline blue adsorption showed Langmuir isotherm with a maximum monolayer adsorption capacity of 870.3 mg g^{-1} and equilibrium time (20 min). The q_m values of aniline blue on CDs@MHILs adsorbent have been compared with those of other absorbents (Table 1).

Table 1. The q_m values for the adsorption of aniline blue on different adsorbents.

Adsorbent	**q_m(mg g^{-1})**
Modified brewer's yeast	228.0
Magnetic PODMP	40.32
Dairy sludge	52.5
Raw Kaolinite clay	2.0
Fe_3O_4@MHILs	870.3

Conclusion: The results show that CDs@MHILs exhibits an enhanced adsorption capacity for aniline blue. The adsorbent provides high adsorption capacity, pseudo-second-order kinetics, adsorption the monolayer dyes onto the homogeneous adsorbent surface, and good reusability.

Keywords: Carbon dots; Aniline blue; Mixed hemimicelles; Ionic liquid.

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Synthesis of ZIF-11 Nanoparticles as Adsorbent

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Background: Zeolitic imidazolate frameworks (ZIFs) constitute highly porous frameworks that have potential to be used as adsorbent in the effective removal of target adsorbate [1, 2]. However, precise control over the size of them in nanoscale still remains a challenge. In this work, nanoparticle of ZIF-11 was synthesized with the ability to absorption of methylene blue (MB).

Methods: At first, 0.24 g of benzimidazole was dissolved in 6.4 g of methanol, together with 9.2 g of toluene and 2.4 g of ammonium hydroxide. Then, 0.22 g of zinc acetate dehydrate was dissolved in 3.2 g of methanol. Both solutions were cooled separately to 18 °C and then mixed in a 50 mL centrifuge flask (10,000 rpm, 10 min). The solid collected was washed with methanol three times and dried at 100 °C overnight. A batch adsorption experiment was carried out.

Results: After filtration of adsorbent, the concentration of MB was determined using UV-VIS spectrophotometer at 668 nm. The uptake was calculated about 60% after 30 min (Fig. 1). Results based on SEM and XRD indicate the formation of ZIF-11 nanoparticles (~ 20 nm) (Fig. 2, 3).

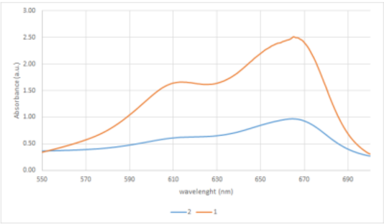

Fig. 1. UV-VIS spectra of MB (10 ppm) during adsorption on ZIF-11 (0.1 gr)

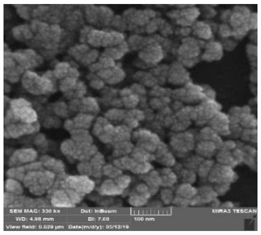

Fig. 2. SEM graph of as-prepared ZIF-11

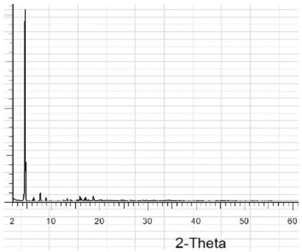

Fig. 3. XRD Spectra of as-prepared ZIF-11

Conclusion: The synthesis of ZIF-11 at temperatures of 18 °C and 10000 rpm at 10 min resulted in the formation of ZIF-11 nanoparticles, which had the good absorption of MB (about 60% after 30 min).

Keywords: Adsorbent; ZIF-11; MOF; Nanoparticle

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Synthesis of Graphitic Carbon Nitride Nanotubes for Efficient Electrocatalytic Hydrogen Evolution Reaction

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Background: Hydrogen production from water using active semiconductor photocatalysts is an attractive solution to increasing energy demand[1]. Recently, graphitic carbon nitride nanotubes (g-C_3N_4 NTs) have drawn considerable attention due to their unique and tunable nanostructure, high nitrogen content, and conductivity[2]. In the present work, g-C_3N_4 NTs were synthesized and their electrocatalytic activity was compared with multiwall carbon nanotubes (MWCNTs) and graphitic carbon nitride nanosheets in the hydrogen evolution reaction (HER).

Methods: In a typical synthesis, $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in deionized water. Subsequently, specific value of melamine was added to the above solution and stirred for 6 h. After filtration and drying, the resulting powder was initially heated under air atmosphere to 340 °C in a tube furnace for 1h, and then the temperature was further increased to 900 °C.

Results: SEM image of the synthesized g-C_3N_4 NTs confirms the existence of high density of nanotubes with diameter of 30-50 nm and length of several µm (Fig. 1(A)). The TEM image in Fig. 1(B) shows that the g-C_3N_4 NTs are bamboo-like structure. The preparation of g-C_3N_4 structure is confirmed with FT-IR spectroscopy (Fig. 1(C)). The performance of the g-C_3N_4 NTs, together with MWCNTs and g-C_3N_4 nanosheets as electrocatalyst for hydrogen production was evaluated for HER. Fig. 1 (D) represents LSVs for above samples in H_2SO_4 solution, indicating the g-C_3N_4 NTs provides a higher specific activity than MWCNT and the nanosheets of g-C_3N_4.

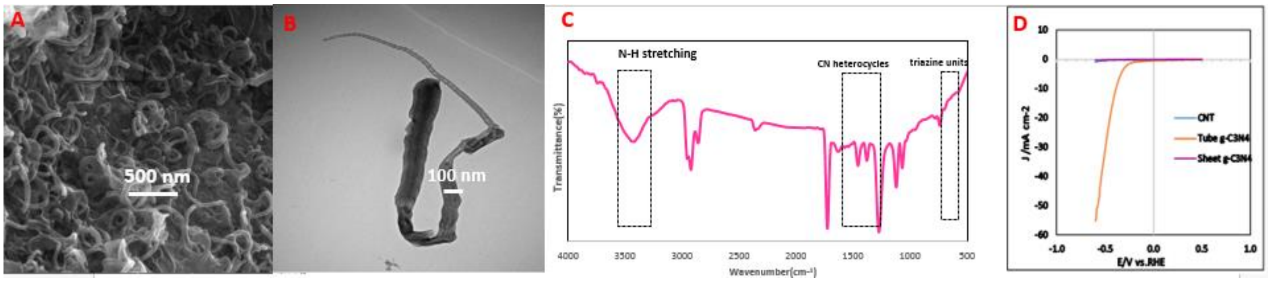

Fig. 1 (A) SEM and (B) TEM images of the g-C_3N_4 NTs¸ (C) FTIR spectra of g-C_3N_4 NTs¸ and (D) LSV curves of MWCNT¸ g-C_3N_4 nanosheets and g-C_3N_4 NTs in 0.5 M H_2SO_4 electrolyte at a scan rate of 5 mV s^{-1}.

Conclusion: The electrochemical studies show that nanotube structure of g-C_3N_4 has an excellent electrocatalytic activity for HER than the other structures.

Keywords: Carbon nitride nanotubes, carbon nitride nanosheets, Hydrogen Evolution Reactions. bamboo-like

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Enhanced Photocataiytic Activitic of (Y, Co) Co-doped BiFeO3 Nanostructures on the Degradation of Methyl Orange (MO)

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Background: In this work $Bi_{0.94}Y_{0.06}Fe_{1-x}Co_yO_3$(x=0, 0.02, 0.04and0.06), (y=0, 0.01, 0.03and0.05), samples are synthesized by sol-gel method. The phase and crystal structure of the samples are confirmed by x-ray diffraction analysis photo catalysis is one of the promising methods for solving such environmental problems, as it decomposes the organic pollutants in to harmless inorganic substances without generating any pollution**.**

Methods: Samples are synthesized by sol-gel method, then photocataiytic activities of the samples are determined by the degradation of methyl orange (MO) dye in the presence of UV light and H_2O_2 at pH 2 which show.

Results: The effect of color concentration parameters, pH, irradiation time, nanoparticle loading percentage and oxygen concentration were studied and optimal conditions were reported

Conclusion: the catalytic performance of nanoparticles of **Y** and **Co** bismuth ferrites for photo catalytic removal of methyl orange color, which is one of the most important pollutants in industrial wastewaters, was investigated by ultraviolet spectroscopy and results showed high performance of Nano Synthesized particles are used to remove contaminants in industrial effluents. The effect of color concentration parameters, pH, irradiation time, nanoparticle loading percentage and oxygen concentration were studied and optimal conditions were reported.

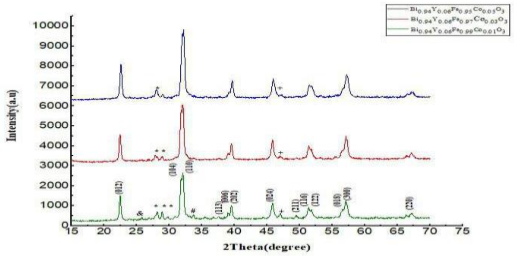

Fig.1 *X*-ray diffraction spectrum of BFO doped with various percentages of Co and Y (0.06)

Keywords: Bismuth ferrite, Photocatalyst, Methyl Orange, Sol_gel.

References*:*

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Synthesis of nano composite chitosan-pumice-acetic acid as low-cost sorbents for removal of dyes from aqueous solutions

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Background: Colored effluents are one of the most important environmental pollution sources. Such effluents usually contain non-used dyes, as well as several organic and inorganic pollutants [1]. Synthetic dyes, often used in these industries, can be divided into acidic, reactive, direct, basic and other groups. Without appropriate treatment, the release of such wastewater into the environment is a serious problem for aquatic environment and human health. For this reason, the treatment of colored waste is necessary. Several methods have been used for dye removal from waste water. Adsorption is the effective method which used for the removal of dyes pollutants from wastewater. Thus, removal of this dyes from aqueous solutions by an effective and inexpensive method is important. Nano sorbents which have higher efficiency have been recently employed, so synthesis of natural, biocompatible and inexpensive nano sorbent such as nano composite chitosan-pumice is important [2].

Methods: Modification of the pumice, was carried out by chitosan based on the method used for different clays[2]. Briefly, pumice powder (200 mesh) treated with oxalic acid to set acidic groups on PMC surface that may increase the amount of adhered to its surface, Acid treated pumice was mixed with chitosan solution in oxalic acid. Chitosan –coated pumice was cross-linked by adding polysulfide drop wise to stirred mixture at room temperature. The result nano composite redisperced in deionized water with aqueous 0.50 M chloroacetic acid maintained at pH 8.0, and treated to convert hydroxyl groups of chitosan to carboxyl groups. Then nanocomposite was treated with con. HCl, for protonation carboxylic groups. The structure and size of resulted nanoparticles were evaluated by using XRD (Figure 1), according to the dedye-scherrer equation, the particle size of the chitosan-coated pumice nanoparticles was 34 nm. The obtained nanocomposite was used as sorbent for removal of Hg^{2+} ions from aqueous solutions.

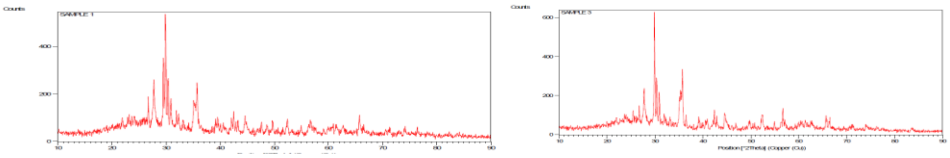

Figure 1: XRD images of the nanocomposite chitosan treated-pumice

Results: Because the synthesis nanocomposite having sufur in its structure, great desire to attract mercury ions. Therefore, it was used as an effective absorbent to remove this ion. For this means different parameter that which influencing removal of Hg^{2+} ions, such as pH, effective buffer, initial concentration Hg^{2+} etc. were investigated.

Conclusion: Purposed new nanocomposite is a super absorbent for mercury ions due to the high porosity of the pumice and the presence sulfur in its structure. This work is going on.

Keywords: Nanocomposite; chitosan; pumice; mercury ion; low-cos sorbent

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Preparation of a New Composite GO/Schiff Base for Detection of Dopamine in Biological Samples

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Background: The accurate detection of dopamine (DA) levels in biological samples such as human serum and urine are essential indicators in medical diagnostics. In this work, we describe the preparation of molybdenum-Schiff base grafted graphene oxide (GO) composite for the sensitive and lower potential detection of DA. The composite modified electrode has been used for the detection of DA in biological samples such as human serum and urine.

Methods: In order to detection of dopamine, GO/Schiff base composite was prepared. The surface morphology and other properties of the GO/Schiff base composite were characterized by various techniques, including TEM, SEM, Raman, FT-IR spectroscopy and thermogravimetric analyses.

Results: The composite modified electrode shows an enhanced oxidation peak current response and low oxidation potential for the detection of DA than that of electrodes modified with bare, GO and Schiff base discretely. Under optimum conditions, the fabricated GO-Schiff base composite modified electrode shows the DPV response of DA in the linear response ranging from 0.04 to 19.41 μM. The detection limit and sensitivity of the sensor were estimated as 0.0042 μM and 6.04 μA μM^{-1} cm^{-2}, respectively.

Conclusion: A novel DA sensor based on GO-Schiff base composite. Low over potential detection of DA with enhanced sensitivity. The LOD of 4.3 nM for DA is achieved. Practicality has been demonstrated in biological samples.

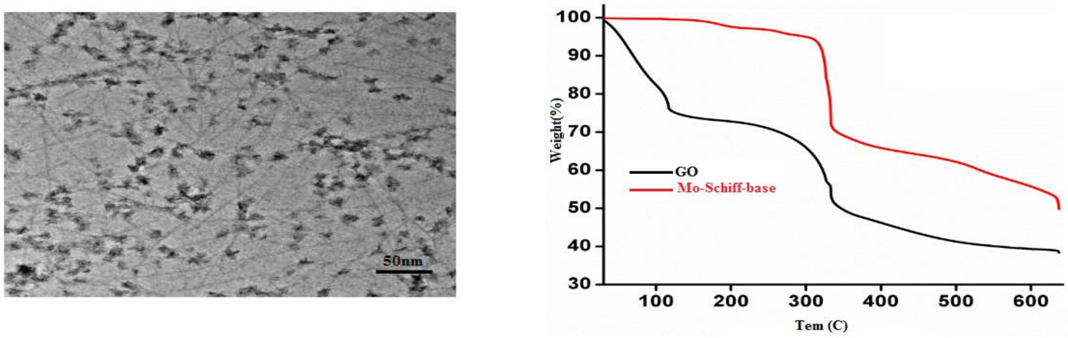

Fig.1. TEM image of Mo-Schiff-base-GO (left) and TGA of GO and Mo-Schiff-base-GO (right)

Keywords: Schiff base; Graphene Oxide; Dopamine; Biological Samples; Composite.

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TiO_2/[$W_{48}P_8Cu_{20}$] Nanocomposite Film Immobilized on Glass for Degradation Methylene Blue

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Background: The wastewater of textile dye draining in to the river without treatment would bring out serious pollution of water resource and threatening of ecology environment and human health [1]. Hence, it is crucial to remove these dyes from colored effluents. Azo dyes are a versatile class of colored organic compounds that have extensively been used in industry for applications such as textiles, paper, leathers, additives and analytical chemistry. Various methods have been used to degrade or remove these contaminates by physical, chemical, photochemical and microbiological process.

Methods: Nanocomposite film of TiO_2//[$W_{48}P_8Cu_{20}$] was prepared via electrostatic layer-by-layer self-assembly method [2]. Atomic force microscopy (AFM) observations and X-ray photoelectron spectroscopy (XPS) analyses show that the positive TiO_2 nanoparticles and [$W_{48}P_8Cu_{20}$] polyanions were successfully incorporated in to multilayer nanocomposite films. XPS spectra clearly demonstrate that the films include Ti and W elements. The Ti 2p XPS spectrum presents two main peaks at binding energy of 459.1 and 465.0 eV. These peaks can be assigned to be Ti^{4+} $2p_{3/2}$ and Ti^{4+} $2p_{1/2.}$ The high resolution W 4f XPS spectrum also displays two main peaks at 35.6 and 37.8 eV, which can be identified to W 4f respectively.The influence of parameters including bilayer number of films, initial dye concentration, and electron acceptor such as H_2O_2 were checked to obtain the optimum conditions of MB photocatalytic degradation.

Results: The experimental results show that the degradation rate of MB decreases with an increase of initial dye concentration. The addition of hydrogen peroxide with concentration over the range 2.5-20 Mm evidently improves the decolorization rate by inhibiting the electron-hole recombination and producing an abundance of ·OH radicals. The kinetics of MB oxidation process was determined to be first-order reaction according to the Langmiur-Hinshelwood kinetics model at different H_2O_2 concentrations.

Conclusion: The TiO_2/[$W_{48}P_8Cu_{20}$] nanocomposite is shown to be effective photocatalyst for the degradation of MB. This nanocomposite was successfully prepared by LbL self-assembly method. The color removal efficiencies increased rapidly by the addition of H_2O_2 as an electron acceptor, which accompanied by a decrease in decolorization time.

Keywords: Methylene Blue; Degradation; Adsorption; Wastewaters.

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Synthesis of mesoporous silica-coated magnetic nanoparticles modified with thiocarbohydrazide applied to analytical chemistry

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Background: Magnetic nanoparticles are a class of nanoparticles that can be manipulated using a magnetic field. Such particles commonly consist of magnetic elements such as iron, nickel, and cobalt and their chemical compounds. Recently iron oxides nanoparticles have a huge potential for different applications such as nickel–iron batteries, catalysts and sorbents for environmental remediation. The use of Fe_3O_4 nanoparticles has been due to its low toxicity and suitable magnetic properties. The sol-gel method is the simplest and most efficient chemical method for the synthesis of magnetic nanoparticles because of its high ability to synthesize a large number of nanoparticles. By using organic and inorganic coatings on the surface of magnetic nanoparticles, the stability of magnetic nanoparticles can be increased. The selectivity of these materials depend on the functional group that is anchored to the surface of magnetic nanoparticles [1,2].

Methods: In this research, a new mesoporous silica-coated magnetic nanoparticles functionalized by thiocarbohydrazide (Fe_3O_4@MCM-41@TCH) was prepared from Fe_3O_4, tetraethoxysilane (TEOS) and 3-chloropropyl triethoxysilane (CPTES) as precursors by a sol-gel method (Fig. 1).

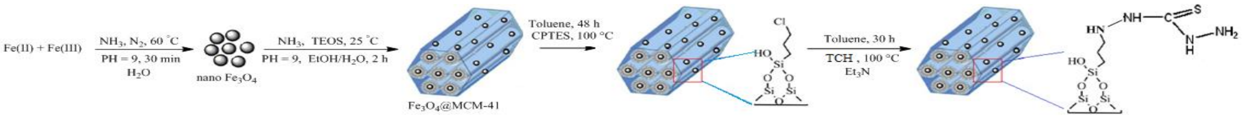

Fig. 1: The reaction sequence for preparation of Fe_3O_4@MCM-41@TCH.

Results: The structure of nanoparticles was fully characterized using by scanning electron microscopy, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and thermogravimetry analysis (Fig. 2). Application of Fe3O4@MCM-41@TCH for some contaminants uptake from contaminated matrix is in progress.

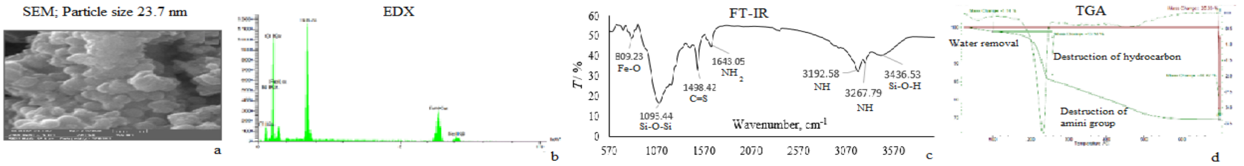

Fig. 2. Studying the structure of nanoparticles: a) SEM image, b) EDX spectrum, c) FT-IR spectrum and d) TGA.

Conclusion: Mild reaction conditions, environment-friendly synthesis and easily prepared starting materials are the key features of the present method. The synthesized nanoparticles can be used as adsorbent for solid phase extraction of heavy metals in water samples.

Keywords: Fe_3O_4 nanoparticle; Thiocarbohydrazide; Heavy metals; Sol-gel.

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Magnetic dispersive micro solid phase extraction based on 2-aminothiophenol as nanoadsorbent for quantification of 2, 4-dinitrophenol

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Background: 2, 4-dinitro phenol (2, 4-DNP) one of the phenolic compounds is primarily used as a chemical intermediate for the production of azo dyes and wood preservatives. Due to their toxicity in the environment, have adverse effects on the environment and human health [1]. 2, 4-DNP can remain in the environment for a long time due to its stability and bioaccumulation.

Methods: In this work, the 2-aminothiophenol as an organosulfur compound is synthesized and characterized by FT-IR, TEM, XRD and TGA techniques and used as nanosorbent in the magnetic dispersive micro solid phase extraction (MD-MSPE) method for the determination of 2,4-DNP [2]. In MD-MSPE method, the adsorbent is dispersed in sample solution by ultrasonic, and after completing the absorption of the analyte, the absorbent is separated by a magnet from the solution, and then the analyte solution is transferred to the UV-Vis spectrophotometry [3].

Results: To examine the most important parameters including amount of sorbent, pH of the solution, extraction time and desorption time on the MD-MSPE, a four factor central composite design (CCD) combined with response surface modeling (RSM) was accomplished [4, 5]. Under optimum conditions, LOD, LOQ and RSD of the method were found to be 5.4 ng mL^{-1}, 17.82 ng mL^{-1} and 7.18 %, respectively.

Conclusion: The MD-MSPE method based on the 2-aminothiophenol as nanosorbent successfully applied to determination of target analyte in various water samples. Furthermore, this method offers significant advantages such as the simplicity of the extraction, speed, high selectivity and sensitivity.

Keywords: *2, 4 Dinitrophenol;* Magnetic nanoadsorbent*;* Dispersive micro-solid phase extraction; Central composite design**.**

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The Performance evaluation of three kind of scale inhibitors using silica nanoparticles on the gypsum scale

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Background: Industrial water contains large amounts of Calcium, Sulfate, Barium and other ions [1]. One of the major problems is deposition of scale precipitates. The main type of oil field scales found are carbonate and sulfate scales. Use of scale inhibitors is the one of the best ways for preventing or reducing scale formation. Silica Nano particles (SNPs) are the newest chemical used as scale inhibitor which can cause to improvement of chemical inhibitors [2].

Method: In this study, effects of (SNPs) on Amino Trimethylene Phosphonic Acid (ATMP), TH-3100 carboxylate sulfonate nonion tri polymer (AC 3100) and poly aldehyde carboxylic acid (POC 2020) inhibitors in the presence of calcium sulfate were investigated. Several test methods are available to measure and evaluate the inhibition and reduced precipitation. In this research, the standard scale inhibition test was used to evaluate the inhibition efficiency (IE %) and using the spectrophotometer device for measuring sulfate ions to predict calcium sulfate scale formation.

Results: The inhibition efficiency (IE %) without/with adding 0.1% (w) of SNP for different scale inhibitors in 2% Na2SO4 solution and The effect of different SNP concentrations on inhibition efficiency were presented from Fig. 1.

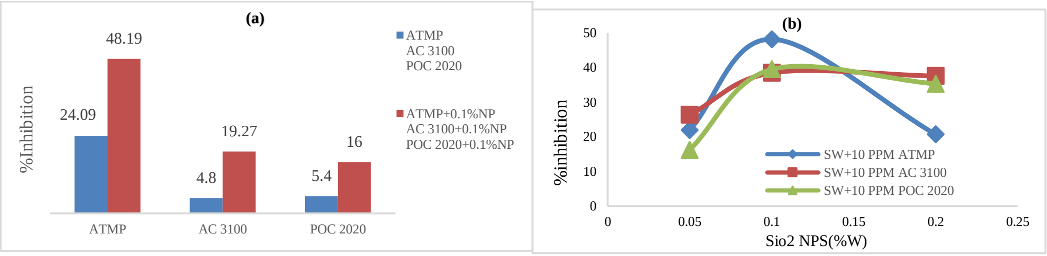

Fig 1. (a) The inhibition efficiency (IE %) without/with adding 0.1% (w) of SNP for different scale inhibitors in 2% Na2SO4 solution and (b) The effect of SNP concentrations on inhibition efficiency.

Conclusion: From the experimental results above, it can be concluded that adding SNPs to water contain calcium sulfate hardness in the presence of scale inhibitors cause to improve the inhibition performance. Using both SNP and inhibitor simultaneously, it was showed that SNPs could improve the effect of scale inhibitors significantly more than before that each of them were used lonely. As shown as Fig. 1(b), the effect of 0.1%w SNP on the type of scale inhibitors was better, and the inhibitory content increased. The maximum inhibition efficiency (up to 90%) was observed for 40 ppm concentration of inhibitors and 0.1%w SNP.

Keywords: Silica nanoparticle, scale inhibitor, calcium sulfate.

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Ir-Mo Alloy as Electrocatalyst for Hydrogen Evolution Reaction

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Background: Electrolysis of water to generate hydrogen is an important issue for the industrial production of green energy[1]. The state-of-the-art electrocatalyst for the hydrogen evolution reaction (HER) is platinum (Pt), but due to high cost and scarcity of Pt, extensive research is devoted for developing cost-effective and efficient non-Pt based electrocatalysts[2]. Herein, we synthesized carbon supported iridium based alloy electrocatalysts. Its electrocatalytic activity of alloy showed that it can be manipulated to achieve a high HER activity surpassing Pt.

Methods: Typically, graphene oxide (GO) was dispersed in deionized (DI) water to obtain a suspension with concentration 9 mg mL^{-1}. Then, $H_3PMo_{12}O_{40}$ (POM) was added to the GO suspension under stirring. The resulting mixture was hydrothermally treated at 180 °C for 12 h. The product was filtered, washed, centrifuged and transferred to DI water. The mixture was homogenized by ultrasonication followed by addition of hydrazine solution as the reducing agent. Finally, $IrCl_3.3H_2O$ was added to suspension and stirred for overnight. The solvent was evaporated and the resulting powder was calcined at 850°C in H_2 atmosphere for 2 h.

Results: Fig. 1(A) shows the XRD spectra of Ir–Mo alloy catalyst deposited on RGO. The diffraction peaks are confirming that the high temperature annealing process resulted in the formation of fcc alloy of Ir-Mo and Ir particles with an average particle size of 12 nm. The electrocatalytic activity of Ir−Mo/RGO for HER was investigated by recording linear scan voltammograms (LSVs) in H_2SO_4 solution. As can be seen in Fig. 1(B), the Pt/C and Ir-Mo alloy after thermal treatment with same loading displayed excellent electrocatalytic activity for HER.

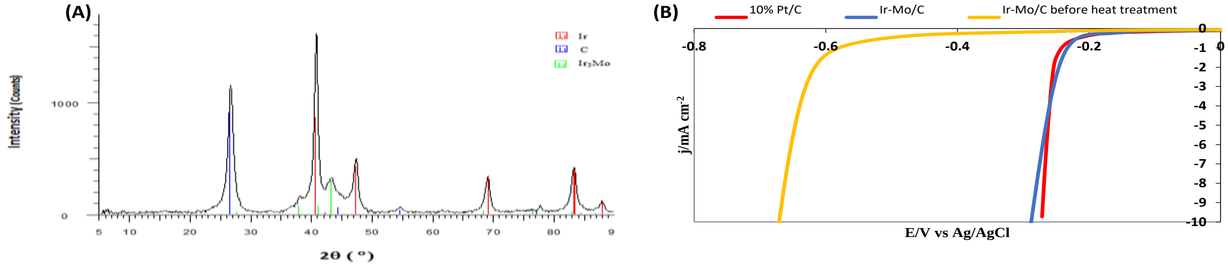

Figure 1. (A) XRD patterns of carbon-supported Ir-Mo alloy and (B) Hydrogen evolution polarization curves of 10% Pt/C and Ir-Mo/C alloy before, after heat treatment in 0.5 M H_2SO_4, at scan rate of 5 mV s^{-1}.

Conclusion: An efficient electrocatalyst, consisting of Ir_3Mo alloy nanoparticles on RGO support, was prepared by simple method. The electrocatalyst displayed excellent HER activity in acidic media, including low overpotential at current density of -10 mA cm^{-2}.

Keywords: Iridium; Polyoxometalate; Alloy; Electrocatalyst; Hydrogen Evolution Reaction.

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Synthesis and study photocatalytic activity of GO/$CuFe_2O_4$/CdS nanocomposite for the degradation of dinoseb and imidacloprid pesticides

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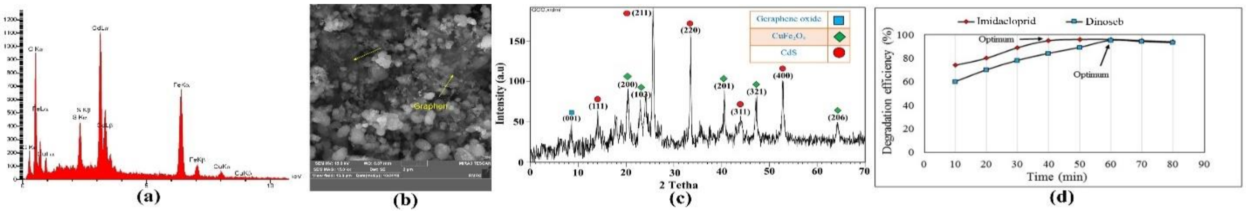
Background: Pesticides play an important role in the agricultural industry due to their efficient advantages. Poisoning with pesticides due to long-term ingestion of their remains in vegetables and fruits can cause nausea, headache, coma and even death [1]. One of the most common types of nitrogenous pesticides is dinoseb and imidacloprid. Exposure to pesticides leads to headache, muscle twitching, convulsions and human birth defects, and has an effect on the male reproductive system. Therefore, elimination of these materials is of particular importance. One of the efficient methods for the degradation of pesticides is advanced oxidation process. Recently, GO-based semiconductor photocatalysts have attracted attention due to their electron conductivity, high specific surface area and good adsorption [2].

Methods: CdS and $CuFe_2O_4$ nanostructures synthesis by their primary materials and graphene oxide synthesis by *modified Hummer's method. Certain weights of* GO, $CuFe_2O_4$ and CdS nanostructures *were refluxed for 24 h to prepare GO/*$CuFe_2O_4$/CdS nanocomposite. This nanocomposite was characterized by FTIR, XRD, FESEM-EDX and TGA. Then, with the UV-Vis spectrophotometer by measuring the wavelength absorbed, evaluated the efficiency of the *GO/*$CuFe_2O_4$/CdS photocatalyst for degradation of dinoseb and imidacloprid pesticides under visible light irradiation. At the end, we also optimized the experimental parameters and the accuracy of the process was investigated.

Results: The photocatalytic degradation of dinoseb and imidacloprid pesticides by using GO/$CuFe_2O_4$/CdS photocatalyst was substantially related on contact time, initial concentration of pesticide, solution pH and amount of the catalyst. Different photocatalysts are prepared under various experimental conditions to degrade pesticides, and they displayed a varied rate constant of degradation. The photocatalyst is easily separated from the mixture with a magnet and re-dispersed for reuse. Finally, the kinetics of the photocatalytic degradation process was investigated.



a) EDS, b) FESEM, c) XRD of the nanocomposite and d) effect of irradiation time

Conclusion: In summary, characterization methods showed that the photocatalysts was properly synthesized. This photocatalysts displayed a good photocatalytic activity, which was achieving 96% of dinoseb and 95% of imidacloprid degradation after 60 min and 40 min by measuring the UV-Vis maximum absorbance, respectively. The kinetics of the process was showed that both of the degradation processes followed the first-order-pseudo kinetic model.

Keywords: Photocatalyst, Magnetic nanocomposite, Pesticide, Dinoseb, Imidacloprid

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Production of a New Optical Sensing Phase for Determination of Gluten

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Background: Gluten is one of the most complex proteins in the wheat family. And it contains 50 different proteins with complex polymorphism [1]. The importance of gluten measurement in the food industry is due to the development of celiac disease [2]. Hence, we have designed a fast, precise, and low-cost nanosenser for determination of gluten by using gold nanoparticles dispersed in shell of functionalized silica nanoparticles.

Methods: The gold nanoparticles dispersed in shell of functionalized silica nanoparticles by using sonochemical method. Then this nanocomposites immobilized on triacetyl cellulose membrane and used for determination of gluten, extracted in lab.

Results: UV-Vis spectrum (Fig. 1a), and SEM image (Fig. 1b), and red color of nanocomposites synthesized (Fig. 1c) was approved the successful synthesis of gold nanocomposites. Fig. 1d, illustrated the nanosensor spectrum, before (1) and after (2) reaction with gluten. This nano sensing phase has a linear range in 22.02–57.26 mg.ml^{-1} for gluten with a limit of detection 4.4 mg.ml^{-1} at wavelength of 530 nm. The response time of nanosensor was 1 min and nano sensing phase has a good performance in neutral pH of gluten solution.

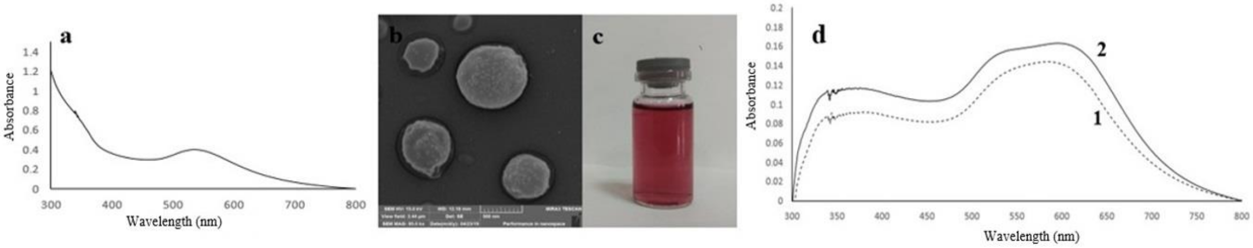

Fig. 1. (a) UV-Vis spectrum (b) SEM image and (c) color of gold nanocomposetes (d) nanosensor befor (1) and after (2) reaction with gluten solution.

Conclusion: A novel, effective, sensitive and precise optical nanosensor based on gold nanocomposites for detection and determination of gluten has been established.

Keywords: Optical nanosensor; gold nanoparticles; triacetyl cellulose.

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Synthesis of Pd supported on mesoporous triazine based carbon as new photocatalyst for degradation of Rhodamine B dye

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Background: Mesoporous carbon- based materials have been widely applied in the photocatalytic degradation of dye due to their unique properties such as high specific surface area and tunable pore size. In a photodegradation process, to improve light absorption, doping of the photocatalyst with metals such as Ag, Au, Pd is required [1]. Therefore, this paper reports Pd supported on mesoporous triazine based carbon (Pd@MTC) as a new carbon-based photocatalyst with a specific structure for Rhodamine B (RB) degradation under UV light.

Methods: The Pd@MTC was synthesized according to our previous literature by applying the pyrolysis process [2]. The characterization of this photocatalyst were confirmed by various analysis (Fig.1).

Results: The results showed that the synthesized photocatalyst has a good and passable activity for degradation of Rhodamine B under UV light. Optimum conditions achieved for photodegradation include: photocatalyst dosage, 4 mg; RB concentration, 20 mg. L^{-1}; and reaction time for an 90% degradation efficiency, 180 min (the result was shown in Fig 1 a).

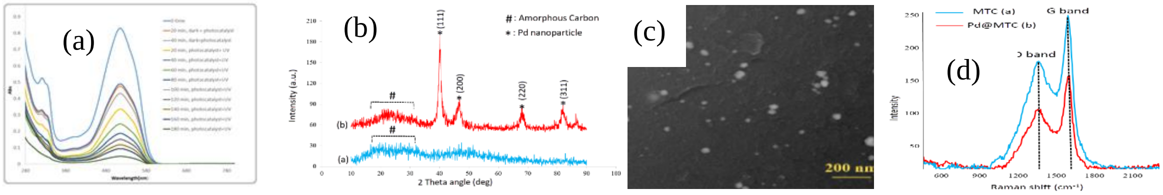

Fig. 1. UV-VIS spectra change (a), XRD (b), FESEM (c) and Raman spectroscopy (d) of Pd@MTC

Conclusion: Pd@MTC was synthesized and applied as a new photocatalyst for the degradation of RB under UV irradiation. According to the result, Pd@MTC, with as little as possible, has been able to exhibit great activity under a UV light source to degradation of dye. In addition, results have shown that palladium metal plays a major role in photocatalytic activity.

Keywords: mesoporous triazine-based carbon; photocatalyst; Rhodamine B; degradation.

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Preparation of mesoporous carbon from cellulose as a green precursor for removal of Methyl orange

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Background: Nowadays, an environmental of dyes pollution became a serious concern, owing to this matter, using of useful technique to remove the dyes is important. One of the most common method is about using the adsorbent [1]. In the present work the mesoporous carbon as a new kind of adsorbent was synthesized and applied for methyl orange (MO) removal.

Methods: Mesoporous carbon was synthesized according to our previous reported literature by cellulose as a green precursor [2]. The removal procedure is as follows: A certain amount of adsorbent was added to 50 mL of methyl orange (MO) solution with pH =7 and after a certain time (min) with different initial dye concentrations (20-200 mg L^{-1}), the absorption spectra of MO were measured by UV-Vis spectrophotometer and finally the recoveries were calculated according to the following equation. ($q_e = (C_0 - C_e)V/W$), Where C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}), q_e is the amount of dye adsorbed on the adsorbent (mg g^{-1}) at equilibrium, V is the volume of the MO.

Results: The characterizations of this synthesized adsorbent were investigated by various analysis (Fig.1(a-c)). The results confirm well synthesized adsorbent. Also, the result of test at room temperature for condition of 20 mg of adsorbent, pH=7, concentration of dye 20 mgL^{-1} was shown in Fig. 1d. According to this Fig., after 15 min, the MO absorption spectrum decrease rapidly and recovery reaches 100%.

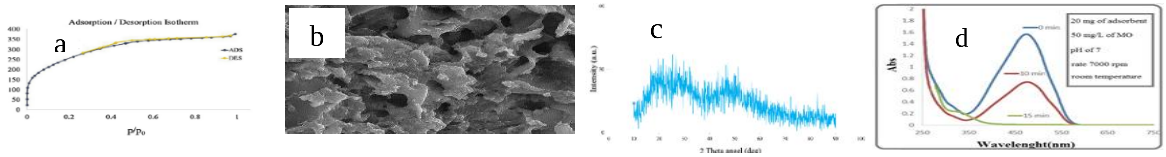

Fig. 1. **N_2 sorption isotherm (a), FESEM (b), XRD (c) and UV-VIS absorption spectra (d) of mesoporous carbon**

Conclusion: In this work parameters of pH, concentration of dye, dosage of adsorbent, temperature and stirrer speed, and also adsorption isotherms study were investigated. In general, it can say that special design of synthesized adsorbent with high surface area and high cavities has resulted the absorption process being carried out in the shortest possible time and with a minimum amount of adsorbent.

Keywords: mesoporous carbon; removal; methyl orange; adsorbent.

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Investigating the Kinetic Mechanism of 2-nitrophenol Photo-degradation with ZnO Nano-photo-catalyst: Multivariate hard modelling approach

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Background: 2-nitrophenol is one of known poisonous compound in drinking water which is highly stable and low biodegradable and remains long in environment [1]. Hence, it is of great importance to find an efficient and economic treatment analysis method for removing this component from aqueous media. In this study, advanced oxidation process based on photo-catalyst was used for degradation of 2-NP.

Methods: ZnO nano-catalyst were synthesized based on the sol–gel method reported in [2]. The starting materials for synthesizing nano-particles were zinc acetate and oxalic acid dehydrate.

Photo-degradation of 2-NP was carried out by the visible light source of 400 W krypton lamp at two acidic and basic condition. At each pH, 100 mL of 2-NP (25 ppm) was transferred to a Pyrex glass vessel and 3mg of ZnO was added to the solution, then the mixture was stirred throughout the reaction. A water jacket connected to a circulating cooling water bath was wrapped around the photo-reactor to maintain the temperature at 320 C throughout the experiment. Three-milliliter samples were taken every 30 min up to the reaction time until no significant changes observed in the signals.

Results: Time-spectral data at each pH was analyzed by multivariate hard modelling method based on consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. Apart from obtaining kinetic parameters, pure spectral profiles of all species were resolved by hard modelling approach. Computed Kinetic rate constants (k_1 and k_2) were 0.06 and 0.013; 0.0503 and 0.0077 for acidic and basic pH, respectively.

Conclusion: Present study illustrates the first report on spectrophotometric monitoring of 2-NP degradation and resolving the data based on a consecutive reaction. It should be mentioned that some previous reports monitored this process at one wavelength and then postulated one step first order kinetic reaction for degradation mechanism of 2-NP while this photo-decomposition obeys a two-step consecutive reaction.

Keywords: ZnO nano-catalyst, 2- Nitrophenol, Degradation, Hard modelling method

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Magnetic solid-phase extraction of mercury(II) ion using a magnetite@carbon/dithizone nano-composite prior to its determination by anodic stripping voltammetry

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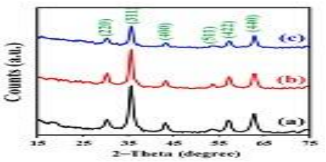
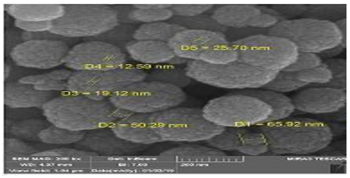
Background: Mercury is a bioaccumulative and highly toxic heavy metal that causes serious humanhealth problems even at low concentrations [1]. Various instrumental techniques have been developed for the determination of the Hg^{2+}. Among these techniques, anodic stripping voltammetry (ASV) have attracted many attentions because of a number of advantages such as low instrumentation cost, high sensitivity, high speed, simultaneous analysis of mixtures, and high selectivity [2]. In general, due to the presence of mercury in environmental samples at low levels, its separation from sample matrix and use of a pre-concentration step is necessary. Therefore, in this research, a magnetic solid-phase extraction (MSPE) method was used for pre-concentration and separation of mercury(II) prior to determination by ASV.

Methods: The adsorbent based on magnetite@carbon/dithizone nanocomposite (Fe_3O_4@C/Dz NC) was synthesized and characterized using energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction (Fig. 1; (a) Fe_3O_4, (b) Fe_3O_4@C NC, and (c) Fe_3O_4@C/Dz NC), and field emission scanning electron microscopy (Fig. 2). For the electrochemical analysis, a 746 VA Trace Analyzer and a system consisting of a glassy carbon electrode as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as a reference electrode were used.

Results: The calibration graph was extended from 0.25 to 30 ng mL^{-1} (Fig. 3), and the detection limit was 27 pg mL^{-1} under the optimized conditions. The pre-concentration factor and intra-day and interday relative standard deviations were 100, 3.8, and 4.5%, respectively and relative recovery values were obtained between 95.3 and 104.4% for the spiked water samples.





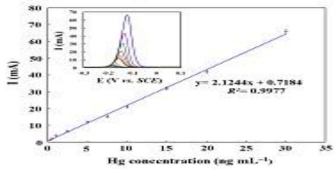


Fig.1. XRD patterns of the prepared nano-materials Fig. 2. FESEM Fig.3. ASV and calibration curve for determination of Hg(II) ion ge

Conclusion: In this research, incorporation of the developed MSPE system with the sensitive ASV technique was used for pre-concentration and sensitive, selective and precise mercury measurement. The results indicate that the presented MSPE-ASV has high efficiency for measurement of mercury(II) ion in water and wastewater samples.

Keywords: Mercury(II) ion, Magnetite@carbon/dithizone nano-composite, Magnetic solid-phase extraction, Anodic stripping voltammetry

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Removal of Methyl Orange from aqueous solution using $La_{0.7}Ba_{0.3}MnO_3$ nanoparticles

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Background: In this work, barium doped lanthanum manganite (*LBMO*) nanostructure was synthesized via hydrothermal method. Using TGA spectra, suitable calcination temperature selected and single phase material was prepared. Properties of materials were characterized by XRD, FT-IR and FESEM. The aqueous Methyl Orange (MO) dye solution was considered as a model of wastewater to study the removal ability of prepared sample via adsorption method.

Methods: The $La_{0.7}Ba_{0.3}MnO_3$ nanoparticles were synthesized using the hydrothermal method which is described in our previous work [1]. The physical removal of aqueous MO solution (10 ppm & pH=2.5) by prepared LBMO nanostructures as adsorbent (0.3 g/L) was carried out in a 50 mL beaker under magnetic stirring [2].

Result: XRD pattern of samples $La_{0.7}Ba_{0.3}MnO_3$ nanoparticles indicated that the sample match with the standard JCPD card number with no extra peak. The results showed that the adsorption process reached a balance point after 30 minutes. The efficiency of the removal of methyl orange at a dye concentration of 10 ppm reached about 97%.

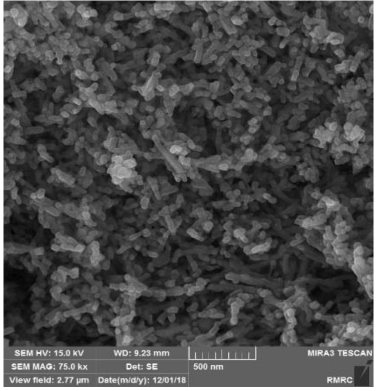

Fig.1. FESEM image of $La_{0.7}Ba_{0.3}MnO_3$

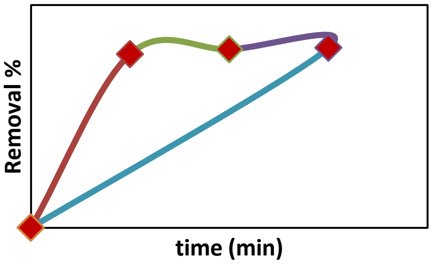

Fig.2. Removal percent of methyl orange in the presence of $La_{0.7}Ba_{0.3}MnO_3$

Conclusion: This research introduced a method for synthesis of visible light photocatalytic material, namely $La_{0.7}Ba_{0.3}MnO_3$, by hydrothermal method. The absorbent performance of removing dyes from the aqueous medium has shown that it can be used as an effective and inexpensive absorbent in the process of treating a variety of colored sewage element.

Keywords: Lanthanum Magnetite ($La_{0.7}Ba_{0.3}MnO_3$), Nanostructure, Methyl Orange, Adsorption.

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Evaluation of Antimicrobial Activity of Silver Nanoparticles Biosynthesized Using Estahban Fig Leaves (*Ficus carica L.*)

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Background: Synthesis of nanosized particles with antimicrobial property is of significance in therapeutic applications [1].The present study reports a rapid method for the biosynthesis of AgNPs and their antibacterial activity. This procedure applied Estahban fig leaves (Ficus carica L. cv. sabz) extract as a reducing and capping agent for the biosynthesis of AgNPs.

Methods: Fig leaves were used to make the aqueous extract. For the synthesis of AgNPs, desired amount of the obtained extract was added into aqueous solution of silver nitrate.The impact of various parameters such as the amount of the extract, the reaction temperature and time were evaluated.We evaluated the antimicrobial activity of AgNPs using agar well diffusion method.

Results: It is well known that silver nanoparticles exhibit a yellowish brown color in aqueous solution due to excitation of surface plasmon vibrations of silver nanoparticles. The absorption spectra of AgNPs solution showed a surface plasmon absorption band with a maximum of 410-430 nm, indicating the presence of AgNPs (Fig 1.a). Also the antimicrobial activity of AgNPs against Escherichia coli were evaluated at different condition of synthesis. The results showed very good antibacterial activity. (Fig 1.b)

Fig 1. UV- Vis spectra of AgNPs and antibacterial activity of AgNPs against Escherichia coli

Conclusion: In this study, a biocompatible, fast and cost effective method for the biosynthesis of AgNPs was presented. The survey on antimicrobial activity revealed very good inhibitory effect of AgNPs against Escherichia coli.

Keywords: Estahban fig leaves; silver nanoparticles; Green synthesis; Antimicrobial; Extraction

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Phyto-assisted Synthesis, Characterization and Applications of Silver Nanoparticles Using Saffron (*Crocus sativus* L) Flower Waste

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Mojtaba Abdi Talebbeygi [a]

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Background: Development of green and reliable processes for the synthesis of metallic nanoparticles is inevitable. An increase in the area of synthesis of nanomaterials employing plants/plant parts have observed [1]. Considering the antioxidant properties of aqueous extract of saffron flower waste, we have made an attempt to apply Estahban saffron flower waste as reducing and stabilizing agent for the low cost and rapid biosynthesis of AgNPs. We studied the antimicrobial activity of AgNPs.

Methods: Saffron flower were used to make the aqueous extract. For the synthesis of AgNPs,The impact of various parameters such as Concentration of $AgNO_3$, the amount of the extract, the reaction temperature and time were evaluated.

Results: The observation of the change in the color of the solution and The appearance of brown color in solution confirmed the AgNPs formation .The UV-Vis spectrum of synthesized AgNPs displays a broad peak in 450 nm. Appearance of this peak, is assigned to a surface plasmon of AgNPs (Fig 1.a) .The biosynthesized AgNPs were tested against Escherichia coli and Staphylococcus Aureus for antibacterial activity using agar well diffusion method (Fig 1.b).

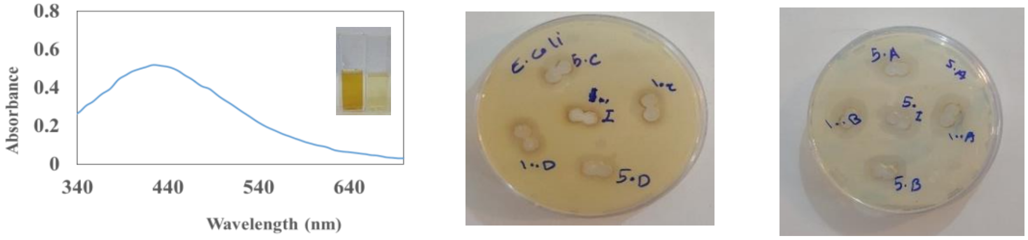

Fig 1. UV- Vis spectra of AgNPs and antibacterial activity of AgNPs against E. coli and

Conclusion: Here, ecofriendly AgNPs were generated using a one step, fast and cost effective process by the aqueous saffron flower waste extract. The results were demonstrated very good bactericidal properties of these nanoparticles to Staphylococcus Aureus and Escherichia coli.

Keywords: Saffron flower; silver nanoparticles; biosynthesis; Antimicrobial; extraction

References

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Functionalized MCM-41 as carriers for release of amlodipine besylate

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Background: There are various methods for loading of drug such as simple mixing, solvent evaporation, vacuum process, loading under high pressure, and layer- by- layer adsorption. Following of loading, the vital question is the releasing of that drug from mesoporous material, for this proposes, it is important to comprehend the mechanism of drug releasing. The classification of drug release can be occurred through four successive steps: the imbibition of release medium, drug dissolution, drug diffusion and convective transport [1]. The drug release process can be controlled by these stages.

Methods: MCM-41 was synthesized and functionalized via grafting by carboxylic acid group to obtain MCM-41@CA. The dissolution technique was performed for release of amlodipine besylate.

Results: The kinetics models of zero order, first order and Hixson–Crowell model were studied using MCM-41 and MCM-41@CA in different pH of 2, 4.5 and 6.8. On the basis of the results it can be deduced that the of release is fairly dominated by diffusion process. To approve diffusion mechanism, the data were fitted into the Korsemeyer-Peppas equation [2].

Conclusion: Results showed that the amount of releasing is exponentially increased with the time. The release process is dependent to the loading efficiency of the drug on the nanoparticles materials. The releasing is high for both carriers in acidic condition (pH = 2). Study of kinetics models revealed that the Hixon-Crowell and first order models are more consistence for the releasing mechanism.

Keywords: Functionalized mesoporous, Amlodipine besylate, Drug releasing, Statistical models

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Fabrication of graphene/ $NiCo_2O_4$ nanocomposite and its supercapacitive study in alkaline medium

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Background: The widening demand for efficient, sustainable energy sources has snowballed active research in the development of novel electrode materials for progressive energy storage devices like batteries and electrochemical capacitors [1]. Generally, supercapacitors (SC) represent a most promising approach for next generation energy storage device due to their higher power and energy densities than batteries and conventional dielectric capacitors. Electrode materials play a crucial role in the development of high-performance supercapacitor in terms of morphology, size and porosity [2].

Methods: In typical experimental procedure, a solution was first prepared by dissolving appropriate stoichiometric amounts of Ni $(NO_3)_2$, Co $(NO_3)_2$ and urea into 50 ml of deionized water. After stirring, the mixture was transferred into an autoclave. The autoclave was sealed and kept in an oven at 150^o C for 6 h. The thus-prepared $NiCo_2O_4$ was dried at 300^o C for 3 h in air after separation and filtration. A conventional three-electrode cell with an Ag/AgCl (in saturated KCl) reference electrode and a Pt wire as counter electrode, were employed for the electrochemical experiments conducted by an Autolab potentiostat/galvanostat instrument (PGSTAT 302N, Netherlands).

Results: The structure and morphology of resulting products were characterized with Fourier transform infrared spectroscopy (FT-IR) (Figure 1), field emission scanning electron microscopy (FESEM) (Figure 2) and the electrochemical behavior of the nanocomposite was investigated by cyclic voltammetry (CV) method in different scan rates (Figure 3). The results confirmed the successful synthesis of the materials and suggest its promising potential as efficient electrode material for electrochemical capacitor.

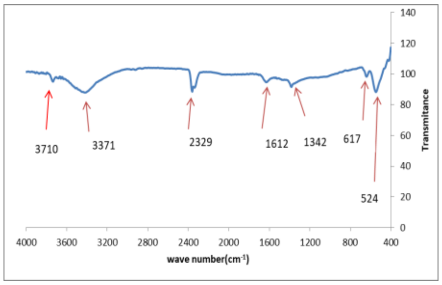

Fig. 1. *FT-IR spectrum of the* $NiCO_2O_4$

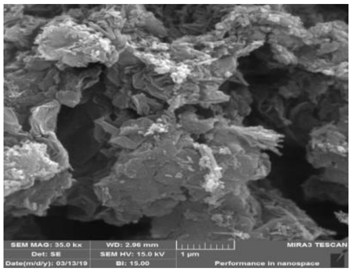

Fig. 2. *FESEM image* $NiCo_2O_4$ */RGO*

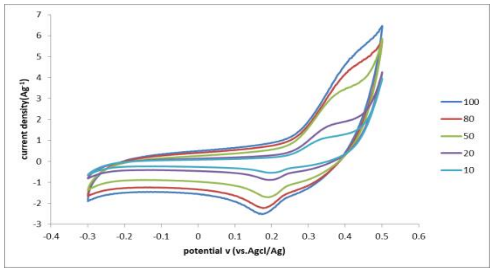

Fig. 3. *Cyclic voltammograms*

Conclusion: The supercapacitive performance of nanocomposite was studied by cyclic voltammetry, indicating good charge propagation within the electrode. The charge storage mechanism of the nanocomposite was investigated and the results indicated the more contribution of electrochemical double layer capacitor (EDLC) mechanism.

Keywords: *Reduced grapheme oxide, Nanocomposite, Hydrothermal, Supercapacitor.*

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Synthesis of Cu_2O- TCN composite and investigation its photocatalytic activities

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Background: The TiO_2 band gap (3.2 eV) and rapid recombination of photogenerated carriers hamper its extensively commercial applications in photocatalysis. Combining TiO_2 with narrow band gap semiconductors has been attested as an attractive approach to improve its visible-light photocatalytic activity [1]. Using of g-C_3N_4 and Cu_2O, with a band gap 2.7 and 2.0 eV, respectively, can improve in visible light response of TiO_2[2]. Herein, we designed and synthesized a Cu_2O- TiO_2@g-C_3N_4 (TCN) composite for improving photoelectrochemical water splitting.

Methods: At first, a certain value of the F127 surfactant was dissolved in H_2SO_4 solution. To this solution was added a mixture of TTIP and AcAc. The resulting mixture were hydrothermally treated. Then the white solid product was separated, washed with water, dried and finally calcined at 550 °C until microspheres of TiO_2 were prepared. To obtain the TCN composite, a value of the TiO_2 microspheres was dispersed in di-cyandiamide solution with stirring. Then the solvent completely evaporated and the sample was calcination at 550 °C in N_2. For preparation of Cu_2O-TCN composite, a solution of copper acetate was added to the solution of TCN composite and stirring for 24 h, then ascorbic acid was added to this solution under N_2 atmosphere and at 60 °C.

Results: Fig. 1 shows SEM images of TiO_2 particles. It can be seen that the particles have a well-defined spherical shape with uniformed surface. Based on the spectroscopy of FTIR in Fig. 2, the formation of a g-C_3N_4 as a layer on TiO_2 microspheres was confirmed. From Fig. 3 it can be noticed that the adsorption intensity of the Cu_2O-TCN composite is clearly stronger than bare TiO_2 through the entire UV and visible light region. As can be seen in the inset of Fig. 4, there is no significant current in the dark, but in the visible light illumination the photocurrents of the Cu_2O-TCN sample increase significantly compare with bare TiO_2 and g-C_3N_4.

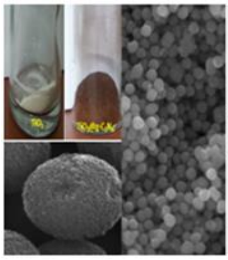

Fig 1. SEM images of TiO_2

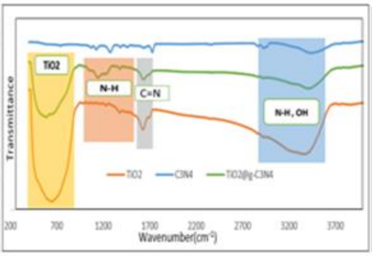

Fig 2. FT-IR spectra of samples

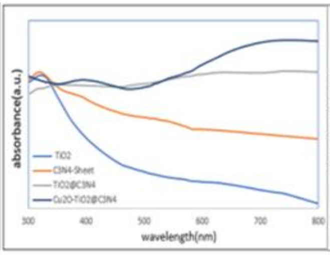

Fig 3. UV–vis spectra of samples

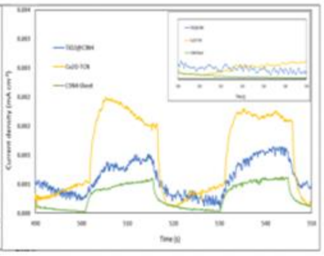

Fig 4. Transient photocurrent density of samples

Conclusion: Spherical TiO_2 microspheres were synthesized via a hydrothermal method. By depositing g-C_3N_4 and Cu_2O on TiO_2 surface, the absorption of TiO_2 is expanded into the visible region. Cu_2O- TCN composite is showing stable and continuous photocatalytic activity under solar irradiation. This study provides a low cost method for hydrogen production using solar energy.

Keywords: Photocatalyst, carbon nitride, spherical titanium dioxide, Cu_2O.

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Preparation of Pt/Py/POM/m-TiO_2/Graphene and investigation its electrocatalytic activity for hydrogen evolution reaction

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Background: The photoelectrochemical water splitting methods are the best method for hydrogen evolution reaction (HER). Decreasing the amount of Pt via increasing its utilization efficiency and replacement of Pt-based catalysts with inexpensive and efficient electrocatalysts or photoelectrocatalysts have been the major concerns during the past decade[1]. In this study, we report the fabrication of a mesoporous photocatalyst based on TiO_2 by using KIT-6/G and then the TiO_2 decorate with Pt nanoparticle by assisting phosphomolybdic acid (POM) as reducing agent. We also investigate the photocatalytic activity of these composite photococatalyst for HER.

Methods: The KIT-6/G was synthesized according to literature [2]. The KIT-6/G template was used for synthesis of mesoporous TiO_2 (m-TiO_2). The KIT-6 in the TiO_2/KIT-6/G composite was removed with NaOH solution. The resulted m-TiO_2/G was functionalized with POM until POM/m-TiO_2/G sample was prepared. Subsequently, pyrrole (Py) monomer was dropped into the suspension for converting the POM to reduced POM. Finally, the Py/POM/m-TiO_2/G composite was decorated with Pt nanoparticles for obtaining of Pt/Py/POM/m-TiO_2/G catalyst.

Results: Fig. 1 (A) and (B) confirm that the KIT-6/G was constructed from KIT-6 and graphene. In Fig. 1 (C), the decreasing of intensity for the (211) reflection, suggesting that the mesopores of template was filled with the guest and anatase and rutile phases of TiO_2 can be detected from XRD pattern. As illustrated the HER activity of Pt/Py/POM/m-TiO_2/G with 4% wt. of Pt increased under dark(D) and illumination (L) conditions than other samples (Fig. 1 (D)).

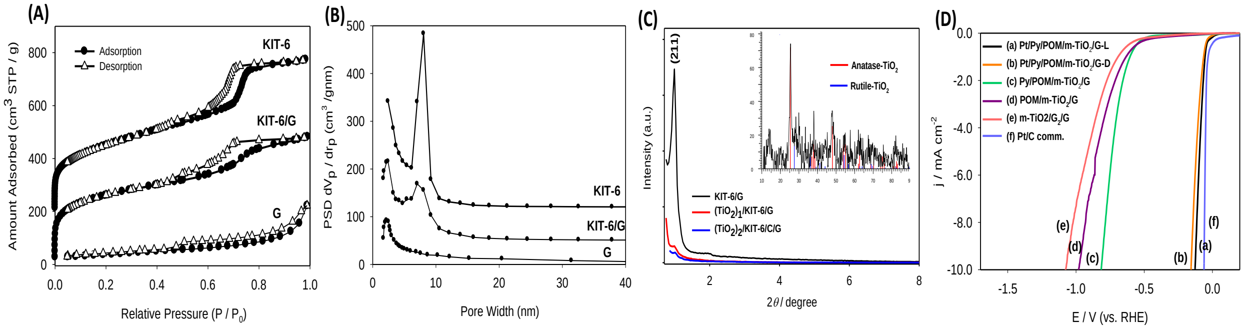

Fig. 1: (A) N_2 adsorption isotherms and (B) pore size distribution of, grapheme (G), KIT-6 and KIT-6/G. (C) Low angle XRD patterns of KIT-6/G and TiO_2/KIT-6/G, inset: XRD pattern of m-TiO_2/G and (D) Typical LSVs of prepared samples in different stages of synthesis procedure in 0.5 M H_2SO_4.

Conclusions: The results clearly demonstrated the effectiveness of a relatively simple route for the preparation of photocatalysts based on m-TiO_2 with well-dispersed Pt nanoparticles by POM.

Keywords: Titanium dioxide, Hydrogen evolution reaction, KIT-6 silica, Graphene, mesoporous

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Spectrophotometric determination of niclosamide and flutamide by graphitic carbon nitride sheets coated by copper nanoparticles

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Background: Niclosamide (NA) belongs to the family of anthelmintic drugs that is especially effective against all the species of tapeworm infections due to its lethal effect on tapeworms upon contact [1]. Flutamide (FLA) is also a synthetic antiandrogenic agent. Flutamide is an unusual example of powerful nonsteroidal androgen antagonist which used in prostate cancer therapy. Due to importance of NA and FLA, sensitive determination of NA and FLA is important.

Methods: A sensitive and simple spectrophotometric method for the determination of niclosamide and flutamide in pure form and their tablets is reported. Hence, graphitic nitride coated with copper nanoparticles (Cu/C_3N_4) was papered and the structural features of this composite was characterized by SEM, EDX-mapping analysis, XRD and FT-IR. Cu/C_3N_4 could catalyze the reduction of NA and FLA (nitroaromatics) to their amine derivatives in the presence of sodium borohydride. Then, the amines were analyzed through a diazotization-azo coupling reaction using N-(1-naphthyl)ethylenediamine in sodium dodecyl sulfate media.

Results: Under optimum conditions, the method showed good linearity in the range of 1-120 μmol L^{-1} and 0.70-120 μmol L^{-1} for NA and FLA, respectively. Also, the limit of detections were found to be 0.64 and 0.33 μmol L^{-1} for NA and FLA, respectively. The Relative standard deviations (RSD) for determination of 20 μmol L^{-1} of NA and FLA were 6.6 and 4.1%, respectively. Some pharmaceutical samples containing NA or FLA were analyzed by the established method and a high performance liquid chromatogravimetric method. The results obtained by the methods were compared by t-test statistical method that showed no significant difference between the results of the two series of the experiments. Applicability of the proposed method on the determination NA and FLA in water samples were also evaluated. Satisfactory results were obtained.

Conclusion: A simple, low cost and rapid niclosamide and flutamide determination method by using a new reducing catalyst has been reported. The proposed method showed its potential application in the analysis of these pharmaceuticals in real samples.

Keywords: Niclosamide, Flutamide, Catalytic Reduction, Determination

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Synthesis, characterisation and application of dithiocarbamate functionalized dendrimer grafted magnetized graphene oxide nano sheets for adsorption of lead

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Background: Dendrimers are an interesting class of macro molecules[1]. Many studies have been done by attaching DTC group for improving their adsorption ability [2-4]. Therefore, coupling of DTC with the polyamidoamine (PAMAM) dendrimers is expected to have enhanced properties in terms of heavy metals adsorption via chemical bonding [5].

Methods: SEM images, EDX spectrum and the corresponding EDS element mapping of DTC-D-MGO was shown in Fig. 1. Also, FT-IR spectrum of GO, D-MGO and DTC-D-MGO in the 400–4000 cm^{-1}, vibrating sample magnetometer, VSM of MGO and DTC-D-MGO and the phase structure of GO, Fe_3O_4 and DTC-D-MGO characterization by XRD shown in Fig. 2.

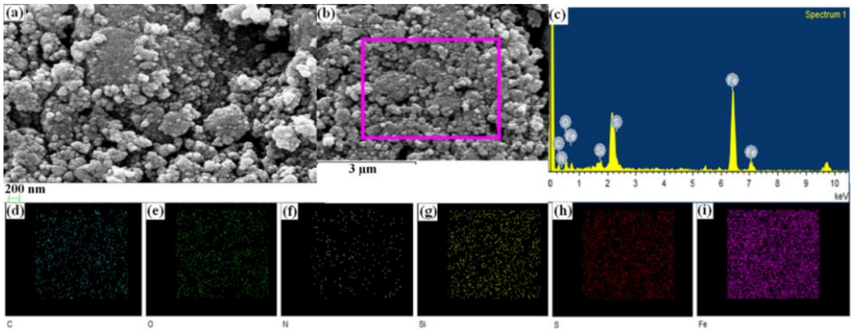

Fig. 1. SEM images at (a) 200 nm and (b) 3µm magnification; (c) EDX spectrum of DTC-D-MGO and the corresponding EDS element mapping of (d) C, (e) O, (f) N, (g) Si, (h) S and (i) Fe.

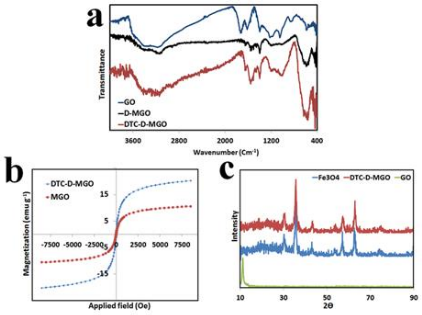

Fig. 2. (a) FT-IR spectrum of GO, D-MGO and DTC-D-MGO, (b) VSM of MGO and DTC-D-MGO and (c) XRD patterns of GO, Fe_3O_4 and DTC-D-MGO.

Results:The results suggest that the Pb(II) adsorption on DTC-D-MGO follow the Langmuir isotherm and pseudo-second-order kinetic models. The maximum amount of Pb(II) that can be adsorbed on the surface of sorbent and obtained from this model is equal to 285.714 mg g^{-1}.

Conclusion: The high density of DTC ligands enclosed within the interior nano cavities makes sorbent especially attractive as high capacity chelating agents for Pb(II) in water. The magnetic separation and easy regeneration made DTC-D-MGO very promising in practical applications.

Keywords: Adsorption, Isotherm, Kinetic, Lead, Dithiocarbamate and Regeneration

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Synthesis and characterization of mesoporous copper oxide and investigation of its catalytic activity for thermal decomposition of ammonium perchlorate

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Background: The development of an efficient catalyst to promote thermal decomposition rate of ammonium perchlorate (AP) is a major challenge for composite solid propellants (CSPs), which have a variety of applications such as gas generators for airbags, propulsion for large space vehicles and tactical missiles [1]. In this regards, mesoporous copper oxide (m-CuO) because of its electrical, catalytic and photonic properties has attracted more attention than other metal oxides [2]. Here, we synthesized m-CuO and its performance for the thermal decomposition of AP was investigated by thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis.

Methods: $Cu(NO_3)_2$ was dissolved in distilled water, and KIT-6 was added by stirring. The solvent was evaporated at 100 °C, and the resulting blue solid was exposed to the vapor of ammonia and dried at 100 °C until the solid turn to purple color. The above process was repeated two times to fill the pores of KIT-6 template completely. The solid product was calcined at 400 °C for 6 h. Finally, the silica template was removed by treating the composite with NaOH solution. The obtained m-CuO was filtered, washed with water and dried. For preparation of m-CuO/AP with 2 wt%, m-CuO particles were added to n-hexane by stirring, then to this solution saturated solution of AP dropwise was added. The mixture was heated for the complete evaporation of the solvents.

Results: The low angle XRD pattern and N_2 adsorption–desorption isotherm for the synthesized KIT-6 in Fig. 1 (A) and (B), respectively, indicating that it is mesoporous with narrow pore size distribution. Fig. 1 (C) and (D) show TG and DSC analysis of AP and m-CuO/AP composite, respectively, which display the catalyst decrease the high temperature decomposition temperature of AP, wherein the decomposition process of AP to volatile products occurs in one regime. Considerable increase in the rate of reaction was observed in the catalyzed system by estimating kinetic parameters for decomposition processes of AP in the presence of the m-CuO.

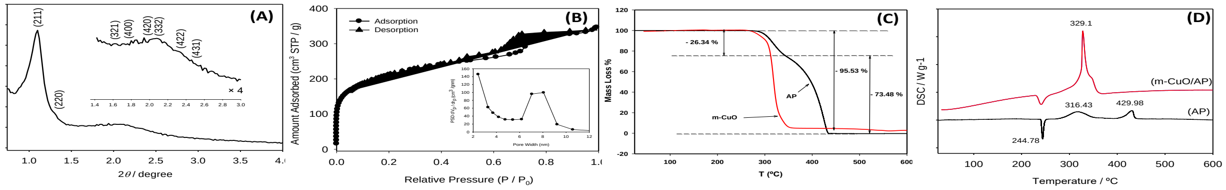

Fig. 1 (A) Low-angle XRD patterns of KIT-6, (B) Nitrogen sorption isotherms and BJH pore-size distribution of KIT-6 (inset plot), and (C) , (D) TGA and DSC diagrams for the thermal decomposition of AP without and with m-CuO.

Conclusion: The m-CuO was synthesized by the hard-templating. The results of characterization techniques confirmed the mesoporosity structure for m-CuO. The TGA and DSC techniques indicated that m-CuO as catalyst has excellent catalytic activity for the decomposition of AP.

Keywords: Ammonium perchlorate, Copper oxide, Catalyst, Thermal decomposition, Mesoporous

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Electrochemical Preparation of Copper nanoparticles

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Background: The development of materials at nanometric scale has been increasing in different fields. The properties of these nanomaterials are critical for the technological revolution worldwide, which mainly depend on the methods of synthesis for the potential applications [1]. Especially, copper nanoparticles are of great interest due to their low cost and easy availability. Copper nanoparticles have drawn the attention of scientists to be used as essential component in the future nano-devices [2]. Herein, we report copper nanoparticles were prepared by electrochemical techniques of cyclic voltammetry and chronoamperometry.

Methods: In this study, the electrochemical setup was a standard three- electrode cell with glassy carbon as a working electrode, platinum wire as a counter electrode and silver-silver chloride as a reference electrode. The experiments were conducted from aqueous solution of 1 mM copper sulfate with 0.1 M ammonium sulfate as supporting electrolytic solution and supplied under a potential range -1.5 to -0.3 V at scan rate 500 mVs^{-1} for 30 minutes. Morphological study of the copper nanoparticles was carried out with scanning electron microscope (SEM) Fig. 1. Diffraction (XRD) was used to determine the size and the shape of copper nanoparticles Fig. 2.

Results: The Cu nanoparticles were successfully synthesized by electrochemical techniques. The sizes of resultant nanoparticles were in the range of 23_45.9 nm. This nanoparticles was used for determination of chlorpromazine.

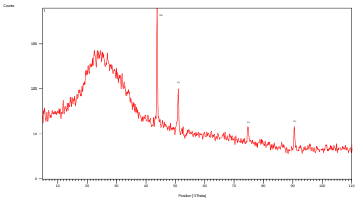

Fig. 1-XRD of Cu nanoparticles

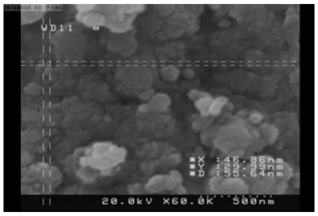

Fig. 2- SEM of Cu nanoparticles

Conclusion: There are various methods for the synthesis of copper nanoparticles. Electrodeposition is a relatively clean, simple, nontoxic, process that can be done at room temperature, environment-friendly, economical and a reliable method for production of novel and interesting morphologies of copper nanoparticles.

Keywords: Copper Nanoparticles; Electrochemical; Cyclic Voltammetric; Chronoamperometry.

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Synthesis, Characterization and Photocatalytic properties of Zeolitic Imidazolate Framework-11

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Background: Organic dyes are chemically stable and not very biodegradable in water, which makes them potentially harmful to the eco- environment. Therefore, an effective and economical technique needs to be developed to reduce the concentration of organic pollutants [1]. Metal-organic frameworks (MOFs), a new class of functional inorganic-organic hybrid materials have been developing rapidly [2]. Zeolitic Imidazolate Frameworks (ZIFs) represent a subclass of MOFs, which are described best as crystalline porous three-dimensional coordination polymers. One of the most promising examples is ZIF-11, which consists of Zn^{2+}-cations connected by benzimidazolate linkers [3]. Despite the large potential of ZIF-11, only few studies have been conducted for this unique yet efficient MOF in which none is about the potential of its photocatalytic activity. In this research Study the synthesis of ZIF-11 and its application in photodegradation process of an organic pollutant is discussed.

Methods: ZIF-11 was successfully synthesized according to the work done by He, et al. 2013[4]. The photocatalytic application of ZIF-11 is illustrated through its possibility to degrade MB in a 300 ml photocatalytic reactor under four 16 watt UV lamps. The resulting photocatalyst is also characterized by XRD, DRS and UV-visible spectra patterns.

Results: The DRS test reveals that this specific powder; ZIF-11 is active under UVC region. Thus, ZIF-11 can be considered as potential photocatalyst to degrade organic pollutants under UV light. The photocatalytic degradation of MB was carried out to evaluate the efficiency of ZIF-11 photocatalyst. The UV visible spectrum indicates that the MB degradation after 20 minutes under four UV visible lights in an alkaline media (pH was set to 12) is 13 percent.

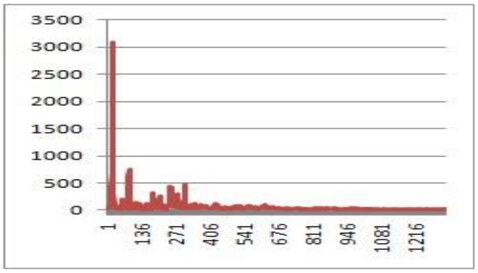

Figure 1. XRD pattern of ZIF-11

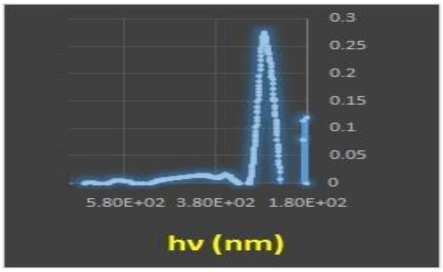

Figure 2. DRS pattern of ZIF-11

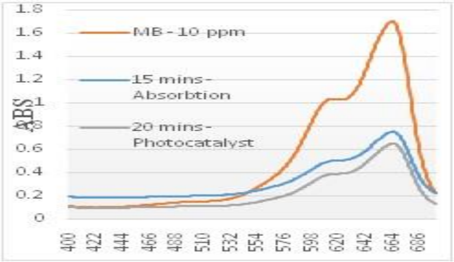

Figure3. UV-visible Adsorption Spectrum

Conclusion: ZIF-11 can be considered as an efficient photocatalyst for degradation of methylene blue under UV light irradiation, which was confirmed by the results of UV visible spectra. It also showed both high adsorption capacity and good degradation efficiency for MB in strong alkaline environment. In all, ZIF-11 can be suggested as potential photocatalyst to degrade organic pollutants.

Keywords: MOF, ZIF-11, photocatalyst, Methylene Blue,

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