Nano-hydroxyapatite/β-CD/chitosan nanocomposite for potential applications in bone tissue engineering

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ABSTRACT

Herein, we report the synthesis of a novel tri-component nanocomposite system incorporating β-cyclodextrin (β-CD) with nano-hydroxyapatite (n-HA) and chitosan (CS). (n-HA/β-CD/CS) at three different temperatures via co-precipitation method. The chemical interactions and surface morphology have been evaluated by TEM, SEM and AFM techniques revealing the agglomerated nanoparticles in CS/β-CD-n-HA binary system whereas the ternary systems produced needle-shaped nanocomposites dispersed homogeneously at low temperature with more porous and rougher surface. The addition of β-CD in CS/n-HA at low temperature decreased the particle size and raised the thermal stability as compared to CS/n-HA. The comparative hemolytic, protein adsorption and platelet adhesion studies confirmed the better hemocompatibility of n-HA/β-CD/CS (RT, HT, LT) nanocomposites relative to CS/n-HA. The cell viability has been evaluated in vitro using MC-3T3 cell line which revealed superior cell toxicity of n-HA/β-CD/CS-LT nanocomposite in comparison to n-HA/β-CD/CS (RT, HT) and CS/n-HA nanocomposites. Thus it may be concluded that the orchestrated organic/inorganic n-HA/β-CD/CS (RT, HT, LT) nanocomposites exhibited relatively higher cell viability of human osteoblast cells, stimulated greater osteogenesis, controlled biodegradation, enhanced antibacterial activity with excellent in-vivo biomimetic and remarkable mechanical parameters as compared to CS/n-HA nanocomposite and thus may provide remarkable cellular potential use as an alternative biomaterial for bone tissue engineering applications.

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1. Introduction

Bone is a highly vascular, organized and dynamic tissue which assembles from nano- to macroscopic building complex structure having interconnected porous network wondrous for its union of regenerative ability and mechanical properties and hence a masterpiece of nature. Bone repair is a prevalent clinical issue with over 2.2 million bone transplantation procedures performed annually worldwide in different fields including dentistry, orthopedics and neurosurgery. Although autografts play better role in terms of biocompatibility and other aspects, they require second surgery to procure donor bone from the patient’s own body. Alternatively, allografts are the attractive option because of their high availability but inherited by the risk of infections and immune responses, which may even intricate other health problems. Therefore, the design and development of ideal biomaterial scaffolds (e.g., ceramics, polymers, metals, and organic bone substitutes) have adequate mechanical properties, biocompatibility, controlled bioreabsorbability, non-toxicity, cost effectiveness and bioactivity, has emerged an area of active research producing synthetic bone substitutes in the field of bone tissue engineering [1,2]. The nanomaterials and nanocomposites enhance protein adsorption, cell adhesion, proliferation, and differentiation compared to conventional materials. The inorganic-organic polymer nanocomposite materials are progressively important because of their exceptional features arising out of synergism between the properties of the components involved. Chitosan being the only cationic polysaccharide in nature composed of N-acetylglucosamine (GlcNAC) and glucosamine (GlcN) residues, has earned marked interest in orthopedic and other biomedical applications [3]. A number of studies have been executed on the diverse chitosan-based implants concluding that chitosan could affect all stages of wound repair in experimental animal models. The biological and mechanical properties of chitosan for bone replacement can be improved by combining it with calcium phosphates [4]. Researches have captivated interests on key bone mineral and the most ubiquitous calcium phosphate, hydroxyapatite (HA) [Ca_{10}(PO_{4})_{6}(OH)_{2}] and its composites for bone repair materials due to its good bone-bonding properties and osteo-

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In vivo cytotoxicity, molecular docking and study of yeast alcohol dehydrogenase on polycarboazole-titanium dioxide nanocomposite

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1. Introduction

The conducting polymers like polyaniline (PANI), polycarboazole (PCz), polypyrrole (PPy), and polythiophene (PTh) are widely used in a variety of applications including the development of next-generation energy storage devices, biosensors, drug-delivery vehicles, fabrication of digital nonvolatile memory device etc. [1–10]. Interestingly, polycarboazole (PCz) has been extensively used in enzymatic immobilization applications due to their low cost, easy synthesis and very good biocompatibility [11,12]. Polycarboazole (PCz) is also very popular in electrical conductivity applications because of its excellent conductivity, high thermal stability, deep highest occupied molecular orbit (HOMO) energy levels, and elevated hole mobility [13–15]. The pristine polymers have not been exploited to their full potentials in biotechnology and biomedical applications due to their inefficient thermal and mechanical stabilities. This has prompted the scientists to produce a wide variety of conducting polymer composites and their blends. Polymer composite materials have replaced pristine polymers due to their enhanced thermal stabilities and mechanical properties. These evolutionary properties of composite polymers have been induced due to synergistic interactions between inorganic materials and polymers and endow the polymer composites with strength, stiffness yet excellent conductivity [16]. Furthermore, titanium-based nanomaterials have even improved enzymatic immobilization and stability because of their extensive surface area, small size, superb thermal and mechanical properties. Owing to the useful properties of titanium-based nanomaterials and PCz, the nanocomposites of titanium-based nanomaterials with PCz expect to further enhance stability of immobilized enzyme [17].

Alcohol dehydrogenases (ADH) are the dehydrogenase enzymes involved in alcohol metabolism that facilitate the alcohol

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Pharmacophore hybrid approach of new modulated bis-diimine Cu\textsuperscript{II}/Zn\textsuperscript{II} complexes based on 5-chloro Isatin Schiff base derivatives: Synthesis, spectral studies and comparative biological assessment

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ABSTRACT

Novel bioactive 5-chloro isatihar based Schiff base ligands, (N,N’-ethylene-N,N’-bis(3-chloroindoline-2,3-diyldiene)bis(5-nitrobenzo[d]isothiole-2-amine), L\textsuperscript{1} and (N,N’-ethylene-N,N’-bis(3-chloroindoline-2,3-diyldiene)bis(5-nitroisothiole-2-amine), L\textsuperscript{2} derived from 2-amino-5-nitrobenzenethiol and 2-amino-5-nitrothiophene and their metal complexes, Cu\textsuperscript{II}(L\textsuperscript{1}), Cu\textsuperscript{II}(L\textsuperscript{2})\textsubscript{2} (1,2), Zn\textsuperscript{II}(L\textsuperscript{1})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}Cl\textsubscript{2} \textsubscript{2} (2), Cu\textsuperscript{II}L\textsuperscript{2}(O\textsubscript{2})\textsubscript{3} \textsubscript{2} (3) and Zn\textsuperscript{II}L\textsuperscript{2}(H\textsubscript{2}O)\textsubscript{2}Cl\textsubscript{2} \textsubscript{4} (4) have been synthesized. The composition, stoichiometry and geometry of the proposed ligands and their complexes have been investigated by the results of elemental analyses and spectroscopic data (FTIR, \textsuperscript{1}H NMR and \textsuperscript{13}C NMR, Mass and EPR). The molar conductivities values of the metal complexes revealed their ionic nature. The thermal stability of metal complexes was demonstrated by TGA/DTA studies while the crystalline nature of the complexes has been ascertained by XRD. Furthermore, a comparative account of in vitro antibacterial study against different bacterial strains with respect to standard antibacterial and scavenging activity against standard control at different concentrations unaided pronounced antibacterial and radical scavenging potencies of the metal complexes as compared to free ligands. In addition, in vitro cytotoxicity of ligands and its metal complexes was also screened on MCF7 (Human breast adenocarcinoma), Hela (Human cervical carcinoma) and HepG2 (Human Hepatocellular carcinoma) cell lines and normal cells (PBMC). The antiproliferative outcomes revealed that metal complexes exhibit superior activity in general as compared to free ligands (L\textsuperscript{1} and L\textsuperscript{2}) where metal complexes (1 and 2) of 5-chloro isatin linked benzothiazole moiety (L\textsuperscript{1}) are found to have better prospect of acting as chemotherapeutic agents which can be explained in terms of greater biopotency, planarity and conjugation against all the tested cancer cell lines with IC\textsubscript{50} \textsubscript{2} 2.80 \mu M.

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1. Introduction

Schiff bases evoked as an interesting class of compounds in the field of coordination chemistry [1] and occupied a position of privileged ligands in view of their ease synthetic approaches through condensation of aldehydes or ketones with amines and their ability to stabilize different metals in various oxidation states of metals [2]. The facile synthesis, wide applications and accessibility of diverse structural modifications of the metal complexes of Schiff bases reflected great significance and interests especially in the field of inorganic and bioinorganic chemistry and have emerged as very promising materials for their use as efficient catalysts, biological sensors, antibacterial, antifungal, antiviral, herbicidal and also as anticancer agents [3]. It has been reported that the Schiff bases proved to be bacteriostatic and carcinostatic upon chelation with metal ion [4].

Cancer being a class of multigenic disease undergoing diversity of genetic and epigenetic alterations and become a leading cause of death worldwide [5]. There has been tremendous search for metal complexes as anticancer drugs which have been used at the forefront of pharmaceutical and genomic research [6]. In view of the fact that metal drugs used in chemotherapy are extremely toxic and usually lead to severe side effects due to the generation of free radicals and reactive oxidant species (ROS) [7,8]. Recently, it has been proved that many antioxidants when used concomitantly in cancer chemotherapy reduce these side effects [9,10]. Therefore, the design and synthesis of drugs possessing both antioxidant and anticancer activities have been preferred in order to scavenge ROS and free radicals as to circumvent the side effects during chemotherapy [11]. Over the last decade there has been increased interest in the development of new non-platinum based metallo-chemotherapeutics to meet the need of treating a
Molecular hybridization approach of bio-potent CuII/ZnII complexes derived from N, O donor bidentate imine scaffolds: Synthesis, spectral, human serum albumin binding, antioxidant and antibacterial studies

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1. Introduction

The alchemy of complexes provides massive prospects for the designing of bioactive scaffolds due to the variety of different accessible metals which have capability to modify the structural reactivity of the complexes by their ligand sphere [1,2]. The transition metal complexes containing Schiff base scaffolds have gained momentous attention among inorganic chemists over the years as Schiff base chromophore acquires substantial absorption of ligands which afford extensive contributions to their coordination ability with various kinds of ligands in view of their structural variability, stability and biocompatibility [3–5]. It is well known that chelation effect enhances the mode of action of drug and efficiency of a therapeutic agent in metal complexes [6]. The therapeutical efficiency of complexes also depends on the properties of the metal ions and the donor sequence of the ligands as different ligand revealed different biological implications [7]. Among the transition metals, copper is a physiologically significant endogenous metal center which carried out a crucial role in CuII/CuI redox couple reactions that are quite substantial in different life processes as copper is found to be an integral cofactor of several enzymes engrossed in different oxidative metabolism. Consequently, the diverse structural aspects of copper (II) complexes and their synergistic activities with drugs have been the focal theme for the large number of researchers [8]. Likewise, zinc also authenticated its vital role for numerous cell processes and is a major regulatory ion in the metabolism of cells [9]. It has also been revealed that zinc (II) complexes exhibit diverse bio-potent activities viz., antibacterial [10], anti-inflammatory [11] and antioxidant [12].

Recently, privileged structure activity conception has been materialized as a triumphant approach for the new-fangled drug discovery in the field of medicinal chemistry [13]. The molecular hybridization (MH) approach has become a potent strategy for the rational design of such ligands or prototypes which depend on the recognition of pharmacophoric sub-units in the molecular framework and directed the design of new hybrid architectures that maintain pre-selected characteristics of the original templates [14] and generate a new hybrid compound with improved affinity and efficiency as compared to the parent drugs. In view of this rational approach, hybrid pharmacophore...
Synthesis and characterization of pharmacologically active 18-membered tetraamidine macrocyclic complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II): In vitro antimicrobial, anticancer screening, DNA interaction and docking studies

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ABSTRACT

The macrocyclic ligand, 2, 4: 11, 13-Dinaphthyl-1, 5, 10, 14 tetraazacyclooctadecane-6, 9, 15, 18-tetraone, (L) obtained from condensation of 1, 8-diaminonaphthalene and succinic acid, was used to synthesize the complexes of the type, [MLCl₂] [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] and characterized by spectroscopic techniques. The calf-thymus DNA interaction and CD studies indicated relatively greater binding ability for...
Synthesis, spectroscopic characterization and in vitro antimicrobial studies of Schiff base ligand, H$_2$L derived from glyoxalic acid and 1,8-diaminonaphthalene and its Co(II), Ni(II), Cu(II) and Zn(II) complexes

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Abstract A novel Schiff base ligand, N,N'-bis (glyoxalic acid carboxaldimine)-1,8-diaminonaphthalene [H$_2$L] obtained by the condensation of glyoxalic acid and 1,8-diaminonaphthalene and its mononuclear complexes of type, [ML]M = Co(II), Ni(II), Cu(II), Zn(II)] have been synthesized and characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements and spectroscopic studies viz., FT-IR, EPR, $^1$H NMR, FAB-Mass, UV–vis and magnetic moment data. A square planar geometry has been assigned on the basis of UV–vis and magnetic susceptibility around Co(II), Ni(II) and Cu(II) ions while conductivity data showed non electrolytic nature of all the complexes. The synthesized ligand, H$_2$L and its complexes have been tested against Streptococcus mutans, Staphylococcus pyogenes, MRSA (Gram positive bacteria), Pseudomonas aeruginosa, Salmonella typhimurium, Escherichia coli (Gram negative bacteria), Candida albicans, Candida krusei, Candida parapsilosis and Candida norvegensis and results suggested that Cu(II) complex has significant antimicrobial activity.

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1. Introduction

Schiff base ligands have played an integral and important role in the development of coordination chemistry since the late 19th century. Metal complexes of these ligands are ubiquitous due to their facile synthesis, wide applications and the accessibility of diverse structural modifications (Coles et al., 1998).
Full Length Article

Photocatalytic degradation of the Paracetamol drug using Lanthanum doped ZnO nanoparticles and their in-vitro cytotoxicity assay

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Abstract

The doping of semiconductor by rare earth metals nanoparticles is an effective way for increasing photocatalytic activity. Zinc oxide and Lanthanum doped Zinc oxide nanoparticles were synthesized by modifying the gel-combustion method. It was found that La can greatly enhance the cytotoxicity and photocatalytic activity of ZnO nanoparticles towards various cell lines and Paracetamol drug. These nanoparticles were characterized by various spectroscopic and other techniques which clearly revealed the presence of lanthanum ions. The absorption edge shifts towards the visible region after doping with La ions. This shift shows that the doping of La ions is favorable for absorbing the visible light. The comparative photocatalytic and cytotoxicity activity revealed that La doped ZnO nanoparticles remarkably enhanced activities as compared to the ZnO nanoparticles. The outcome of these studies offers valuable for planning La doped ZnO nanoparticles having cytotoxicity and photocatalytic activities helpful for the formulation of anticancer product and waste water remediation.

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1. Introduction

The presence of pharmaceutical compound even at low concentration in waste water effluents raised the environmental problems on aquatic and human life in recent years [1]. Several drugs are extensively used as antibiotics, antiseptics, anti-inflammatory and disinfectants [2]. Out of which Paracetamol (PARA) a familiar analgesic and antipyretic drug which is heavily used all over the world [3]. In view of huge production and quantitative use of PARA, it has been frequently found in the environment, particularly in the aquatic environment with 0.01-0.03 mg/L leading to hazardous effect proving that it is not an absolutely safer drug [4]. PARA could cause liver failure, hepatic necrosis, nephrotoxicity and even death in human and animal [4]. Keeping in view the above, it is important to propose an efficient treatment method which may transform PARA to non-toxic product. Many advanced oxidation processes like ozonation [5], electrochemical [6], sonolysis [7], UV oxidation [5] and heterogeneous photocatalysis [8] are utilized to get rid of such compounds. Several metal oxide semiconductors (TiO2, ZnO, WO3 and graphene based metal oxide, etc.) with a large band gap have been established to be capable of catalyzing the disinfection of the

organic pollutants under UV light irradiation [9,10]. Among various semiconductor, ZnO nanoparticles have been proved to be the perfect candidates because of their high photocatalytic activity for water pollutants, decomposition of organic molecules, certain organisms, photoreduction of halogenated benzene derivatives and toxic metal ions, use in self-cleaning surfaces and ability to detect biological species [11,12] have extended their applications into environmental remediation and biomedical research. ZnO which is "generally recognized as safe (GRAS)" substance by the US Food and Drug Administration. It is also additionally used as a typical additive and a element in cosmetics and sun screens [13]. Due to cytotoxicity of ZnO nanoparticles which is recently reported in prokaryotic and eukaryotic system is a matter of great concern [14,15]. ZnO nanoparticles are among the foremost toxic engineered nanomaterials, particularly among other metal oxide nanomaterials [16-18]. Many reports of the remarkably high toxicity of ZnO nanoparticles and their intensive use in various application cause important health and environmental issues. It invites attention for the detailed investigation to identify the specific material features and properties which contribute to their strong cytotoxic effect [13]. The data might facilitate researchers to design new synthetic approaches to provide safer and reduced cytotoxicity of ZnO nanoparticles without affecting their vital physiochemical properties like their optical and crystal structure that makes them striking for their general use in technological applications.
Human Topoisomerase I mediated cytotoxicity profile of l-valine-quercetin diorganotin(IV) antitumor drug entities

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ABSTRACT

New chiral l-valine-quercetin diorganotin(IV) complexes [(CH3)2Sn(QX-val)] 1lp, [(Cd2H)2Sn(QX-val)] 2lp were synthesized and thoroughly characterized by elemental analysis, mass spectrometry, IR, 1H NMR, 125Sn NMR spectroscopy. Preliminary comparative DNA binding studies on enantiomeric complexes 1lp and 2lp were carried out by UV–vis, fluorescence titrations, thermal denaturation and circular dichroic techniques to ascertain their DNA binding propensity. Thermal denaturation studies of complexes in the absence and presence of CT-DNA have been carried out and ΔTm was calculated to be 2–3 °C depicting electrostatic mode of binding corroborated well with the results of UV–vis and fluorescence studies. The intrinsic binding constant, K, and binding constant, K values revealed that both l-enantiomers of complexes 1 and 2 exhibited exceptionally high binding propensity as compared to their D-enantiomers and between l-enantiomers 1l exhibited greatest binding affinity and followed the trend: 2l > 1l > 2p > 1p. The cytotoxicity profile of 1l and 2l was studied on four different human cancer cell lines; HepG2, HepG2, MiaPaCa-2 by SRB assay which revealed remarkably good cytotoxic activity (with G1S values of ≤10 μg mL-1) and 2l exhibited better cytotoxic activity than 1l. Furthermore, the chemotherapeutic action of drug entities was found to be mediated by human Topoisomerase I enzymatic inhibition.

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1. Introduction

Quercetin (3,5,7,3',4'-pentahydroxyflavone), a natural bioflavonoid pharmacophore has attracted considerable interest due to its diverse biological properties viz. antioxidant, antibacterial, antifungal and antitumor via apoptosis [1,2]. The chemical structure of quercetin possesses conjugated electron rich aromatic rings and a number of labile hydroxyl groups which make them very good hydrogen and electron donors [3]. Quercetin as a pharmacophore is therefore, highly desirable motif for the robust drug design strategy particularly, in combination with other recognition element domains [4]. In the recent past, many quercetin metal complexes were synthesized and thoroughly characterized. It has been observed that incorporating metal ions in quercetin scaffold dictates the geometric spatial orientation at the active site which is responsible for better pharmacokinetic responses both in vitro and in vivo [5,6].

Tin and organotin(IV) derivatives have gained much attention recently as a notable class of antitumor chemotherapeutics [7,8]. Organotin compounds are coordinatively unsaturated and can expand their coordination number from four to seven upon addition of neutral organic donor ligands, therefore they could exhibit wider possibilities of hybridisation beyond sp, sp2 and sp3 [9]. Functionalization of organotin(IV) complexes with tailored ligand scaffolds could yield drug entities with altered pharmacological properties, such as improved biocompatibility, reduced systemic toxicity, target specificity and selectivity [10,11]. A plethora of organotin derivatives have been prepared and tested in vitro and in vivo, firstly against murine leukemia cell lines and after that, against different panels of human cancer cell lines [12]. Organotin(IV) complexes have been identified as effective drug candidates in organometallic oncology with remarkably good IC50 values (63 ng mL-1 against MCF-7 and 121 ng mL-1 against WIDr cell line as compared to 600 and 976 ng mL-1, respectively for cisplatin) [13]. Several diorganotin and triorganotin(IV) compounds which were conjugated to bioactive donor ligands have also shown high
Research paper

A comparative analyses of bioactive Cu(II) complexes using Hirshfeld surface and density functional theory (DFT) methods: DNA binding studies, cleavage and antibiofilm activities

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1. Introduction

Biofilm formation by pathogenic bacteria is considered a major step for establishing successful colonization on implanted medical devices, stents, catheters and endocarditis or lung infections in hospitals [1]. These biofilms being tolerant to both antibiotics and immune system are therefore difficult to treat and result in severe pathological conditions for host [2]. There is therefore, a huge demand of efficacious therapeutic molecules for combating bacterial biofilms, and new innovative strategies are required for the development of novel, potent as well as less toxic antibacterial agents [3].

In recent past, much attention has been focused for the development of DNA targeted antimicrobials [4] as previous literature reveals that DNA is an important primary cellular target for most of the therapeutic drugs in clinical use [5]. Considering the role of DNA (both extracellular and intracellular) in the development and maturation of biofilms [6], DNA targeting molecules can be considered as potential antibiofilm agents. Therapeutic agents exert their cytotoxic and antibacterial effect by binding to DNA, thereby cleaving the DNA and inhibiting the growth of the cells, preventing further aggregation or uncontrolled division of cells leading to colonization [7].

Currently, tremendous efforts are directed for the design and synthesis of metal-based therapeutics and much focus is on the development of DNA-targeted drug candidates involving the interaction with specific domain of DNA helix preferably by non-covalent mode (e.g., intercalation, groove binding and surface interaction with negatively charged oxygen atoms of the phosphate linkage) [8]. Among the metal ions utilized in drug design, copper being an endogenous bio-essential element plays a pivotal role in the functioning of several metalloenzymes and proteins [9]. Due to its high redox activity, copper has potential to catalyze the generation of reactive oxygen species (ROS), disrupt the redox equilibrium of cell and also intervene in the redox mediated cellular signaling pathways [10]. It is speculated that ROS are capable of

Abbreviations: dip, [(2,6-dipropionylphenyl)methyl]methylphenol; dmp, [(2,6-dipropionylphenyl)methyl]methyl)6-methoxyphenol; CT DNA, calf thymus DNA; EL, ethidium bromide; QM, quantum mechanical.

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Research paper

Synthesis and crystal structure determination of cobalt(II) mixed-ligand complex containing 1,10-phenanthroline and 5-(2-carboxybenzyloxy) isophthalic acid: Their biological evaluation viz. DNA/protein binding profile, pBR322 DNA cleavage activity

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ABSTRACT

New metal-based cancer chemotherapeutic agent Co(II) complex of the type [(CoMe\(_2\)Phen](o-cblAl) (H\(_2\)O)\(_2\)]H\(_2\)O \((1)\) was synthesized from ligand 5-(2-carboxybenzyloxy)isophthalic acid (o-cblAl) and thoroughly characterized by spectroscopic and single crystal X-ray diffraction method. Complex 1 crystallizes in a slightly distorted octahedral Co\(_{12}\)O\(_2\) coordination environment. In vitro DNA binding studies of ligand and complex 1 with CT DNA were carried out by using biophysical techniques viz. electronic absorption and fluorescence spectral studies which indicated that 1 binds to DNA more avidly as compared to ligand via electrostatic binding mode. Complex 1 shows significant DNA photo cleavage activity through the formation of hydroxyl radicals via photo-redox pathway. The affinity of 1 towards HSA was also investigated by the fluorescence spectroscopic technique and 3D scan measurements revealing that 1 quenches the fluorescence intensity of HSA more strongly than o-cblAl. Furthermore, magnetic drug targeting shows the accumulation of complex 1 in the target site under the influence of an externally applied magnetic force.

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1. Introduction

The metallic drug-DNA interaction is a new thrust area of research in inorganic pharmaceutical research. The interaction of cobalt(II) transition metal complexes containing a planar heterocyclic aromatic ligand with molecular target DNA is of particular interest for understanding their cytotoxic activities owing to their tunable coordination geometry, versatile redox and spectroscopic properties, which make them suitable for the synthesis of new metal-based therapeutic agents \([1-4]\). These compounds can bind with DNA duplex through non-covalent interactions viz. intercalation between the bases, surface groove-binding and electrostatic attraction with anionic sugar-phosphate backbones \([5]\). The different loci present in the DNA are involved in various regulatory processes such as gene expression, gene transcription, mutagenesis, carcinogenesis, etc \([6]\). On the other hand, metal-based artificial nucleases for the hydrolytic cleavage of the phosphodiester bond that cleave DNA different from natural enzymes, thus providing leads for the development of chemotherapeutic agents \([7-9]\). The hydrolytic cleavage of DNA offers important advantages as compared to the oxidative one because nucleic bases and deoxynucleoside sugar moiety are not modified and no additional reagents is necessary when they are hydrolytically cleaved which allows the cleaved fragments to be religated enzymatically, while the oxidative process involves the oxidation of nucleobases and/or H abstraction from the sugar moiety \([10-12]\). Among several transition metal complexes used as synthetic hydrolyases, Co(II) complexes are better suited for the hydrolysis of DNA due to their strong Lewis acid and redox properties to produce reactive oxygen species that ultimately cleave DNA, yielding direct strand scission \([13,14]\).

Cobalt is a bioessential trace element and its complexes can mimic metalloenzymes cobalamin (vitamin B\(_{12}\) \([15]\) and have been widely studied for the development of DNA-cleaving agents,

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Synthesis and crystal structure elucidation of new copper(II)-based chemotherapeutic agent coupled with 1,2-DACH and orthovanillin: Validated by in vitro DNA/HSA binding profile and pBR322 cleavage pathway

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In vitro DNA binding
HSA binding
Photoinduced DNA cleavage

ABSTRACT
New copper(II)-based complex (1) was synthesized and characterized by analytical, spectroscopic and single crystal X-ray diffraction. The in vitro binding studies of complex 1 with CT DNA and HSA have been investigated by employing biophysical techniques to examine the binding propensity of 1 towards DNA and HSA. The results showed that 1 avidly binds to CT DNA via electrostatic mode along with the hydrogen bonding interaction of —NH2 and C—N groups of Schiff base ligand with the base pairs of DNA helix, leads to partial unwinding and destabilization of the DNA double helix. Moreover, the CD spectral studies revealed that complex 1 binds through groove binding interaction that stabilizes the right-handed B-form of DNA. Complex 1 showed an impressive photoinduced nuclear activity generating single-strand breaks in comparison with the DNA cleavage activity in presence of visible light. The mechanistic investigation revealed the efficiency of 1 to cleave DNA strands by involving the generation of reactive oxygen species. Furthermore, the time dependent DNA cleavage activity showed that there was gradual increase in the amount of NC DNA on increasing the photoexposure time. However, the interaction of 1 and HSA showed that the change of intrinsic fluorescence intensity of HSA was induced by the microenvironment of Trp residue.

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1. Introduction

The interaction of transition metal complexes with DNA and proteins provide an excellent platform for the development of new chemotherapeutic agents that control primary and malignant secondary tumors [1,2]. Among the transition metals, copper is a physiologically important endogenous metal center that plays a crucial role in redox reactions and triggers the generation of reactive oxygen species (ROS) which induce apoptosis in cancer cells. Copper possesses high affinity for nucleobases and have wide anticancer activity due to the selective permeability of cancer cell membranes to copper complexes [3,4]. There is a positive correlation between serum copper concentration and tumor incidence, stage of the diseases and mass of the growth in a variety of cancers essential for the tumor angiogenesis processes [5]. Additionally, copper is an important cofactor of several enzymes involved in oxidative metabolism, ceruloplasmin, superoxide dismutase, ascorbic acid oxidase and tyrosinase etc. [6].

The present treatment regimes for chemotherapy involves platinum based drugs, which have failed in terms of severe systemic toxicity, intrinsc drug resistance (due to off-target binding of the drug at the molecular level), and high cost issues [7,8]. Therefore, it is necessary to synthesize new therapeutic modalities derived from endogenous metal ions which show promise (i) to increase the survival rates of patients with maximal therapeutic efficacy, (ii) to reduce the systemic dose-limiting toxicity and overcoming drug resistance, (iii) more prone to anti-proliferative activity against tumors leaving behind healthy cells unaffected.

An understanding of the binding modes to DNA would give insights into the understanding of the biochemical mechanism of action of the metal complexes [9]. Transition metal complexes interact with DNA via different binding modes such as covalent, intercalation, groove or electrostatic binding. The interaction of the Schiff-base transition metal complexes with DNA is of particular interest due their use as new structural probes in nucleic acid chemistry as well as development of therapeutic agents [10]. By changing both the metal ions and ligands, it is possible to modify the mode of interaction of the complex with nucleic acids [11–13]. Reesdik and co-workers reported the DNA binding and cleaving ability of a new Cu(II)-Schiff base complex which
A dinuclear copper(II) complex with piperazine bridge ligand as a potential anticancer agent: DFT computation and biological evaluation

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1. Introduction

Cancer is a multifaceted class of disease in which cells divides wildly away from the normal limits, consequently, intruding to the near or distant tissues (metastasis), and ultimately leads to death [1]. There are different types of cancers (more than 100 phenotypes) derived from numerous organs or tissues with multiple etiologies and endless combinations of genetic and epigenetic alterations. The primary treatment modalities include surgery, chemotherapy, radiotherapy, and immunotherapy etc. [2]. However, the mainstay treatment is based on chemotherapy involving various natural and synthetic compounds that have potential to kill or control the unwanted proliferation of cancerous cells. In this bioinorganic chemistry has emerged as the potential field for scientific fraternity around the globe. Medicinal inorganic chemistry offers additional opportunities for the design of the therapeutic agents not accessible to organic compounds due to their wide range of coordination number, geometries, available redox states, thermodynamic and kinetic individuality and intrinsic properties of the cationic metal ion and ligand itself offer variety in activities [3–5]. In this milieu, cisplatin and the follow-on Pt(II) metallo-drugs (carboplatin and oxaliplatin) are well-established anticancer agents, which have achieved worldwide clinical acceptance with exemplary success in treating testicular, ovarian and colorectal cancers [6]. However, their remarkable success is marred by clinical limitations, including acquired or intrinsic resistance problems, a limited spectrum of activity, and high toxicity leading to various side effects [7]. This open up the window for the extensive search and prompted chemists to search for alternative metals viz., transition metals, Cu, Zn, Fe, Ru, etc. and several
Review

Current and future potential of metallo drugs: Revisiting DNA-binding of metal containing molecules and their diverse mechanism of action

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ABSTRACT

Cancer treatments regimes which include conventional chemotherapy have not proved so successful in curing human malignancies. Failures to these treatment modalities include inherent resistance, systemic toxicity and severe side effects. Out of 50% patients administered to chemotherapy, only 5% undergoes survival. Therefore, identification of new drug design and therapeutic strategies that could target cancer cells leaving normal cells unaffected still continues to be a challenge. Despite advances that have led to the development of new therapies, treatment options are still limited for many types of human cancers particularly with those undifferentiated phenotypes. This review provides an overview of metal based antitumor drugs in clinical trials and the serious side effects caused by these drugs led the chemists to search for the new diagnostic and therapeutic agents. In particular, we focus on metal complexes of copper, zinc, silver and gold complexes with an emphasis on the new strategies used in the development of new antitumor agents.

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1. Introduction

Medicinal inorganic chemistry is a field of increasing prominence as metal-based compounds offer possibilities for the design of therapeutic agents not readily available to organic compounds. Numerous metal ions play a vital role in biological systems and currently many metal-based drugs are routinely administered to patients for therapeutic and diagnostic benefit. Among this, anticancer drug screening is becoming the most attractive field due to the increasing threats of cancer to our health. There is a growing interest in metal containing drugs, and medicinal inorganic chemistry covering applications of metals in therapeutics and diagnostics is a field of increasing prominence [1–7]. The major advantage of metal based over organic based drugs is the ability to vary coordination number, geometry, and redox states. Metals can change the pharmacological properties of organic-based drugs by forming coordination complexes with them. Metal-based pharmaceuticals can be arranged into seven categories depending on the function of the metal and ligand moieties according to Hambly et al. [8]: (1) the metal complex is active in its inert form, (2) the metal complex is active in its reactive form, (3) the metal serves as a radiation enhancer, (4) the compound contains a radioactive metal, (5) the metal or its biotransformation product

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0020-1693/© 2016 Elsevier B.V. All rights reserved.
Vibrational dynamics (IR, Raman, NRVS) and a DFT study of a new antitumor tetrannuclearstannoxane cluster, Sn(IV)-oxo-[di-o-vanillin] dimethyl dichloride†


The vibrational dynamics of a newly synthesized tetrannuclearstannoxane was characterized with a combination of experimental (Raman, IR and tin-based nuclear resonance vibrational spectroscopy) and computational (DFT/B3LYP) methods, with an emphasis on the vibrations of the tin sites. The cytotoxic activity revealed a significant regression selectivity against the human pancreatic cell lines.

The resurgence of organotin(IV) as active metallopharmaceuticals in cancer oncology is well recognized and much attention is being devoted to the design and synthesis of therapeutically active compounds of organotin(IV) embedded in organic frameworks with N-O, O-O, N-N donor atoms. o-Vanillin, 2-hydroxy-3-methoxy benzaldehyde is a useful drug precursor that has been used for the preparation of many Schiff base complexes and conjugate supramolecular motifs that display exceptional biological activities viz., anti-inflammatory, antibacterial, antiviral and antitumor. Organotin(IV) compounds possessing ligand skeletons with Sn-N, Sn-S and Sn-O bonds are considered to be therapeutically potent, and it was observed that the organotin complexes which have covalent bonds between the Sn and O atoms are very active compounds compared to those which have coordinate bonds between them. Furthermore, it was observed that amongst the organotin(IV) compounds, the activity of diorganotin(IV) was highest for most of the human cancer cell lines. Previous literature reports reveal that the biological activity of diorganotin compounds, R₂SnX₃, is determined by the R organic group which exercises control on the cytotoxic activity, while X groups control the delivery of the active R₂Sn₄ species.

Many studied organotin(IV) complexes are mononuclear, although tetrannuclear or polymeric species have also been investigated. Since metal nuclearity plays a key role in imparting pharmacological responses to drug entities, many organotin(IV) complexes that are polymeric or have an appropriate coordination number were found to exhibit a better biological activity as compared to mononuclear derivatives. Recently, X. Shang et al. reported ladder-like tetranuclearstannoxane complexes formulated as [R₂Sn₄(C₆H₅-COO)₂]([µ₄-O](µ₄-OH)] (R = Et, Bu, Oct and Ph) possessing a Sn₄O₄ core. The therapeutic potential of these complexes was assessed by their cytotoxic activity against the human tumor cell lines, viz., Hela, BGC-823 and KB with cisplatin as a control. The IC₅₀ values (μM) of these complexes showed good antitumor activity. Several other organooxotin clusters have also been synthesized and chemically modified by organic ligands using selective spacers or bridged groups, such as carboxylic acids, phosphonic acid, phosphinic acid and arsanates.

Organooxotin clusters are considered a new class of pharmaceutical drug motifs owing to their remarkable structural diversity and exceptional biological applications. Recently, organooxotin clusters with methylene[4]circulane cavities were found to be suitable for drug delivery at the target site with specificity. It was further revealed that the organo substituent attached to tin atoms through an oxo bridge in stannoxane complexes could be responsible for good anticancer activities. Furthermore, probing vibrations coupled to localized electronic excitations during chemical reactions could be crucial for depicting the interactions at the active site at the molecular level. The experimental identification of in-plane and out-of-plane vibrational modes could significantly contribute to understand binding interactions with biological molecules and their reaction dynamics. In tetrannuclearstannoxane, the presence of four tin atoms contributes to a larger molecular system and therefore, many vibrational frequencies that could be responsible for more intimate binding emerge. Among the out-of-plane vibrations, the most significant modes in the low frequency region are
Facile fabrication of highly efficient modified ZnO photocatalyst with enhanced photocatalytic, antibacterial and anticancer activity

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Abstract

The degradation of organic pollutants in the aqueous medium using semiconductor photocatalysts has become an attractive method for detoxification of water. ZnO is an efficient photocatalyst with few

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(Prof. S. Tabassum)
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Research paper

Synthesis, characterization and interaction studies of 1,3,4-oxadiazole derivatives of fatty acid with human serum albumin (HSA): A combined multi-spectroscopic and molecular docking study

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Highlights

- Fatty acid derivatives of 1,3,4-oxadiazole were synthesized and characterized.
- Comparative study of conventional heating and microwave irradiation method described.
- Binding of compound 2C with HSA was investigated.
- Compound 2C binds at subdomain III A at binding site II of HSA.

Synthesis and multi-spectroscopic DNA binding study of 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives of fatty acid

Mohammad F. Hassan, Abdul Rauf

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Highlights

- Synthesis of a series of fatty acid derivatives of 1,3,4-oxadiazole and 1,3,4-thiadiazole has been described.
- The binding affinity of 3a and 6a with CT-DNA has been evaluated using various spectroscopic studies.
- This work can benefit in understanding the binding mechanism of small heterocyclic molecules at molecular level.

Abstract

A facile and convenient synthesis of a series of fatty acid derivatives of 1,3,4-oxadiazole and 1,3,4-thiadiazole has been described. The key step of this protocol is the cyclization of acyl thiosemicarbazides via iodobenzene diacetate and methanesulfonic acid under mild conditions. The newly synthesized compounds were characterized by FT-IR, $^1$HNMR, $^{13}$CNMR and mass spectral study. The binding affinity of 5-(pentadecyl)-N-propenyl-1,3,4-oxadiazole-2-amine (3a) and 5-(pentadecyl)-N-propenyl-1,3,4-thiadiazole-2-amine (6a) with calf thymus DNA (CT-DNA) was assessed by the melting temperature ($T_m$) method.
A novel and facile synthesis of fatty acid chain substituted benzoazadiazepine and naphthoazadiazepine derivatives

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ABSTRACT

A series of novel benzoazadiazepine and naphthoazadiazepine (4a-e and 5a-e) were synthesized by nucleophilic attack of selected fatty acid hydrazides (1a-e) on 2,3,5,6-Tetrachloro-1,4-benzoquinone and 2,3-dichloro-1,4-naphthoquinone in appreciable yield.

Key words: Fatty acid hydrazides, 2,3,5,6-Tetrachloro-1,4-benzoquinone, 2,3-dichloro-1,4-naphthoquinone, benzoazadiazepine, naphthoazadiazepine.

INTRODUCTION

Modern organic chemistry is more and more related to heterocycles. Developing novel heterocycles and relating synthetic methods is the eternal goal in synthetic chemistry [1]. Particular interest on nitrogen-containing heterocycles is due to their existence in many natural or synthetic molecules [2]. Despite diverse synthetic utility, exploring novel synthetic methods to meet increasing scientific and practical demands is still an active area. Fused ring systems are very well-known and interesting molecules from several points of view [3-5]. The addition of nitrogen nucleophiles to benzo- and naphthoquinone represents a common synthetic route to many fused heterocyclic rings which have been used as synthetic intermediates in medicinal chemistry [6-7] and for food science [8]. Numerous studies have been reported [9-11] on the synthesis of a variety of azadiazepine derivatives covering a wide range of bioorganic, natural products and medicinal chemistry. Considering potential safety risk implications of a compound with even further medicinal chemistry effort was focused towards design of novel fatty acid chain substituted naphthoazadiazepine and benzoazadiazepine derivatives using fatty acids. In present work, we developed a method for preparing fatty acid chain substituted benzoazadiazepine (4a-e) and naphthoazadiazepine (5a-e) derivatives using readily available 2,3,5,6-Tetrachloro-1,4-benzoquinone (2) and 2,3-dichloro-1,4-naphthoquinone (3). Compounds (4a-e) and (5a-e) were prepared by using procedure [12].

MATERIALS AND METHODS

1. Experimental
   1.1. Chemicals and Instruments
   Undec-10-enoic (purity 98%), (9Z)-octadec-9-enoic (purity 97%), octadecanoic (stearic) and hexadecanoic (palmitic) acids were purchased commercially from Fluka Chemicals, (Buck: Switzerland), (9Z, 12E)-12-Hydroxyoctadec-9-enoic (ricinoleic) acid was isolated from Ricinus communis (castor) oil following Gunstone's partition procedure. Melting points were determined on a Koehler apparatus and are uncorrected. IR spectra were
Spectroscopic, Viscositive, DNA Binding and Cytotoxic Studies of Newly Synthesized Steroidal Imidazolidines

Ayaz Mahmood Dar, Shamsuzzaman & Shakir Khan

Abstract

A series of new steroidal imidazolidine derivatives (4–6) were synthesized after reacting steroidal thiosemicarbazones with chloro ethylacetate in absolute ethanol. After characterization by spectral and analytical data, the interaction studies of compounds (4–6) with DNA were carried out by UV–vis, fluorescence spectroscopy, hydrodynamic measurements, molecular docking and gel electrophoresis. The compounds bind to DNA preferentially through electrostatic and hydrophobic interactions with $K_{b1}$: $2.63 \times 10^3$ M$^{-1}$, $1.81 \times 10^3$ M$^{-1}$ and $2.06 \times 10^3$ M$^{-1}$, respectively indicating the higher binding affinity of compound 4 towards DNA. Gel electrophoresis demonstrated that compound 4 showed strong interaction during the concentration dependent cleavage activity with pBR322 DNA. The molecular docking study suggested the intercalation of imidazolidine moiety of steroid derivative in minor groove of DNA. During in vitro cytotoxicity, compounds (4–6) revealed potential toxicity against the different human cancer cells (MTT assay). The uptake of compound 4 by MCF-7 and HeLa cells was studied by confocal microscopy which determined cell shrinkage and hence leading to the apoptosis. The results revealed that compound 4 has better prospectus to act as cancer chemotherapeutic candidate which warrants further in vivo anticancer investigations.
Synthesis, characterization, antimicrobial and anticancer studies of new steroidal pyrazolines

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KEYWORDS
Cholest-5-en-7-one;
2,4-Dinitrophenyhydrazone;
Pyrazoline;
Antimicrobial;
Anticancer

Abstract A convenient synthesis of 2'-[2',4'-dinitrophenyl]-5z-cholestan-1,3(2H,4H)-pyrazolines 4-6 from cholest-5-en-7-one 3 was performed and structural assignment of the products was confirmed on the basis of IR, 1H NMR, 13C NMR, MS and analytical data. The synthesized compounds were screened for in vitro antimicrobial activity against different strains during which compound 6 showed potent antimicrobial behaviour against Corynebacterium xerosis and Staphylococcus epidermidis. The synthesized compounds were also screened for in vitro anticancer activity against human cancer cell lines during which compound 5 exhibited significant anticancer activity.

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1. Introduction

In the last few decades there has been an extensive focus of research towards the rational modification of steroid molecules. This is due to the fact that such type of compounds are less toxic, less vulnerable to multi-drug resistance (MDR) and highly bioavailable because of being capable of penetrating the cell wall. Recent studies reveal that incorporation of heterocarom (N/O/S) enhances the biological activities of steroid molecules. This is proved by various activities shown by these systems like antimicrobial, anti-inflammatory, hypotensive, hypcholesterolemic and diuretic activities (Manson et al., 1963; Hirschmann et al., 1963, 1964; Wang et al., 1993; Gupta et al., 1996). As a result, a number of different heterocyclic systems have been introduced into the core structure of steroids with pyrazolines, pyrazolines, isoxazoles, isoxazolines, thiazoles, thiadiazoles, pyridines, pyrimidines, imidazoles, etc. as the notable ones. Among these heterocycles, pyrazolines occupy a unique place in the realm of natural and synthetic organic chemistry (Jung et al., 2005).

Pyrazoline derivatives are synthetic targets of utmost importance for the researchers, since such type of compounds have a wide range of biological and pharmaceutical properties such as analgesic, antipyretic and antinflammatory activities (Jung et al., 2005; Amr et al., 2005). Pyrazolines also possess antidepressant, anti-inflammatory and antirheumatic activities (Palaska et al., 2001; Bansal et al., 2001). Besides this pyrazolines are also used as potent antidiabetic agents (Villhauer et al., 2002; Ahn et al., 2004). Recently, pyrazolines were reported as a DP-IV inhibitors and antitumor agents (Amr, 2000; Hammad et al., 2000; 2003).
Turmeric/polyvinyl alcohol Th(IV) phosphate electrosyn fibers: Synthesis, characterization and antimicrobial studies

Mohd Imran Ahamed, Inamuddin, Lutfullah, Gaurav Sharma, Anish Khan, Abdullah M. Asiri

1. Introduction

During last few decades, organic and inorganic ion exchange materials have been used for the treatment of wastewater. Inorganic ion exchange materials are well known for their good ion exchange capacity, thermal stability and ease of synthesis, whereas, organic ion exchange materials are considered good due to their granulometric properties suitable for column operation. Inorganic as well as organic ion exchange materials have their own merits and demerits. For example, inorganic ion exchangers are less stable in high acidic and alkaline media while organic ones are less thermally stable. To overcome these obstacles, organic-inorganic hybrid materials which possess the synergetic properties of both the materials have been developed. Organic-inorganic hybrid materials have established themselves as a distinct class of materials, as they are combining the properties of inorganic and organic parts [12]. Electrosyn is one of the globally acknowledged modern economical and versatile techniques to produce smooth fibers in nanometer range [3-4]. Electrosyn fibers offer several outstanding properties such as large surface to volume ratio, excellent flexibility, small width and multi-scale porosity and hence are extensively utilized for fabrication of bioengineering materials [5-6] for various applications in the emerging areas of medical science like wound dressing, drug delivery, tissue engineering, bone regeneration etc., [7-11]. The name turmeric i.e. Curcuma longa, coined from the Arabic name Tarkum and has miscellaneous biological properties like antimicrobial and antifungal properties due to the presence of bioactive agents mainly “curcumin” [12]. Polyvinyl alcohol (PVA) is a polymer that is well known for its easy processability, smooth film forming capacity, high hydrophilicity, biocompatibility and chemical resistance properties [13]. PVA is water soluble and almost non-toxic polymer. Thus, it can be effectively utilized in medical fields. In this study, inorganic ion exchanger Th(IV) phosphate was used to prepare the hybrid material with PVA and turmeric in view of combining the favorable features of individual components, such as ion exchange properties of Th(IV) phosphate, antimicrobial properties of turmeric and bioincompatibility of PVA. These properties of hybrid ion exchange nanofibers make them suitable for the treatment of wastewater along with the antimicrobial
Lanthanum immobilized on chitosan: a highly efficient heterogeneous catalyst for facile synthesis of novel (α,β-unsaturated) β-aminoketones

Saima Taranum and Zeba N. Siddiqui*

A new heterogeneous catalyst, lanthanum immobilized on chitosan, was synthesized and used for the aza-Michael reaction of β-enameinone under microwave irradiation. The characteristic structural features of the catalyst were determined using Fourier transform infrared spectroscopy, powder X-ray diffraction, energy-dispersive X-ray spectroscopy, transmission and scanning electron microscopies and inductively coupled plasma atomic emission spectroscopy. The stability of the catalyst was evaluated using thermogravimetric analysis. The use of recyclable catalyst and glycerol as solvent makes this procedure environmentally benign and economically viable. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: Heterogeneous; aza-Michael; glycerol; microwave

Introduction

The chemistry of lanthanides has rapidly developed over the last few decades. In the 1970s, lanthanides were introduced as shift reagents due to their paramagnetic nature.[11] Recently, lanthanides have found widespread use as mild, stable and water-compatible Lewis acids.[12] Their low toxicity and inexpensiveness make them attractive to chemists. The trivalent lanthanides (most common oxidation state) have found widespread use in carbon–carbon bond forming reactions and functional group transformations.[13-15] In this regard, lanthanum salts have shown much potential for use as water-tolerant Lewis acids in various organic transformations.[12-15] But from the environmental point of view, their recovery and recyclability from reaction media remain major limitations. Therefore, heterogenization of lanthanum salts remains a major objective in organic synthesis.

Chitosan is one of the most abundant natural biopolymers and has excellent properties such as biocompatibility, biodegradability and non-toxicity. The presence of abundant surface polar hydroxyl and amino groups on chitosan provide high sorption capacity for metal ions and make chitosan an excellent candidate as a support for heterogeneous catalyst.[3] In recent years, a surge of interest has been directed towards combining the effects of metal ions and chitosan in catalyst design and their applications in various organic reactions.[16-18] The use of metal immobilized on chitosan in heterogeneous catalysis is encouraged by easy elimination of chitosan by dissolution in acidic water solutions that allows a quantitative metal recovery.[19]

The aza-Michael addition is one of the most convenient procedures for carbon–nitrogen bond formation between α,β-unsaturated carbonyl compounds and nitrogen nucleophiles.[20] It provides an efficient way to obtain β-aminocarbonyl scaffolds which are important building blocks in organic synthesis for the production of a variety of biologically important natural products, antibiotics, anticancer agents and other drugs.[21-23] Although a number of procedures have been developed for aza-Michael reactions of α,β-unsaturated carbonyl compounds with N-nucleophiles, catalytic aza-Michael reactions of β-enameinones remain rare. To our knowledge, only a few reports are available in the literature of aza-Michael reactions of β-enameinones using AcOH, conc. H2SO4, Mg-Al hydrotalcites and silica-supported sulfamic acid.[18-21] A few drawbacks associated with these protocols include the use of homogeneous and corrosive catalysts and limited substrate tolerance.[18,20] In this regard, protocols for the synthetic improvement of this reaction are still desirable. Hence, we have synthesized a novel lanthanum immobilized on chitosan (La/chitosan) and evaluated its catalytic activity for aza-Michael reaction.

Experimental

Chemicals and apparatus

Melting points of all synthesized compounds were obtained on a Büchi Thermonov instrument and are uncorrected. Fourier transform infrared (FT-IR) spectra (KBr) were recorded with a PerkinElmer RXI spectrometer. 1H NMR and 13C NMR spectra were recorded with Bruker DRX-300 and Bruker Avance II 400 spectrometers using tetramethylsilane as an internal standard and deuterated dimethylsulfoxide (DMSO-d6)/CDCl3 as solvent. ESI mass spectra (ESI-MS) were recorded with a Quattro II (ESI) spectrometer. Elemental analyses (C, H and N) were conducted using an Elemental Vario EL III elemental analyser and their results were found to be in agreement with calculated values. Enaminone was synthesized

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Spectroscopic study of charge transfer complexation between doxepin and π–acceptors and its application in quantitative analysis

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ABSTRACT

Charge transfer complexes of the doxepin with π–acceptors such as 2,3-dichloro-5,6-dicyano-1,4-benzochinone (DDQ), tetracyanoquinodimethane (TCNQ) and p-chloranilic acid (p-CA) have been studied spectrophotometrically. The stoichiometry of the reactions was studied by Job's method of continuous variations which show that the complexation ratio was 1:1 (acceptor: donor) for DDQ, TCNQ and p-chloranilic acid with doxepin base. The data were discussed in terms of association constant (K), molar absorptivity (ε), free energy change (ΔG), oscillator strength (f), transition dipole moment (μ0), resonance energy (E0) and ionization potential (I0). These simple, fast and sensitive spectrophotometric methods were proposed for the quantification of doxepin hydrochloride in pure form and drug formulations. The methods (A, B and C) were based on the reaction of doxepin base as n-donor with DDQ, TCNQ and pCA resulting in coloured species which absorbed maximally at 570 nm, 840 nm and 530 nm respectively. Beer's law was obeyed in the concentration range of 5–45 μg mL⁻¹, 40–360 μg mL⁻¹ and 40–400 μg mL⁻¹ for the methods A, B and C, respectively. A series of variables were studied to optimize the reaction conditions. The developed methods were successfully applied for the determination of doxepin in its formulations with high accuracy and precision and without interference from common excipients. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

Doxepin hydrochloride belongs to the family of first generation anti-depressant [1] and is chemically known as 1-propanamine, 3-dibenzo[b, e]oxepin-11 (6H) -ylidene - N, N-dimethyloctahydrochloride. Doxepin is widely used in the treatment of depression and anxiety. It has been found to be effective in the management of chronic neuropathic pain [2]. It has anaesthetic and analgesic activity in oral mucositis when administrated as a topical oral rinse [3]. Doxepin promotes sleep through resynchronization of circadian rhythm and hence approved for the treatment of insomnia characterized by difficulties in maintaining sleep [4]. Low dosage doxepin (1, 3 and 6 mg) has been recommended for the treatment of primary insomnia in adults and geriatric patients because it binds with high specificity and affinity to the histamine H1 receptor. Therefore at low doses, doxepin selectivity antagonizes H1 receptors and promotes the initiation and maintenance of sleep [5,6]. The over dose of doxepin hydrochloride may lead to coma, seizures, dysrhythmias and hypotension [7,8]. Therefore, the assay of doxepin is required for the quality assurance in pharmaceutical preparations.

Several analytical methods such as high-performance thin layer chromatography [9], HPLC with UV detection [10–12], electrochemical detection [13], MS detection [14,15] or resonance Raleigh scattering detection [16], capillary electrophoresis [17,18], cathodic adsorptive stripping voltammetry [19], differential pulse voltammetry [20], electrochemical sensors [21,22] and spectrophotometry [23,24] have been reported for the determination of doxepin in various matrices. Spectrophotometry based on natural absorption and chemical reactions has been playing a significant role in drug analysis due to its high efficiency and versatility, low cost, low labour consumption and less time of analysis. Thus, spectrophotometry has become the high-throughput technique for quality control of active pharmaceutical ingredients in pharmaceutical formulations [25–27]. Revanasiddappa and Manju [28] developed a spectrophotometric method for the determination of doxepin hydrochloride in commercial dosage forms. The method was based on the oxidative coupling of drug with 3-methylnitrosoazoline-2-one hydrzone in presence of iron (II) chloride to give coloured product which absorbed maximally at 620 nm. The oxidation of doxepin with Ce(IV) in acid medium followed by reaction with leuco crystal violet lead to the formation of violet coloured dye which absorbed maximally at 590 nm [29]. Beer's law was obeyed in the concentration range of 0–60 μg mL⁻¹ with detection limit of 0.35 μg mL⁻¹. Spectrophotometric methods [30,31] based on the extraction of ion association complexes of doxepin with Hg(II) thiocyanate, Fe(III) thiocyanate and Cu(II) thiocyanate into mixture of butyl alcohol chloroform (2:3 v/v; 1:4 v/v) and 1,2-dichloroethane have been reported for determination of doxepin hydrochloride. The characteristic of light scattering of doxepin with fast green was employed to develop analytical method.

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Amitriptyline-molybdovanadate/-molybdtungstate based ion-selective membrane electrodes for determination of amitriptyline in pharmaceutical formulations and water samples

Nalisus Rahaman, Sumaiya Khan

ABSTRACT

Poly(vinyl chloride) membrane electrodes for the determination of amitriptyline hydrochloride were fabricated based on the use of molybdovanadate and molybdotungstate as ionic transport materials and diocetylphthalate as the plasticizer. The effect of membrane composition on the electrode response was studied. The membrane electrodes containing amitriptyline-molybdovanadate (electrode A) and amitriptyline-molybdotungstate (electrode B) showed a fast and selective response over the amitriptyline hydrochloride concentration range of \(1 \times 10^{-4} \text{ to } 1 \times 10^{-1} \text{ mol L}^{-1}\). Under the optimum conditions, the slope of the calibration curve and detection limits were found to be \(57.2 \text{ mV decade}^{-1}\) and \(4.05 \text{ mV decade}^{-1}\) and \(0.007 \text{ to } 1 \text{ mmol L}^{-1}\) and \(0.0007 \text{ to } 0.1 \text{ mmol L}^{-1}\), respectively. The electrodes were successfully applied to the determination of amitriptyline hydrochloride in tablets and water samples by direct potentiometric method.

1. Introduction

Amitriptyline hydrochloride (AMT), C22H24ClN3O2S, is a tricyclic antidepressant which belongs to the dibenzodiazepine drug group [1]. The drug has a cardiotoxic structure with an enantiomeric double bond at C5 which is substituted with an N,N-dimethylpropylamine moiety. Amiptyline is chemically and physically available in the form of hydrochloride salt. The mechanism of AMT is widely used to treat symptoms of depression and psychic disorders [1]. It inhibits uptake of both norepinephrine and serotonin which contributes to its antidepressant properties [4]. AMT is also used in long-term prophylaxis for the management of children with cyclic vomiting syndrome aged over 6 years [1]. A change in the concentration of AMT in the body may influence its bioavailability and consequently, its magnitude of action. In view of this, control of active pharmaceutical ingredients is required to achieve better remedial effect and lower toxicity. AMT is covered in United States Pharmacopeia, European Pharmacopeia, and British Pharmacopoeia. The non-specific titration is described in USP methods while base titration is laid out in BP and PhTr [1] for the assay of AMT.

The literature review revealed that various analytical techniques such as HPLC [1-3], HPTLC [2, 3], gas chromatography [1-3], capillary electrophoresis [1-2], fluorimetry [1-3], and spectrophotometry [1-2] have been employed for the determination of AMT in pharmaceutical preparations. However, the aforementioned techniques have often suffered diverse disadvantages with regard to cost and selectivity. Potentiometry with ion selective electrodes is a promising analytical technique that has been used to measure directly the concentration of various active organic cations in amounts of pharmaceutical interest, by various instances, without separation of active pharmaceutical ingredients from the formulation matrix. Potentiometric sensors are used in pharmaceutical analysis mainly due to their easy fabrication, inexpensive, adequate accuracy and selectivity, fast response and reduced time of analysis. AMT has been determined by potentiometry with liquid membrane ion selective electrodes prepared from the salts of amitriptyline with cesium and tetrabromophenyl ether in p-nitrophenone [1-4]. The electrode exhibited response in the concentration range of \(6 \times 10^{-5} \text{ to } 6 \times 10^{-4} \text{ mol L}^{-1}\). Serious interferences were observed from cations of similar structure or cations that form water insoluble cesium or tetrabromophenyl ether salts extractable in p-nitrobenzene. Amitriptyline selective plastic membrane electrodes based on amitriptyline tetraphenylborate and ammitriptyline-tetrathionophenylborate ion pairs complexes embedded in poly (vinyl chloride) matrix has been tested for determination of AMT in commercial dosage forms [1-2]. However, the response time of the electrodes was about 1.0 min. Amitriptyline-molybdovanadate ion pair complex dissolved in nitrobenzene was used as a liquid membrane electrode for the drug determination...
Nitrate removal using poly-o-toluidine zirconium(IV) ethylenediamine as adsorbent: Batch and fixed-bed column adsorption modelling

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Nitrates are the most widespread contaminants of ground and surface waters all over the world. Agricultural over-application of natural and synthetic fertilizers, aquaculture, municipal wastewater, human and animal waste, overflowing septic tanks, processed food, dairy and meat products, detergent manufacturing and mineral processing industries are the sources of nitrate into the aquatic environment. A high level of nitrate in drinking water may cause adverse health effects such as blue-baby syndrome, especially in infants, cancer of the alimentary canal, and diabetes. The European Community established a maximum contaminant level of 50 mg/L, and recommended level of 25 mg/L. Therefore, the monitoring and removal of nitrate from water is relevant due to its potential dangerous impact on both environment and human health.

The conventional methods used for the removal of nitrate can be divided into three main groups: physical, chemical and biological treatment processes. Among them, adsorption methods are generally considered to be more promising and effective because they allow simple and economical operation, resulting in less sludge production and disposal problems. In recent years, several studies have been performed to explore the application of zirconium(IV) based materials for adsorption of anionic pollutants. In our earlier studies, PTEZ was synthesized which showed affinity for nitrate in the pH range 3-6. The equilibrium sorption data fitted well to Freundlich isotherm model. A single-stage batch adsorption system was developed from Freundlich adsorption isotherm parameters for removal of nitrate from water. A new inorganic-sugar beet pulp composite was prepared from sugar beet pulp after loading with zirconium(IV) ions and used for removal of nitrate from water. The adsorption of nitrate by chitosan hydrogels was increased with increase in the pH of solution and depends on the temperature with an optimum activity at 30 °C. The kinetic results corresponded well with the pseudo-second order rate equation and the intraparticle diffusion also played a significant role in the initial stage of adsorption process [1-3].

Aroa et al. [4] have modified the surface of natural zeolite by coating with a chitosan layer. The chitosan coated zeolite was protonated and used as adsorbent for removal of nitrate from water. Nitrate can also be removed from aqueous solution by modified clinoptilolite zeolite. The investigation of kinetic equations indicated that nitrate adsorption followed pseudo first order kinetic model. Adsorption of nitrate from aqueous solutions on amionium functionalized mesoporous MCM-48 silica was investigated [5-7]. The adsorbent was prepared via a post synthesis grafting method using aminosuccinimide dichloroethanesulphonate. At ambient temperature, the removal of nitrate was maximum at pH 8.

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Optimized and validated spectrophotometric method for the determination of palladium(II) in synthetic mixture and automobile workshop area samples

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Palladium (II);
Spectrophotometric determination;
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Validation

Abstract An optimized and validated spectrophotometric method has been developed for the determination of Pd(II) in synthetic mixture and automobile workshop area samples. The method was based on the complex formation of Pd(II) with cysteine in methanol-distilled water medium in the presence of Na2HPO4-citric acid buffer solution of pH 2.6 at room temperature. The complex showed a maximum absorption wavelength at 352 nm. Beer's law was obeyed in the working concentration range of 0.7502-16.5004 µg mL -1 with apparent molar absorptivity of 1.22 × 104 L mol -1 cm -1 and Sandell's sensitivity of 0.002 µg cm -2 0.001 absorbance unit. Limits of detection (LOD) and quantitation (LOQ) for the proposed method were 0.07 and 0.21 µg mL -1 , respectively. The effect of diverse ions such as Cu(II), Mg(II), Mn(II), Fe(II), Fe(III), Cr(III), Ni(II), Al(III), Fe(III), Cd(II) and Zn(II) has been studied in the presence of Pd(II) and the maximum tolerance limit of each metal was calculated. The proposed method was successfully applied for the determination of Pd(II) in synthetic mixture and automobile workshop area samples.

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1. Introduction

A tremendous effort has been taken for the determination of traces of palladium in a variety of sample types (Sharma et al., 2012; Ozgur et al., 2011; Soyaks and Altin, 2013; Soyaks et al., 2000; Serencem et al., 2013). Pd is used in jewelry, dentistry applications, line instruments such as watches and some surgical tools for electrical contacts and for the purification of hydrogen gas (Brazzoni et al., 2003). The largest application of palladium is in the catalytic field. The extensive use of Pd in automotive catalytic engines.
Determination of thorium(IV) with rifampicin in synthetic mixture and soil samples by spectrophotometry

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Spectrophotometry, Thorium nitrate pentahydrate, Rifampicin, Validation

Abstract A validated spectrophotometric method has been described for the determination of thorium(IV) in synthetic mixture and soil samples. The method is based on the complexation of thorium(IV) with rifampicin at room temperature which absorbs maximally at 525 nm. Beer's law is obeyed in the concentration range 1.16–23.2 μg mL⁻¹ with apparent molar absorptivity and Sandell's sensitivity of 8.23 × 10⁴ L mol⁻¹ cm⁻¹ and 0.0301 μg cm⁻², respectively. The influence of variables was investigated and optimized. Interference due to other metal ions was studied and the tolerance limit was achieved. The proposed method was applied to the analysis of thorium(IV) in a synthetic mixture containing various other metal ions and in soil samples. The results of analyses of the proposed method were statistically compared with the reference method showing acceptable recovery and precision.

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1. Introduction
Thorium is a naturally occurring actinide element found in the environment or associated with other metal ions in different complex matrices, nuclear fissile products, monazite sands, and geological materials. Thorium is known to have acute toxidological effects on human and progressive and irreversible renal injury (Sahoo et al., 2004). The determination of thorium(IV) in the presence of various metal ions found in soil and rivers is of special interest. Various analytical techniques such as thin-layer chromatography (Soran et al., 2005), gravimetry (Arora and Rani, 1981), titrimetry (Muralidharan and Srinivasan, 1982), reversed phase liquid chromatography (Hao et al., 1996), fluorimetry (Pavoni et al., 1989), potentiometry (Baumann, 1982; Chandria et al., 2005), X-ray fluorescence (Gibson et al., 1983) and inductively coupled plasma mass spectrometry (Aydin and Soylik, 2007) have been reported for Ti(IV) determination. These reported methods such as liquid chromatography, X-ray fluorescence, and inductively coupled plasma mass spectrometry are sensitive but expensive due to high cost of production and cost.
Spectrofluorimetric determination of doxepin hydrochloride in commercial dosage forms via ion pair complexation with alizarin red S

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KEYWORDS
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Ion-pair complex

Abstract A simple and sensitive spectrofluorimetric method has been developed for the determination of doxepin hydrochloride in pharmaceutical preparations. It is based on the formation of ion-pair complex between doxepin and alizarin red S at pH 3.09. The ion pair complex was extracted in dichloromethane and the fluorescence intensity was measured at 580 nm after excitation at 490 nm. The optimum conditions for determination were also investigated. The linear range and detection limit were found to be 2-14 and 0.55 μg/ml respectively. The method has been successfully applied for the analysis of drug in commercial dosage forms. No interference was observed from common pharmaceutical adjuvant. Statistical comparison of the results obtained by the proposed method with that of the reference method shows excellent agreement and indicates no significant difference in accuracy and precision.

1. Introduction
Doxepin hydrochloride is a dibenzoazepin class of antidepressants. It is chemically known as 1-propynamine-3, 6-didecahydroy-1H,11H-dibenz[a]azepine-N,N-dimethylhydrochloride with a molecular weight of 315.8. It is a white crystalline solid readily soluble in water. The inert ingredients used in the formulations are magnesium stearate, sodium lauryl sulfate and starch. It has been widely used as an effective tricyclic antidepressant in the treatment of psychiatric disorders over the past decades (Choloswka et al., 2003; Uddin et al., 2008). The starting daily dose of 75 mg is recommended for patients with mild to moderate severity. The dosage may be increased or decreased depending upon the patient’s response. The usual optimum dosage range is 75-150 mg/day. However, overdoses of doxepin hydrochloride may lead to some disorders like cardiac arrhythmias, severe hypertension and hypothermia among other disorders (Geissel and Bricker, 1994; Lata et al., 2005). In view of above considerations, an analytical procedure is needed for quality assurance in pharmaceutical preparations.
Circular dichroism spectroscopy: An efficient approach for the quantification of ampicillin in presence of cloxacillin

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Abstract

Ampicillin exhibited a negative and a positive Cotton effect on the circular dichroism (CD) spectra in the wavelength range of 200-750 nm. Cloxacillin showed a positive Cotton band peaking at 228 nm. Three sensitive, precise and accurate CD spectroscopic methods have been developed for the determination of ampicillin and cloxacillin. Method A was used for the determination of ampicillin in presence of cloxacillin by measuring ellipticity at 206 nm. Method B and C were employed to determine ampicillin and cloxacillin based on evaluation of ellipticity at 233 nm and 228 nm, respectively. Methods A and B showed linearity in the concentration range of 10-40 μg/mL, 5-40 μg/mL of ampicillin and 10-80 μg/mL of cloxacillin, respectively. The method A was successfully applied to the determination of ampicillin in commercial dosage forms containing equal amount of cloxacillin.

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1. Introduction

Ampicillin,[25,98,19,122,123] 2-amino-2-phenylacetylaminobenzoic acid (Amp1), is a β-lactam semisynthetic β-lactam antibiotic that inhibits bacterial cell wall synthesis by binding to peptidoglycan synthesizing enzymes[1,2,3]. It has broad spectrum of antibacterial activity and is widely used against gram-positive and gram-negative organisms as well as for enterococcal infections resistant to penicillin G. It is also useful in the prophylaxis and treatment of exacerbations of chronic bronchitis. It is ineffective against penicillin-resistant staphylococci[3] and ampicillin is a highly recommended therapy in clostridia infections in chicken [4]. However, the dose adjustments are suggested during oral administration in chicken infected with colibacillosis. In aqueous solution ampicillin exists mainly in three different forms [13] (H2O) in the media, depending on the pH and ionic strength. The COOH and NH2 groups of AmpH2 are successively deprotonated in the pH range 2-4 (pK1 = 2.55) and 6-8 (pK2 = 7.05), respectively [5]. Cloxacillin, chemically designated as monosodium (2S,5R,6R,7R,8S,9R)-2,6-dimethyl-7-oxo-3-(2-oxo-1,3-dihydroxy-2H-1,4-benzodiazepin-2-yl) heptane-2-carboxylic acid, is a semisynthetic β-lactam antibiotic. It is a semisynthetic β-lactam antibiotic resistant antibiotic in the monobactam penicillin which has dissociation constant (pK2) of 2.7.[6] The presence of unstable four-membered ring in the β-lactam moiety makes cloxacillin prone to degradation by heat and in presence of alcohol and water [8,9]. It is widely used in non-methicillin-resistant Staphylococcus aureus infections. There are some side effects of cloxacillin which include gastrointestinal manifestations like vomiting or diarrhea and different hypersensitivity reactions.[10] The quality assurance and quality control of active pharmaceutical ingredients and excipients is imperative in order to achieve better remedial effect and a lower toxicity. It is, therefore, necessary to develop simple, sensitive and efficient methods for determination of ampicillin and cloxacillin in pharmaceutical preparations. With increasing regulatory stringency on the control of drugs, variety of analytical methods has been developed to monitor impurities and degradation products in pure and commercial dosage forms.[11,12] It is noteworthy that several attempts have been made for the determination of ampicillin and cloxacillin either individually or in combination. High performance liquid chromatography has been used most frequently for analyzing ampicillin and cloxacillin in different matrices [9,22]. Capillary electrophoresis[13,24] has played a significant role in the analysis of β-lactam antibiotics. Other analytical methods reported in the literature include spectrophotometry [15,16], spectrophotometry [20-31], FT-IR [17], potentiometry [18,19], and voltammetry [32,33].

Circular dichroism spectroscopy is an excellent technique with a high degree of analytical selectivity and hence, it can be used for direct determination of optically active drugs. CD has two major advantages: (i) it is extremely sensitive to absolute configuration as well as to conformational features, which are often completely obscured in ordinary absorption spectrum [34], and (ii) a wide range of solvents can be used to study with relatively much smaller sample amounts. The degree of...
Synthesis, characterization, electrical and dielectric studies of AgCu1 and Co-SnO2 composite solid electrolytes

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ABSTRACT

The composite solid electrolytes of AgCu1 (SCI) and Co-SnO2 (CDS) were prepared by direct mixing method. The phase structure, composition, and surface morphology of the composites were explained by X-ray diffraction (XRD). Far infrared spectroscopy (FAR IR) and Scanning electron microscopy (SEM). AC impedance spectroscopy revealed that the ionic conductivity was effectively increased with the increase of temperature. Presence of a semicircle in the impedance spectrum shows the greater contribution of grain than the grain boundary. Addition of CDS particles enhanced the ionic conductivity of the composites, which reached a maximum value $\sigma = 129 \times 10^{-4}$ cm$^{-1}$ at room temperature for $x = 0.4$ composition. The dielectric values of the composite were gradually increased upon increasing the temperature, followed by a sharp change observed at 440 K. The electrical modulus of the sample was decreased with the increase of temperature and exhibits a single relaxation.

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1. Introduction

Composite solid electrolytes have attracted much attention from the perspectives of applications and scientific research, since these materials have some novel properties and functions distinct from those of the individual components [1–11]. These materials have to satisfy specific criteria for effective operation at low and moderate temperatures such as high ionic conductivity and ionic transport number, chemical and physical stability at the operating conditions, accessibility and low cost of raw materials and easy mass production. Therefore, they have various applications in electrochemical devices such as solid-state batteries, fuel cells, electrochromic devices and smart windows. The most common and simplest way to prepare a composite is to add some oxide into normal ion-conducting solid, to improve conductivity. This method was first reported by Liang in 1973 that the Li–Al2O3 composites have the lithium ion conductivity up to 12 times higher than that of pure Li10. Subsequently, a number of studies such as AgX (X = SiO2, Al2O3, TiO2), CaCl2/Al2O3, TiO2/X (Al2O3, TiO2), Li2SO4/Al2O3, Na2SO4/R2O3, and NH4PO4/SiO2 have been reported by various workers to explain this effect [12–17]. Although a detailed mechanism of these materials has not been clarified, it is considered that film interfacial layers generated in the heterogeneous system act as the additional source of point defects, resulting the enhancement in ionic conductivity [16–17]. The crystal lattices of the pure Ag and Cu resemble each, and forms complete solid solution. The structure and phase diagram of mixed system has been extensively studied experimentally by various workers and it has been observed that Ag1–xCu1x (0 < x < 0.5) undergoes a phase transition in temperatures between 430 K and 660 K change into the most probable α-form (amorphous form FCC structure) crystal structure [18–19]. Various properties such as high temperature phase structure, phase transition, conductivity, ionic transport number and intrinsic parameter defects of Ag1–xCu1x based solid solutions and glasses have been reported in literature by various investigators [20–24]. In this work, a series of SCI/CDS composite system was prepared by direct mixing method. The as prepared composite was confirmed through XRD, FAR IR and SEM analysis. The investigation about dependence of the conductivity, dielectric and modulus properties over the temperature was discussed in detail. It has good thermal stability and high conductivity indicating that the composite might have great importance from both fundamental and industrial points of view.

2. Experimental

2.1. Sample preparation

In this typical procedure to prepare the SCI solid solution, a drop wise addition of required molar aqueous solutions of Ag and Cu nitrates (having the ratio of 2:1 in 100 ml), under continuous and vigorous stirring, into a 2–5% excess solution of KI at 80 °C, causing
Preparation, characterization, electrical conductivity and dielectric studies of Na$_2$SO$_4$ and V$_2$O$_5$ composite solid electrolytes

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**ABSTRACT**

Composite solid electrolytes (1 - x) Na$_2$SO$_4$ - x V$_2$O$_5$ were prepared and characterized by various techniques such as XRD, FT-IR, DTA and SEM. AC impedance spectroscopy revealed that the contribution of grain is strong enough over the grain boundary. Arrhenius plot of the Na$_2$SO$_4$ shows a sharp increase in conductivity at 253 K due to the structural phase transition (phase V $\rightarrow$ I). Composites show the enhanced ionic conductivity than the pristine Na$_2$SO$_4$ over the entire temperature range. The maximum conductivity is 3.03 S cm$^{-1}$ at 773 K with the lowest activation energy of 0.28 eV was observed for the x = 0.4 sample. The enhanced value of dielectric constant and dielectric loss in the case of composites was obtained because of increase of conductivity, resulted from the increase of space charge polarization and charge motion.

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1. Introduction

As far as the search for new solid electrolyte is concerned, composite solid electrolyte is a class of material that focuses not only the improvement at room temperature conductivity but also chemical stability and favorable mechanical properties [11, 12]. Typically, dispersion of minute or submicron size of inert and insulating particles such as Al$_2$O$_3$, SiO$_2$, CeO$_2$, ZrO$_2$ and SnO$_2$ into normal ionic conductors like CaF$_2$, Li$_2$SO$_4$, AgI and AgBr leads to the formation of composites. The insulating oxide particles displayed less solubility with the salt and their interaction formed amorphous type interfaces [13]. Such type of interface itself has the capacity to increase the mobile ion concentrations that supplies the unusual bulk properties from both fundamental and applied aspects, especially in the applications for intermediate temperature fuel cells and batteries [10, 12]. The conduction mechanism of polyanphosphate (composite) materials can also be understood by the anisotropy of boundaries that explain the transport along and across the interfaces. The enhancement in ionic conduction along the interfaces can be observed for two reasons. First one the interface core itself is a disordered region where defects formation and migration of energies are especially reduced and another is the defects and dopant interactions with interfaces that induces concentration profiles of point defects near the interface in ionic materials (space charge layers). The concentration profiles of mobile charge carriers adjacent to interfaces are because of thermodynamic defect equilibrium [14]. The conductivity enhancement at interface is mainly due to the presence of high conducting space charge regions [14]. It strongly depends on different factors such as ionic salts, heterogeneous components and their interfaces [15]. The composite solid electrolytes based on Na$^+$ ions have received great importance in electrochemical cells and batteries applications. The composite solid electrolyte based on Na$_2$SO$_4$ was successfully studied and examined by various
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Enhanced ionic conduction of CdI₂–Ag₂CrO₄ and Al₂O₃ composite solid electrolytes

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(Prof. S. Tabassum)
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Structural, electrical conductivity and dielectric behavior of Na$_2$SO$_4$–LDT composite solid electrolyte

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A B S T R A C T

A series of composite materials of general molecular formula (1 - x) Na$_2$SO$_4$ - x LDT was prepared by solid state reaction method. The phase structure and functionalization of these materials were defined by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) respectively. Differential thermal analysis (DTA) revealed that the hump of phase transition at 250 °C has decreased while its thermal stability was enhanced. Scanning electron microscopy signifies the presence of improved rigid surfaces and interphases that are accountable for the high ionic conduction due to dispersion of LDT particles in the composite systems. Arrhenius plots of the conductance show the maximum conductivity, $\sigma = 4.56 \times 10^{-2}$ S cm$^{-1}$ at 500 °C for the $x = 0.4$ composition with the lowest activation energy 0.34 eV in the temperature range of 573 – 773 K. The value of dielectric constant was decreased with increasing frequency and follows the usual trend.

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Introduction

Fabrication of composite solid electrolytes having mesoscale interface is an attractive approach for the development of high performance ionic conductors both in fundamental and application point of view [1–3]. The absence of electrolyte leakage, light weight, ease of roll–roll fabrication and improved safety makes the composite solid electrolyte as a suitable candidate for the batteries and electrochemical cells [4]. Dispersion of submicrometer insulating oxide particles such as Al$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$, TiO$_2$ and ZrO$_2$ is a well known technique to enhance the transport characteristics as well as the thermal and mechanical properties of the several modest ionic conductors at room temperature [3–10]. Generally, ionic conductivity of the solid electrolytes varies with the particle size, concentration and type of the dispersoids. If the particle size of inert component is relatively large then the effect is described satisfactorily by the space charge model [11,12]. If the size of particle of inert component is so small i.e. less than 100 nm then the heterogeneous doping can lead to a significant change in the bulk properties of ionic salts [13]. It has been proposed that the major cause of conductivity enhancement in the composites is due to the strong interaction between matrix and additives. This type of interaction supplies an unusual disordered
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Transport studies of ions across polystyrene based composite membrane: Evaluation of fixed charge density using theoretical models

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Synthesis of Phosphonated Poly(vinyl alcohol)-Based Composite Membrane: Effects of Counter and Co-Ions on Its Electrochemical Properties for Separation Applications

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Supporting Information

ABSTRACT: A new composite ion-exchange membrane of phosphonated poly(vinyl alcohol)-zirconium isodiphosphate (ppVA/ZIP) was synthesized by incorporating ZIP as an additive in organic polymer matrix with varying ratios to improve membrane performance. The membrane was characterized to prospect its application in technologies that require advanced ionic electrolytes. The membrane with 20% acid and 25% additive shows optimal results: good water uptake, thermal stability, transport properties, and high permselectivity (P). Membrane potential was calculated for aqueous solutions of NaCl, KCl, NaHCO$_3$, and KHCO$_3$ with varying concentrations (1 M to $10^{-4}$ M). Membrane potential, transport number, and mobility ratio followed the same trend NaCl > KCl > NaHCO$_3$ > KHCO$_3$. The membrane fixed-charge group was compared with theoretical models to better understand transport properties. Membrane potential and $P_i$ are the two important factors for various separation processes. We analyzed the two interconnected parameters governing $P_i$ of the membrane. First, the binding affinity of the counterions with polymer fixed-charge sites and, second, the electrostatic exclusion of co-ions due to different hydrated radii and charge density. Thus, with a good tendency to discriminate between counter and co-ions, the membrane serves to be the suitable candidate in separation technology.

1. INTRODUCTION

In recent past, composite membranes have drawn more interest in the arena of ion-exchange membrane for electrochemical separation and energy technologies because of their energy saving and eco-friendly nature. Poly(vinyl alcohol) membranes have applications mainly in the field of pervaporation, but its swelling in aqueous solution is a major concern. However, the use of acidic and basic polymer blend membranes can improve its property, and in this context, phosphonation of the membrane has shown positive effects on electrochemical and transport properties of the membrane. Improved thermal properties of PVA can be achieved with addition of a small amount of a mineral acid, preferably phosphoric acid.

Although PVA has excellent biocompatibility, chemical resistance, and gas barrier properties, the poor mechanical integrity and low water retention behavior forced the incorporation of inorganic fillers. The inorganic fillers increase various properties of the polymer due to their reinforcement effect when they are well-dispersed as they provide additional pathways for transport by promoting protonation-deprotonation. Nowadays, metal phosphates serve as a promising candidate for fillers. Thus, phosphonated PVA-inorganic composite ion-exchange membranes attracted our attention as they show good thermal stability, easy film formation, and controllable electrochemical properties, and they have C-OH groups attached to its chain that can be easily modified for diverse applications. Composite membranes also have applications in the area of material science, heterogeneous catalysis, separation science, and fuel cells.

Separation membranes are an indispensable part of our daily life because of their diverse applications in food and...
Solid electrolytes are a class of solids which show high ionic conductivities despite their rigid structure. These materials are characterised by their high ionic conductivities with a similar order of magnitude to that usually found in molten salts. Composite solid electrolytes are prepared by mixing two or more conducting solids. Polymer solid electrolytes refer to the polymeric systems which enable efficient ion migration even in the solid state—comparable to that in the solution state. Polymer electrolytes are ion-conducting materials with values of ionic conductivity as high as $10^{-3}$ S/cm or more. This research studied polymer-based composite solid electrolytes, where polyaniline doped with sodium sulfate was used. Different compositions based on sodium sulfate concentrations ranging from 25 to 90% (by weight) were studied over the temperature range of 50-300°C by using techniques such as scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and impedance spectroscopy. The observed conductivities lie in the range of $10^{-4}$-$10^{-1}$ S/cm. Maximum conductivity was observed for the composition 50:50, which showed an activation energy of 0-12 eV.

1. Introduction

Solid electrolytes are a class of solids which show high ionic conductivities despite their rigid structure. Their ionic conductivities are of the same order of magnitude as the ionic conductivities usually found in molten salts. In solid electrolytes, the high ionic conductivity is due to the movement of one kind of ion between sites provided by the amobile ion sublattice. Composite solid electrolytes are prepared by mixing two or more conducting solids. Polymer electrolytes are solid solutions of alkali metal salts in polymers (not to be confused with polymeric electrolytes, in which either the cation or the anion is covalently linked to the polymer repeat unit). Solid polymer electrolytes (SPEs) usually show lower ionic conductivities, but they have high mechanical strength and can be applied as thin films. The applicability of polymer electrolytes as thin films opens their area of applications and practical use. The interest in polyaniline (Pani) as an important conducting polymer has increased significantly over the past decade, resulting in a number of review articles published a few years ago. This research studied the electrical properties of heterogeneously doped Pani. The concept of doping is the most important concept in conducting polymers, and it distinguishes intrinsically conducting polymers from all other types of polymers. By treatment of the neutral form of a polymer with small quantities of chemical species, the electronic, electrical, magnetic, optical and structural properties of the polymer changes dramatically. The electrical conductivity of a doped material is typically about five to ten orders of magnitude higher than that of a non-doped material. It should be noted that doping and dedoping are generally reversible processes which do not change the chemical nature of the original polymer backbone. Use of sodium sulfate (Na$_2$SO$_4$) as a solid electrolyte was first demonstrated by Jacob and Rao in a sulfur dioxide (SO$_2$)-oxygen (O$_2$)-sulfur trioxide (SO$_3$) concentration cell in place of potassium sulfate (K$_2$SO$_4$). Sodium sulfate was preferred because of its higher stability and electrical conductivity over potassium sulfate. This research studied the effect of the addition of Pani to sodium sulfate solid electrolyte and the resulting changes in its electrical and structural properties. Polymer electrolytes are known to exhibit conductivity in both crystalline and amorphous phases. Conventionally, an SPE comprises one or more conducting (or sometimes non-conducting) polymers and an ionic salt with a fairly high conductivity. Other modifications can also be included in order to enhance conductivity further, by using a common organic solvent or a filler. The organic solvent serves as a medium for the efficient mixing of the organic polymer and inorganic ionic salt, while the filler provides a structural backbone to the SPE for better...
Volumetric, compressibility and viscosity studies of binary mixtures of [EMIM][NTf₂] with ethylacetate/methanol at (298.15–323.15) K

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ABSTRACT

Densities, speeds of sound and viscosities of pure and binary mixtures 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [EMIM][NTf₂] + ethyl acetate; methanol have been measured experimentally over the entire composition range and at six temperatures from 298.15 K to 323.15 K at pressure 0.1 MPa using Anton Paar Density and Sound velocity meter DSA 5000 M and Louis microviscometer 2000 M. From these experimental data, the excess molar volumes (vₑ) viscosity deviations (Δυₑ) and isentropic compressibility deviations (Δkₑ) have been evaluated. The vₑ values are negative for [EMIM][NTf₂] + ethyl acetate system up to xₑ = 0.00 and positive above this xₑ value at all temperatures of study. However, the vₑ values are negative for [EMIM][NTf₂] + methanol system at entire mole fraction range and at all temperatures. The vₑ values in both studied systems decrease with increase in temperature. The Δυₑ and Δkₑ are found to be negative over the entire range of mole fraction and decrease with increasing temperature in both binary systems. The computed data of vₑ, Δυₑ and Δkₑ have been correlated with Redlich-Kister polynomial equation. The measured and computed data have been interpreted in terms of ion-dipole, ion-ion and dipole-dipole interactions and structural effects between like and unlike molecules upon mixing. The experimental data of vₑ have also been used to examine the applicability of Prigogine-Flory-Patterson (PFP) theory in predicting the vₑ of the binary systems. The minimum and maximum percent deviations of experimental and calculated by PFP vₑ values are 0.017 and 3.01 for [EMIM][NTf₂] + ethyl acetate and 1.19 and 2.10 for [EMIM][NTf₂] + methanol systems, respectively.

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1. Introduction

Ionic liquids (ILs) are considered as potential substitutes to organic solvents in reactions and separation processes [1–5]. The potential applications of ionic liquids are mainly founded by their unique properties such as negligible vapour pressure, wide temperature range for the liquid state, high thermal and electrochemical stability, high solvating power, non-flammability, high density and high polarity [6–9]. The main applications of ILs are in chemical processing and fine chemicals as solvents for organic, organo-metallic syntheses, homogeneous and heterogeneous catalysis, in electrochemistry and electrolysies, in polymers and biopolymers, in metal processing, in engineering and functional fluids, and separation processes [10–13]. Besides these, ILs are also applicable for the stationary phase in chromatography, supporting immobilization of enzymes, in separation technology, liquid crystal templates in the synthesis of mesoporous, nano-materials and ordered films, materials for embalming and tissue preservation [13–15]. Thermodynamic studies of mixtures of ionic liquids with the organic solvents are of relevance both for understanding their solution behavior and providing data for various industrial applications. Moreover, a detailed knowledge of the thermophysical properties of ILs mixtures are also important in relating microscopic and macroscopic behavior of ILs. The design of technological processes also requires in-depth knowledge on thermodynamic and transport properties of ionic liquids and their mixtures. The addition of a co-solvent may improve the properties of ionic liquids for their applications in various chemical processes. Therefore, the measurements of thermophysical properties of mixtures of ILs with organic solvents are rapidly gaining importance [16–17]. Despite the importance and applicability of ionic liquids and molecular solvents mixtures, the accurate and extensive studies of their fundamental physical and chemical properties are scarce or even not present. Studies on physical and chemical properties of ionic liquids, property measurement methodology, high-quality data on reference systems, standards for reporting thermodynamic data and the creation of a comprehensive database have been promulgated by NIST [18], IUPAC [19] and DDB (the Dortmund Data Bank) [20]. The ionic liquid containing imidazolium cation has been chosen in this study because it is among the most promising ion for applications despite its cost and its somewhat poor chemical stability in the presence of impurities. We have, thus undertaken the study of the thermophysical properties of a possibly green solvent, namely, the ionic liquid containing the popular cation 1-ethyl-3-methylimidazolium ([EMIM]+) with the anion bis(trifluoromethanesulfonyl)imide ([NTf₂]−). Due to its low viscosity...
Interaction of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with methanol/dimethyl sulfoxide at (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K: Measurements and correlations of thermophysical properties

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Abstract

Densities, speeds of sound and viscosities of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + methanol/dimethyl sulfoxide mixtures have been measured experimentally over the entire composition range and at six temperatures, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K, under 0.1 MPa pressure using Anton Paar density and sound velocity meter DSA 5000 M and Liova microviscometer 2000Mr. From these experimental data, the excess molar volumes, \( V^E \), enthalpic compressibility deviations, \( \Delta S_h \), and the viscosity deviations, \( \Delta n \), have been evaluated. The computed data have been adequately fitted to the Redlich–Kister polynomial equation. The measured and computed data have been interpreted in terms of ion–dipole interactions and structural effects between like and unlike molecules upon mixing. The \( V^E \) results have been correlated to the Prigogine–Flory–Patterson (PFP) theory. The experimental and PFP correlated values are quite close to each other.

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1. Introduction

Ionic liquids exhibit unique physical properties such as negligible vapor pressure, low melting point, a wide liquid range, suitable viscosity and high thermal stability. They are good solvents for both polar and non-polar organic and inorganic substances, good electrical conductor, and have wide electrochemical windows, which suggest many applications as green and possibly benign replacements for traditional volatile organic solvents [1,2]. They have wide commercial applications namely as lubricants, as catalysts, as electrolytes, as solvents for reactions, in azotropic and extractive distillations and absorption media for gases [3]. The physicochemical properties of ionic liquids can be finely tuned by slight structural changes of the corresponding cations and anions [4,5]. Due to their combined low viscosity, broad temperature range of liquid stability, and absence of halogen atoms in potentially chemically reactive forms, the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ([BMIM][NTf2]) is considered one of the most promising ionic liquid to become important in diverse applications [6]. Gadzuric et al. [6] reported the density, excess properties, electrical conductivity and viscosity of 1-butyl-3- methylimidazolium bis(trifluoromethylsulfonyl)imide + 2-butyl-2-oxazoline binary mixtures at temperatures (293.15 to 323.15) K and at atmospheric pressure over the whole composition range. Smith et al. [7] reported the densities at pressures up to 200 MPa and viscosities at atmospheric pressure and at (293-373) K. Lee et al. [8] reported the P–P–T properties of binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with n-propanol and acetophenone at elevated pressures over temperatures ranging from 298.15 to 348.15 K and pressures from (0.1 to 50) MPa. Rabello et al. [9] reported the densities, heat capacities and enthalpies of fusion of [BMIM][NTf2] within the temperature intervals (278.15 to 333.15) K.

The densities, (\( \rho \)), speeds of sound, (\( u \)) and viscosities, (\( \eta \)) of binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ([BMIM][NTf2]) with methanol/dimethyl sulfoxide, (DMSO) over the entire composition range and at temperatures (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K, and at \( P = 0.1 \) MPa have been measured in this study. The excess molar volumes (\( V^E \)), enthalpic compressibilities (\( \Delta S_h \)), isentropic compressibility deviation (\( \Delta S_h \)) and viscosity deviation (\( \Delta n \)) have been computed using measured data. The PFP theory has

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Synthesis, characterization, and crystal structure of RNA targeted L- and D-phenylalanine-(1,10-phen)-copper(ii) conjugate complexes: comparative in vitro RNA binding profile of enantiomers and their biological studies by morphological and antibacterial activity†

Surbhi Sharma, Loic Toupet, Musheer Ahmad and Farukh Arjmand

New ternary chiral Cu(II) complexes 1a and 1b derived from L- and D-phenylalanine and 1,10-phenanthroline were synthesized and characterized thoroughly by single crystal X-ray diffraction and other spectroscopic techniques viz. UV-vis, IR, EPR, ESI-MS and elemental analysis. The complexes crystallized in the monoclinic P2₁ space group, possessing the lattice parameters a = 5.7469(10) Å, b = 20.6365(2) Å, c = 9.2801(10) Å, α = γ = 90°, and β = 98.82(10)° in complex 1a, and a = 5.7283(9) Å, b = 20.587(5) Å, c = 9.252(5) Å, α = γ = 90°, and β = 98.30(8)° in complex 1b per unit cell, respectively. Comparative in vitro RNA binding studies of the L- and D-enantiomeric complexes 1a and 1b were carried out by a variety of optical spectroscopy techniques viz. UV-vis, fluorescence, and circular dichroism. Because copper is a redox metal ion, cyclic voltammetry was employed to evaluate the enantiopurestic RNA binding of the complexes. The results demonstrated that the L-enantiomer of Cu(II) complex 1a binds more strongly to the t-RNA motif than the D-enantiomer, thereby underlying the differential disposition of the enantiomers and the site preference of RNA for the L-enantiomer over the D-enantiomer. Furthermore, the comparative K_{d} and K_{a}, values of the L- and D-complexes demonstrated significant increases for the L-enantiomer of the copper complex 1a, in comparison to its D-enantiomeric form, 1b. SEM analysis divulged surface morphological alteration of complexes 1a and 1b, evidenced by the formation of hollow tubes and a concrete-like structure with the RNA condensate, which was less pronounced in SEM micrographs of the complex 1b condensate. Complexes 1a and 1b were evaluated by the agar well diffusion method and demonstrated significant antibacterial activity.

Introduction

The interaction of transition metal complexes with nucleic acids is one of the most interesting areas of bioinorganic chemistry and medicinal chemistry owing to the possible applications of these complexes as therapeutic agents for drug design,12 nucleic acid structural probes2 and artificial nucleases.2,13 Nucleic acids, particularly DNA and RNA, are primary targets for most drugs for treating infectious diseases,2,14 viz., HIV, AIDS, hepatitis C and cancer.2 RNA, particularly microRNA (miRNA), plays an indispensable role in various biological processes, including development, cell proliferation, differentiation and apoptosis. Thus, altered miRNA expression is likely to contribute to many human diseases, including cancer.10-12 RNA differs from CT-DNA not only in the composition of the bases but also in structure. CT-DNA has a B-form double-helical configuration with a wide major groove and a relatively narrow minor groove, while yeast t-RNA has an A-form conformation with an L-shaped tertiary structure (mainly unipolar), a deep major groove, and a wide, shallow minor groove. These differences are expected to lead to different binding modes and affinities.13-14

The in vivo structures of DNA and RNA are very different; whereas DNA typically remains in the helical double stranded form, RNA folds into diverse structures, adopting folds that are similar to proteins; this is responsible for its diverse functions in cells.15 The specific recognition of pockets available in RNA by suitable ligands, involving non-covalent binding usually
A comparative analyses of bioactive Cu(II) complexes using Hirshfeld surface and density functional theory (DFT) methods: DNA binding studies, cleavage and antibiofilm activities

Mohammad Usman *, Farukh Arjmand *, Musheer Ahmad b, Mohammad Shavez Khan c, Iqbal Ahmad c, Sartaj Tabassum a, b, c

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Highlights

- Copper(II) complexes have been synthesized and characterized by single crystal X-ray analysis and other spectroscopic techniques.
- B3LYP/DFT calculations have been carried out to elucidate the tentative assignments of N-Cu-N/O-Cu-O/O-Cu-N and other significant vibrational modes.
- Hirshfeld surface analyses to explore H-bonding, C-H/π and Cu...H–C interactions.
- Copper complexes damaged pBR322 plasmid DNA by oxidative pathway via ROS species viz., O₂⁻, ¹⁰₂ etc.
- Antibiofilm activity was evaluated against E. Coli 25922.
Estimating the Richardson-Zaki index n for non-spherical irregular natural sediments in a concentrated suspension

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English Abstract
The hindered settling velocity (uh) of the particles is considered as a part of the terminal (free) settling velocity (ut). Richardson and Zaki investigated this relation and derived an equation known as R and Z formula \((n \times u_{h} = u_{t})\) for spherical particles. Currently work is modified the R & Z index n to become suitable for nonspherical irregular natural sediments that settled in concentrated suspension known as palm oil mill effluent (POME). Aspect ratio (AR) adopted as a shape factor to determine the particle diameter. The n-indexes modified at different Reynolds number (Re) taking into consideration the wall effect (λ). The obtained results shows that the index n for non-spherical irregular particles has close values of index n for the spherical particles in comparison to the previous published data.

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Kinetics and thermodynamic studies of phenol adsorption on nanocomposite

Meraj Alam Khan & Anees Ahmad

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Abstract

An inorganic–organic hybrid nanocomposite materials has been used as a stable extractor for the removal of phenol and characterized using Fourier transform infrared (FTIR), and scanning electron microscopy (SEM) analyses. Batch adsorption experiments were employed to study the main parameters of kinetic study under various conditions (e.g. contact time, solution pH, initial metal ion concentration, temperature etc.). The most favourable pH for the optimum sorption of phenol was found to be 3–5. Langmuir and Freundlich isotherms were tested to describe the adsorption mechanism. The monolayer adsorption capacity of polyaniline Sn(IV) silicophosphate (PTSP) for phenol was found to be 3.76, 5.58 and 8.2 µg g⁻¹ at 30, 40
Supercritical carbon dioxide extraction of essential oils from leaves of *Eucalyptus globulus* L., their analysis and application†

Aarti Singh, Anessa Ahmed and Rani Bushra

Author affiliations

Abstract

A comparative study on the extraction of essential oil from the leaves of *Eucalyptus globulus* was conducted using traditional methods such as hydrodistillation (HD), solvent extraction (SE), ultrasonic-assisted extraction (UAE) and an innovative supercritical carbon dioxide (SC-CO₂) extraction technique. Each oil was evaluated by HPTLC (high performance thin layer liquid chromatography) and FTIR (Fourier transform infrared spectroscopy) fingerprinting with qualitative and semi-quantitative composition of the isolated essential oil determined by gas chromatography–mass spectrometry (GC–MS). The yield of essential oil was found to be 2.0%, 2.2%, 2.6% and 3.6% v/w, via HD, SE, UAE and SC-CO₂, respectively. A total of 53 compounds were identified by GC–MS. Comparative studies have shown that the SC-CO₂ technique is favourable for the extraction of monoterpene, sesquiterpene and oxygenated sesquiterpene hydrocarbons. HD, SE and US techniques are also important in the extraction of aliphatic saturated hydrocarbons, organic acids and esters. The maximum separation of compounds was observed at 254 nm by HPTLC fingerprinting. The present research paper covers different extraction methods, which may lead to different yields of essential oils; this further shows that the choice of the appropriate extraction method is very important to obtain the desired components in products with

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Development of PANI/MWCNTs decorated with cobalt oxide nanoparticles towards multiple electrochemical, photocatalytic and biomedical application sites†

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In the present work, a ternary nanocomposite of Co3O4-doped/PANI/MWCNTs (cobalt oxide-doped polyaniline multi-walled carbon nanotubes) was synthesized via the in situ oxidative polymerization of aniline. The composite was fully characterized using instrumental analysis, and further tested for its potential in electrochemical, photocatalytic and biomedical applications. The Co oxide nanoparticles were first synthesized using the sol–gel approach in the presence of starch as a capping agent so as to prevent agglomeration and characterized using Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), EDX, elemental mapping and high-resolution transmission electron microscopy (HRTEM). For the measurement of electrochemical activity, the electrodes were synthesized with MWCNTs and functionalized with a conducting polymer (PANI). For the composite, the Co metal oxide provides a pseudo-capacitance which, in general, improves the performance characteristics of the electrode and has been the focus of many researchers. Furthermore, the specific capacitance of the prepared composite was tested using cyclic voltammetry (CV) and impedance spectroscopy. The capacitive studies reveal that the composite has a synergistic effect and is observed to have the highest specific capacitance of 382 F g−1 run at a scan rate of 1.0 mV s−1. The composite was also found to have excellent photocatalytic degradation properties and outstanding antibacterial activity against both Gram positive and Gram negative bacterial strains. The minimum MIC (6.25 µg ml−1) and MBC (12.5 µg ml−1) values against E. coli and maximum values against B. amyloliquefaciens (25 and 50 µg ml−1) at fourth dilution were observed. Furthermore, the anticancer efficiency of the composite was tested by making use of two different cancer cell types (MCF-7 and MDA-MB-231) confirming the importance of its biological activity for biomedical applications.

1. Introduction

In recent years, many nanomaterials with exceptional properties have been developed in the nanotechnology sector and one among them, multi-walled carbon nanotubes (MWCNTs), as a single nanostructure or as a nanocomposite, has received significant attention in this field. The development of CNT-based composites has become a major topic of interest for researchers around the world.† With their distinctive structure and extraordinary properties MWCNTs are extensively used in electronic devices, solar cells, hydrogen storage materials and supercapacitors, to mention a few.† Also, the inclusion of MWCNTs can certainly improve the electrochemical reactivity of biomolecules and also promote the electron transfer of red-ox reactions in electro-polymerisations. Further, the high surface to volume ratio of MWCNTs provides a large number of nucleation centers which makes them promising sorbents for the removal of toxic contaminants from the environment. This property of MWCNTs is responsible for their high sorption efficiency and enhancement of catalytic activity.† In addition, the MWCNTs can also be successfully employed for exhibiting strong biological activity against bacterial spores, Gram positive and
Research Article


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Cauliflower leaf powder (CLP), a biosorbent prepared from seasonal agricultural crop waste material, has been employed as a prospective adsorbent for the removal of a basic dye, methylene blue (MB) from aqueous solution by the batch adsorption method under varying conditions, namely, initial dye concentration, adsorbent dose, solution pH, and temperature. Characterization of the material by FTIR and SEM indicates the presence of functional groups and rough coarse surface suitable for the adsorption of methylene blue over it. Efforts were made to fit the isotherm data using Langmuir, Freundlich, and Temkin equation. The experimental data were best described by the Freundlich isotherm model, with an adsorption capacity of 169.22 mg/g at room temperature. To evaluate the rate of methylene blue adsorption onto CLP, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were employed. The experimental data were best described by the pseudo-second-order kinetic model. Evaluation of thermodynamic parameters such as changes in enthalpy, entropy, and Gibbs’ free energy showed the feasible, spontaneous, and exothermic nature of the adsorption process. On the basis of experimental results obtained, it may be concluded that the CLP prepared from agricultural waste has considerable potential as low-cost adsorbent in wastewater treatment for the removal of basic dye, MB.

1. Introduction

The increasing demand for commercial dyes by various industries leads to the vast production of dyes. Over 100,000 commercial dyes are available and more than 7 × 10^6 tons are produced annually, of which a significant portion is being discharged directly into the aqueous media [1, 2]. In developing nations, environmental pollution, particularly water pollution, which arises due to the discharge of unprocessed industrial effluents into main water streams is of major concern. These effluents containing dyes and pigments are regularly discharged into the natural water bodies by industries like food, textile, cosmetics, rubber, plastics, paper, pharmaceutical, and so forth. These dyes have so many adverse effects not only on the aquatic flora and fauna but also on the human health. Large water bodies can be colored even with small quantities of dyes, which not only affect visual quality but also diminish light penetration and photosynthesis. Many of these dyes are of toxic nature and have cancer-causing and mutagenic effects. So the effluents containing these coloring agents have to be removed appropriately earlier that they are discharged into the aquatic forms [3, 4]. Among these dyes, methylene blue (MB) is frequently used coloring substance for dyeing cotton, wood, and silk. Although methylene blue is not so harmful, it can cause harmful effect upon inhalation. Severe contact to methylene blue can cause increased heart rate, vomiting, tremor, Heinz body formation due to damage of hemoglobin component, cyanosis or blue disease, jaundice, quadripelgia, and tissue necrosis in humans [5], while ingestion through the mouth creates a hot feeling causing nausea, diarrhea, and gastric problems. Accidental large dose creates pain in abdomen and chest and head, abundant sweating, mental confusion, painful micturition, and methemoglobinema [6]. This shows the necessity for effective removal of
Redetermination of diaqua[N,N'-bis(3-methoxy-2-oxidobenzylidene)ethylenediamine-κ⁻O,N,N',O']-manganese(III) perchlorate at 100 K

Shabana Noor, Rüdiger W. Seidel, Richard Goddard, Sarvendra Kumar and Suhail Sabir

Keywords: crystal structure; redetermination; Jahn–Teller effect; manganese(III) coordination complex.

CCDC reference: 1512691

Structural data: full structural data are available from icrdata.iucr.org

The crystal structure of the organic–inorganic title salt, [Mn(C₁₈H₁₆N₂O₄)·(H₂O)₂]ClO₄, has been redetermined at 100 K. In contrast to the crystal structure determinations at room temperature [Akitsu et al. (2005). Acta Cryst. C61, m324–m328; Bermejo et al. (2007). Eur. J. Inorg. Chem. pp. 3789–3797], positional disorder of the ethylene bridge in the Schiff base ligand and the perchlorate anion is not observed at 100 K. The Mn(III) ion is six-coordinated with the tetradentate Schiff base chelate ligand N₂N'-bis(3-methoxy-2-oxobenzylidene)ethylenediamine occupying coordination sites in the equatorial plane and the aqua ligands residing in the two axial positions. The octahedral coordination sphere of the Mn(III) ion exhibits an axial elongation due to the Jahn–Teller effect, which is characteristic of a d⁷ high-spin electronic configuration.

Structure description

Transition metal complexes of Schiff bases show an interesting chemistry, including various aspects of organometallic and bioinorganic chemistry (Yamada, 1999). Schiff base complexes find application in a variety of catalytic transformations as they have the ability to coordinate to metal ions and stabilize unusual oxidation states. Metal complexes containing salen-type Schiff bases are important owing to their resemblance to metalloproteins with respect to their electronic structure and catalytic activities in the way that they mimic enzymatic oxidations (Groves, 2005). Interest in the coordination chemistry of manganese complexes in high oxidation states is largely centred on the...

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Synthesis of CdS nanoparticles using different sulfide ion precursors: Formation mechanism and photocatalytic degradation of Acid Blue-29

Nida Qutub, Bilal Masood Pirzada, Khalid Umar, Suhail Sabir 9, 89

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Abstract

Cadmium sulphide (CdS) nanoparticles were synthesized by different combinations of chemical precursors using H₂S, Na₂S and (NH₄)₂S as sulphide ion sources. The reactions were carried out by a single pot chemical precipitation method under ambient conditions. The X-ray diffraction (XRD) patterns obtained for the synthesized nanoparticles (NPs) were used to determine their crystal structure and the crystallite size. The average particle sizes of the synthesized nanoparticles were determined by transmission electron microscopy, UV–vis spectra and XRD techniques. Electron dispersive spectroscopy and Fourier transform infrared spectroscopy were used to investigate the purity of the synthesized CdS nanoparticles. The smaller particle size for CdS was obtained with Na₂S, followed by H₂S and (NH₄)₂S and that the quantization in the band gap was directly in correlation with decreased particle size effects. In addition, mixed phase of wurtzite–zinc blende was synthesized with H₂S, while phase pure zinc blende and wurtzite phase was obtained with Na₂S and (NH₄)₂S, respectively. The series of synthesized CdS nanoparticles were exploited for photocatalytic degradation of an organic dye derivative, Acid Blue-29, under visible light and the effect of different precursor combinations on photocatalytic efficiency was analysed. An increase in photocatalytic rate was observed by the decrease in particle size on using different sulfide ion precursors, which can be attributed to the increase in the catalyst surface.


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A highly efficient visible-light-driven novel p-n junction \( \text{Fe}_2\text{O}_3/\text{BiOI} \) photocatalyst: Surface decoration of \( \text{BiO} \) nanosheets with \( \text{Fe}_2\text{O}_3 \) nanoparticles

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ABSTRACT

Novel \( \text{Fe}_x\text{BiO}_1(y=0.25, 0.35, 0.45 \) molar ratios\( ) \) with a p-n heterojunction were prepared for the first time through an in situ hydrolysis method under solvothermal conditions. The phase, structure, morphology and optical properties of the composites were studied using several characterization tools including X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), Fourier transform infrared (FTIR), N\(_2\) adsorption-desorption isotherms (BET), and UV–vis diffuse reflectance spectroscopy (UV–DRS). The characterization results suggest square shaped nanosheets of \( \text{BiO} \) with \( \text{Fe}_2\text{O}_3 \) nanoparticles well distributed on the surface of \( \text{BiO} \) nanosheets. The photodegradation performances of the \( \text{Fe}_x\text{BiO}_1 \) samples were investigated using aqueous solution of Rhodazine B (RHB) dye. The \( \text{Fe}_x\text{BiO}_1 \) composites displayed much higher photocatalytic efficiencies for RHB degradation than the single \( \text{BiO} \) under visible light \( (\lambda > 400 \text{ nm}) \). Specifically, the degradation rate of \( \text{Fe}_x\text{BiO}_1 \) samples at molar ratio of 0.35 is 4.24 times higher than single \( \text{BiO} \). The novel \( \text{Fe}_x\text{BiO}_1 \) heterojunction was found to be highly stable in cyclic experiments. Based on the results of BET, PL and DRS analysis, the enhanced photocatalytic efficiency can be mainly ascribed to the formation of stable p-n heterojunction between \( \text{Fe}_2\text{O}_3 \) and \( \text{BiO} \), which facilitates the transfer and separation of photogenerated electron–hole pairs.

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1. Introduction

In recent years heterogeneous photocatalysis has been considered as a promising process for the degradation of organic pollutants in waste water and air. Extensive efforts towards environmental purification and solar energy conversion have been made by development of highly efficient photocatalysts. The most studied semiconductor photocatalyst till date is \( \text{TiO}_2 \). It has high stability, low cost and is also non-toxic but the main drawback with \( \text{TiO}_2 \) is that it can absorb only 4% of the total spectrum because of its large band gap of 3.2 eV [1–3]. Since the discovery of \( \text{TiO}_2 \) by Honda and Fujishima [4], the development of visible light driven photocatalysts has attracted massive research interest for effective utilization of solar energy.

Up to now, many novel and highly effective visible light responsive photocatalysts have been developed. Among them bismuth based series of novel layered ternary oxides such as \( \text{BiOX} (\text{X} = \text{Cl}, \text{Br}, \text{I}) [5–9] \), \( \text{Bi}_2\text{Ti}_2\text{O}_7 \) [10–12], \( \text{Bi}_2\text{WO}_6 \) [13–15], \( \text{BiVO}_4 \) [16, 17], \( \text{Bi}_2\text{O}_3 \) [18], \( \text{BiNbO}_4 \) [19], and \( \text{Bi}_2\text{Mo}_6\text{O}_{17} \) [20], have received much attention because of their excellent photocatalytic performance and intriguing electronic structure.

An attractive p-type semiconductor with fermi level close to the valence band possess a layered structure consisting of \( \text{Bi}_2\text{O}_3 \) slabs separated by double slabs of halogen atoms [21–26]. \( \text{BiO} \) has a band gap of 1.78 eV which makes it to exhibit strong photoresponse in visible light region [27]. However, by itself, \( \text{BiO} \) shows poor photocatalytic activity due to high racombination rate of photogenerated electron–hole pairs [28, 29]. Since \( \text{BiO} \) is a typical p-type semiconductor [30, 31], therefore to facilitate the separation of photoinduced charge carriers, it is extremely fit to couple it with n-type semiconductor which will result in the generation of internal electric field. \( \text{BiO} \) has been previously selected to couple with n-type \( \text{TiO}_2 \) [32, 33], \( \text{ZnSnO}_3 \) [34], \( \text{ZnTiO}_4 \) [35], \( \text{ZnSnO}_4 \) [36], etc. We therefore choose n-type \( \text{Fe}_2\text{O}_3 \) to couple with p-type \( \text{BiO} \). To the best of our knowledge no efforts have been made till date to couple p-type \( \text{BiO} \) with n-type \( \text{Fe}_2\text{O}_3 \). We choose to couple \( \text{Fe}_2\text{O}_3 \) with \( \text{BiO} \) based on following advantages [37–43].

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ORIGINAL ARTICLE

Antimicrobial Agents from Selected Medicinal Plants in Libya

Hasan MH Muhaisen, Mutlah Malailoud Ab-Mous, Fadel A Ddeeb, Aboclaid Ali Rami, Omer M Tabaa, and Mehtab Parveen

ABSTRACT Objective: To test the in vitro antimicrobial efficacy of water and methanol extracts of 23 plant species that are commonly used in Libyan folk medicine. Methods: The antimicrobial activity was determined using the well-diffusion method. Four test microorganisms were used namely, Escherichia coli, Salmonella species, Staphylococcus aureus and Bacillus subtilis. The minimum inhibitory concentration (MIC) was determined for the high biologically active crude plant extracts. Results: Among 23 medicinal plants used in the study, only 5 methanolic extracts (Rosmarinus officinalis L. Carduus marianum L. Lantana camara L. Rhus tripartite (vera) Grande, and Thymus capitatus (L.) Hoffm (link)) showed the highest antimicrobial activity against Staphylococcus aureus, Bacillus subtilis and Salmonella species, while 22 methanolic and aqueous extracts showed moderate to weak antimicrobial activity on all tested organisms. However 19 of the extracts showed no activity at all against Gram-ve and Gram +ve microorganisms. MIC was found to be 1.25 mg/mL (Thymus capitatus), 3 mg/mL (Rhus tripartite), 4 mg/mL (Carduus marianum), 5 mg/mL (Rosmarinus officinalis) and 5 mg/mL (Lantana camara), respectively. Conclusions: The present results revealed that, crude methanolic extracts of the investigated Libyan folk medicinal plants exhibited mild to high in vitro antibacterial activities against Gram-positive and Gram-negative microorganisms.

KEYWORDS medicinal plant extracts, antimicrobial activity, minimum inhibitory concentration, Libyan folk medicine

Nature has been a source of medicinal agents for thousands of years and an impressive number of modern drugs have been isolated from natural sources, many based on their use in traditional medicine. Today it is estimated that more than two thirds of the world's population relies on plant derived drugs, some 7,000 medicinal compounds used in the Western pharmacopoeia are derived from plants. In USA approximately 25% of all prescription drugs used contain one or more bioactive compounds derived from vascular plants. However, fewer than 10% of the world's plant species have been examined for the presence of bioactive compounds. Hence screenings of antimicrobial plants for new agents poses an enormous challenge and are important especially with the emergence of drug resistant disease strains. It is valuable to screen ethno-medicinal plants commonly used by Libyans for their antimicrobial potentials to disclose which of them might be useful for curing infectious diseases based on analytical basis.

Recently much attention has been paid to extracts and biologically active compounds isolated from plant species and analyze their pharmacological activities. Antimicrobials of plant origin have enormous therapeutic potential; they are effective in the treatment of infectious diseases while simultaneously mitigating many of the side effects that are often associated with synthetic antimicrobials.

Infectious diseases caused by bacteria, fungi, viruses and parasites are still a major threat to public health, despite the tremendous progress in human medicine. Extracts from Citrus aurantium (Rutaceae), Punica granatum (Punicaceae), Phyllanthus acidus (Euphorbiaceae) and Tamarindus indica (Caesalpinaceae) possess strong in vitro antibacterial activity against many microorganisms. The recent appearance of bacterial strains with reduced susceptibility to antibiotics raises the specter of untreatable bacterial infections and adds urgency to the search for new infection-fighting strategies.

In the present investigation, the antimicrobial potential of 23 medicinally important plants Artemisia campestris (L.) Compositae, Artemisia herba-alba (alba)
Microwave-assisted green synthesis of silver nanoparticles from *Fraxinus excelsior* leaf extract and its antioxidant assay

Mehtab Parveen1 · Faheem Ahmad1 · Ali Mohammed Malla1 · Shaista Azaz1

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Abstract The biosynthesis of nanoparticles has been proposed as a cost effective and environmentally benevolent alternative to chemical and physical methods. In the present study, microwave assisted synthesis of silver nanoparticles (AgNPs) has been demonstrated using leaf extract of *Fraxinus excelsior* reducing aqueous AgNO3 solution. The synthesized nanoparticles have been characterized on the basis of fourier transform infrared spectroscopy (FT-IR), UV–Vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis. The presence of a characteristic surface plasmon resonance (SPR) absorption band at 425 nm in UV–Vis reveals the reduction of silver metal ions into silver nanoparticles. FT-IR analysis was carried out to probe the possible functional group involved in the synthesis of AgNPs. Further leaf extracts and AgNPs were evaluated for antiradical scavenging activity by 1,1-diphenyl-2-picryl-hydrazyl (DPPH) assay.

Keywords Microwave · Biosynthesis · *Fraxinus excelsior* · Silver nanoparticles · Antioxidant activity

Introduction

Exploitation of biological materials in synthesis of nanoparticles is one of the hottest thrust areas in the modern nanoscience. The application of nanoscale materials and structures, usually ranging from 1 to 100 nm, has become an emerging area in the field of nanoscience and nanotechnology since from the past few decades (Wang and Wang 2014). Nanoparticles exhibit completely new or improved properties based on specific characteristics such as size, distribution and morphology. The potential benefits of nanoparticles in biomedical and industrial applications for human health and environment are now well documented (Lanone and Boczkowski 2006). Among the various nanoparticles, metal nanoparticles assume special importance because they are easier and cheaper to synthesize and possess promising applications (Jian et al. 2012). Additionally, metal nanoparticles display a surface plasmon resonance (SPR) absorption in the UV–Vis region which arises from the coherent existence of free electrons in the conduction band due to the small particle size (Burdz et al. 2005; Tessier et al. 2000). The band shift is dependent on the particle size, chemical surrounding, adsorbed species on the surface and dielectric constant (Mulvaney 1996). A unique characteristic of these synthesized metal particles is that a change in the absorbance or wavelength gives a measure of the particle size, shape and interparticle properties (Mulvaney 1996; Knoll and Keilmann 1999). To date, noble metals like Ag, Au, Pd, Pt have been widely used for the synthesis of metallic nanoparticles (Doria et al. 2012). Among these, silver nanoparticles (AgNPs) have become the focus of much research interest due to their unique optical, electrical and biological properties which offers a number of exciting potential applications in various fields including catalysis, electronics and biology (Prabha and Poulou 2012). They possess an excellent biocompatibility and low toxicity (Pauksch et al. 2014). Silver nanoparticles have been documented in the field of biomedical (Chaloupka et al. 2010), drug delivery (Prow et al. 2011), food...
SiO₂/ZnBr₂ mediated expeditious approach to 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one derivatives in water under microwave irradiation

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Abstract

A new one-pot three-component green approach has been developed for the synthesis of a series of pyrazolone derivatives 2 (a−s) from differently substituted aldehydes, ethylacetocacetate and phenylhydrazine/2,4-Dinitrophenylhydrazine in excellent yields (94−98%), employing SiO₂/ZnBr₂ as a recyclable Lewis acid catalyst in water under microwave heating. The molecular structure of compounds 2a and 2d were well supported by single crystal X-ray crystallographic analysis. The present protocol bears wide substrate tolerance and is believed to be more practical, efficient, eco-friendly and compatible as compare to existing methods.

Keywords: SiO₂/ZnBr₂, Pyrazolone, Microwave, X-ray analysis, Eco-friendly.

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Synthesis, X-ray crystallography, spectroscopic (FT-IR, $^1$H & $^{13}$C NMR and UV), computational (DFT/B3LYP) and enzymes inhibitory studies of 7-hydroximinocholest-5-en-3-ol acetate

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A B S T R A C T

The present study reports the synthesis of 7-Hydroximinocholest-5-en-3-ol acetate (syn. 3β-acetoxycholest-5-en-3-one oxime; in general, steroidal oxime). The identity of steroidal molecule was confirmed by NMR, FT-IR, MS, CHN microanalysis and X-ray crystallography. DFT calculations on the titrated molecule have been performed. The molecular structure and spectra interpreted by Gaussian hybrid computational analysis theory (B3LYP) are found to be in good correlation with the experimental data obtained from the various spectrophotometric techniques. The vibrational bands appearing in the FTIR are assigned with great accuracy using harmonic frequencies along with intensities and animated modes. Molecular properties like HOMO-LUMO analysis, chemical reactivity descriptors, MEP mapping, dipole moment and natural atomic charges have been presented at the same level of theory. Moreover, the Hirshfeld analysis was carried out to ascertain the secondary interactions and associated 2D fingerprint plots. The percentages of various interactions are pictorialized by fingerprint plots of Hirshfeld surface. Steroidal oxime exhibited promising inhibitory activity against acetylcholinesterase (AChE) as compared to the reference drug, tacrine. Molecular docking was performed to introduce steroidal molecules into the X-ray crystal structures of acetylcholinesterase at the active site to find out the probable binding mode. The results of molecular docking admitted that steroidal oxime may exhibit enzyme inhibitor activity.

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1. Introduction

Over the past few decades research towards the rational modification of steroidal molecules has received considerable attention in tribute to their significant role in biological processes and having potential to be developed as therapeutic agents for various diseases [1]. Introduction of certain functional groups to the various positions of steroidal skeleton can cause major changes in the biological behaviour of steroidal moiety [2]. Among them, the steroidal oximes due to its unique structural features with wide spectrum of pharmacological activities gained significant attention in the late 1990s, along with a large number of physiologically active sterols [3]. Steroidal oximes have always attracted substantial consideration because of being a fundamental class of biological signalling molecules with well validated biological, scientific and clinical properties [4]. Moreover, a plethora of medicinally important steroidal compounds bearing oximes in their structural framework have been reported possessing antineoplastic [5], anti-inflammatory [6], anti-microbial [7], hypotensive [8], anthelmintic [9], antitumor [10], hypoletholesterolmic [11], gestagenic [12] and antibody binding properties [13]. These compounds have also been reported to exhibit valuable biological activities such as cytotoxicity [14] and aromatase inhibitory activity [15]. Oximes have wide application in synthetic organic chemistry as promising intermediates for the transformation into nitriles, amides, nitro compounds, nitrones, amines [16–20] and for the synthesis of azaheterocycles [21]. They are also useful for selective e-activation [22]. These versatile oximes are also used for protection.

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Structure elucidation and DNA binding specificity of natural compounds from Cassia siamea leaves: A biophysical approach

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ABSTRACT

A novel isoflavone, 5,6,7-trimethoxy-3’(3’,4’,5’-trimethoxyphenyl)-4H-chromen-4-one (1) along with a known pyranocoumarin, Seselin (2) have been isolated from the ethanolic extract of the leaves of Cassia siamea (Family: Fabaceae). Compound 1 has been reported for the first time from any natural source and has not been synthesized so far. Their structures were elucidated on the basis of chemical and physical evidences viz. elemental analysis, UV, FT-IR, 1H-NMR, 13C-NMR and mass spectral analysis. Structure of compound (1) was further authenticated by single-crystal X-ray analysis and density functional theory (DFT) calculations. A multi-technique approach employing UV-Visible spectroscopy, fluorescence, KI quenching studies, competitive displacement assay, circular dichroism and viscosity studies have been utilized to probe the extent of interaction and possible binding modes of isolated compounds (1–2) with calf thymus DNA (CT-DNA). Both the compounds were found to interact with DNA via non-intercalative binding mode with moderate binding affinities. Groove binding was the major interaction mode in the case of compound 2 while compound 1 probably interacts with DNA through electrostatic interactions. These studies provide deeper insight in understanding of DNA-drug (natural products) interaction which could be helpful to improve their bioavailability for therapeutic purposes.

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1. Introduction

The genus Cassia (Family: Fabaceae) comprises of 580 species of herbs, shrubs and trees, which are widely distributed throughout the world, of which only twenty species are indigenous to India [1]. Cassia siamea Linn. (syn. Senna siamea), commonly known as the Kassod tree, belongs to family Fabaceae is a medium-sized, evergreen tree native to the countries of South and Southeast Asia. Cassia siamea is better known in folklore medicine for the treatment of fever, arthritis, skin disease, constipation, hyper tension and insomnia [2]. The literature survey revealed that Cassia siamea possess promising biological properties such as antihelmintic [3], antimicrobial [4], antiplasmodial [5], antiviral [6], antidiabetic [7], antioxidant [8], antitumor [9], anti-inflammatory and analgesic [10]. Previous phytochemical investigations of Cassia siamea have shown the presence of different phytochemicals viz. alkaloids, anthraquinones, chromones, chromone-alkaloids, tripeptidones, steroids, flavonoids and coumarins [11–22].

Motivated in quest of new bioactive metabolites from Cassia siamea and in continuation of our previous work [21,22], our research group has investigated the chemical constituents of the leaves of this plant, which led to the isolation of a novel isoflavone, 5,6,7-trimethoxy-3’(3’,4’,5’-trimethoxyphenyl)-4H-chromen-4-one (1) along with a known pyranocoumarin, Seselin (2). To the best of our knowledge, compound (1) has neither been isolated from any plant source nor has its synthesis been reported so far. However, literature survey revealed the reports of compound 2 from Cassia siamea by Basudan et al. [23] and also from some other plant sources [24–28]. In the present study the structures of the isolated compounds 1 and 2 has established on the basis of physical and chemical evidences (elemental analysis, FT-IR, UV, 1H-NMR, 13C-NMR and MS spectral analysis). The molecular structure of compound (1) was further authenticated by X-ray crystallographic analysis and DFT studies. DNA binding studies of the isolated compounds have been carried out to probe the binding mode and extent of interaction of these compounds with calf thymus DNA (CT-DNA).

2. Materials and Methods

2.1. General Experimental Procedures

Meltng points were determined on a Kofler apparatus and are uncorrected. Elemental analysis (C, H and N) has been conducted using a Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Fourier

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Potent acetylcholinesterase inhibitors: Synthesis, biological assay and docking study of nitro acridone derivatives

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Abstract

The reaction of α-haloacetic acid with aniline derivatives and their subsequent cyclization reaction yielded the acridone derivatives. The series of nitro acridone derivatives were prepared by Ullmann condensation in presence of copper as catalyst and were characterized by FTIR, 1H, 13C NMR and mass spectra. The structure of 5-nitro-(2-phenyl amino) benzoic acid (4) was confirmed by X-ray crystallography and was found to crystallize in P21/c space group. The in vitro efficacy of the compounds for their acetylcholinesterase (AChE) and antioxidant inhibitory activities have been evaluated against the standard drugs Amanitin and Gentamicin against Gram positive and Gram negative bacteria, 1,7-Diiodoacridone was found to be the most potent AChE inhibitor (IC50 = 0.22 μM). Moreover, the compounds have been screened for their antioxidant activity using the DPPH assay. Also, docking study results were found to be in good agreement with the results obtained through in vitro experiments. The docking study further predicted possible binding conformation.

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1. Introduction

Chemical modification of bioactive components is one of the most commonly employed approaches in drug discovery research because of its promising results [1]. The occurrence of heterocyclic derivatives in bioactive natural products and pharmaceuticals has made them significant synthetic targets. Acridones are an exclusive kind of heterocycle, a subclass of acridines with a basic structure consisting of 9(10H)-acridone which is present in a large number of natural products and synthetic compounds that are known as multi-targeted agents with biomedical perspective. Acridone-based derivatives were first pursued for their antibacterial activity against bacteria, parasites and fungi [2,3]. It is an important organic compound bearing tricyclic nitrogen containing ring was first used in 19th century against malaria [4]. Acridone consists of two benzene rings fused together having a keto group and a nitrogen atom at 9th and 10th position, respectively, resulting in a planar structure. This chemical scaffold bears a wide range of biological activity including anti-cancer [5], anti-malarial [6], anti-viral [7,8] and modulation of multi-drug resistance (MDR) [9–11]. On the molecular level, the planar structure of acridone molecule facilitates its interaction with nucleotides leading to intercalation with DNA and RNA strands. Interaction of DNA with various biologically important organic molecules has been extensively reviewed in the literature [12–14]. A series of 1-amino thiacridones were designed as DNA intercalating agents with covalent bond formation potential [15]. The intercalation of acridone molecule with DNA and RNA is primarily based on its π–π stacking interactions with base pairs of double-stranded nucleic acids. These interactions of acridine analogs have also been confirmed by X-ray crystallography revealing ring overlap between acridine ring and base pairs of nucleic acid [16]. The biological consequence of these interactions is the disruption of DNA functions in the cells, serving as a prerequisite for effective anti-cancer activity of acridine analogs [17]. Moreover, acridone molecule also possesses hydrophilic and lipophilic balance which facilitates its transverse through biological membranes to reach into the nucleus, exerting their action [18].

Acridone is highly fluorescent and stable against photo degradation, oxidation, and heat [19,20]. It is a small molecule with no charge. Several acridone derivatives have been used as fluorescent labels for peptides [21], amino acids [22], antibodies [23] and substrates for catalysis [24]. A series of acridone linked with nitro group have been developed as potential anticancer agent, among which antiarrhythmic appeared to be very...
Silica Bonded N-(Propylcarbamoyl)sulfamic acid (SBPCSA) Mediated Expeditious Approach to C–C Bond Formation: An Innovative Pathway for Acrylonitrile Derivatives

Mehtab Parveen1 · Shaista Azaz1 · Faheem Ahmad1 · Ali Mohammed Malla1 · Mahboob Alam2

Received: 18 April 2016/Accepted: 11 June 2016

Abstract A new silica bonded N-(propylcarbamoyl)sulfamic acid (SBPCSA) catalyst has been prepared for the highly efficient synthesis of a series of acrylonitrile derivatives via solvent-free facile Knoevenagel condensation between differently substituted heterocyclic/aromatic aldehydes 1 (a–o) and 2-thiopheneacetonitrile (2). The catalyst was characterized by FT-IR, SEM-EDX and XRD techniques. The thermal stability of the catalyst was evaluated with TGA and DT analysis. The remarkable features of the present protocol are solvent free synthesis, recyclability of the catalyst, mild reaction conditions, shorter reaction profile, excellent yield of products with applicability to broader substrate scope (electron rich and electron deficient) and exclusive formation of E-isomer of the product. DFT calculations also revealed that E-isomer of compound 3f is stabilized by 12.53 kcal mol⁻¹ more than the Z-isomer.

Graphical Abstract Efficient and economical synthesis of acrylonitrile derivatives.

Keywords Acrylonitrile · SBPCSA · Knoevenagel condensation · E-isomer · DFT studies

1 Introduction

In the last few decades, there has been an upsurge usage for environmentally benign and sustainable catalyst in the chemical industry [1, 2]. Recycling of homogeneous catalysts is the main issue in large-scale production of chemicals [3]. In this regard, substantial research efforts have been devoted to develop catalysts with high efficacy, selectivity and stability. Immobilization of catalysts on solid support, leads to clean chemical synthesis for environmental as well as economical point of view [4, 5]. Heterogeneous catalysts have gained much attraction of
Original article

An Experimental Study of Ethanolic Extract of *Myristica fragrans* in Morphine Dependence

Zaheer F, Rahman S, Khan RA, Parveen M

Abstract:
Objective: To evaluate the role of ethanolic extract of *Myristica fragrans* in morphine dependence. Methods: Wistar albino rats were made moderate and severe grade morphine dependence by administering morphine sulphate in dose of 10 mg/kg (i.p.), twice daily for 4 days and by increasing doses of 10-100 mg/kg (i.p.), twice daily for 7 days, respectively. The signs of spontaneous abstinence syndrome were recorded 12 hours in both studies after the last dose of morphine for 30 minutes and quantified by ‘counted’ and ‘checked’ signs. Ethanolic extract of *Myristica fragrans* (EEMF) was administered p.o. in different regimens: (a) EEMF 200 mg/kg along with morphine twice daily for 4 days and 7 days in moderately and severely induced morphine dependence group, respectively. (b) EEMF 400 mg/kg (p.o.), single dose 10 hours after the last dose of morphine in both moderately and severely induced morphine dependence rats. Result: Oral administration of EEMF in both study groups caused significant reduction in the scores of counted and checked signs of morphine abstinence syndrome as compared to active morphine control group. The reduction was significantly more in regimen 'a' as compared to regimen 'b'. Conclusion: Ethanolic extract of *Myristica fragrans* seed significantly reduced the mean scores of various 'counted signs' and 'checked signs' of morphine withdrawal syndrome and might give a solution as a substitute therapy in morphine de-addiction.

Keywords: *Myristica fragrans*; De-addiction; morphine sulphate

Introduction

Morphine addiction is worst affected socio-economic problem worldwide. It causes mild to severe dependence resulting into difficult withdrawal at the time of de-addiction. A number of therapeutic medicines have been described in indigenous system of medicine to overcome the addiction. *Myristica fragrans*(Nutmeg) belongs to the family Myristicaceae, is one of the important spices used in indigenous system of medicine in India. Its usefulness is reported in inflammation, cephalgia, helminthiasis, halitosis, dyspepsia, flatulence, nausea, vomiting, diarrhoea, dysentery, colic, asthma, catarrh, neuralgia, lumpago, stangury, amenorrhoea, menorrhagia, dysmenorrhoea, ulcers, liver and splenetic disorders, eye diseases, impotency, skin diseases, freckles, cracks in feet, insomnia, delirium tremens, hyperdyspia, cardiac disorders, fever and general debility. Its psychoactivity such as hallucinations, feelings of euphoria, unreality, and delusions is documented since the middle ages. Under the cover of its

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An experimental study of ethanolic extract and methanolic fraction of *Delphinium denudatum* Wall in morphine withdrawal syndrome

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**Abstract**

Objective: To evaluate the role of ethanolic extract and methanolic fraction of the roots of *Delphinium denudatum* Wall in morphine dependence. Methods: Wistar albino rats were made moderately and severely morphine dependent by administering morphine sulphate in a dose of 10 mg/kg (i.p.) for 4 days and by increasing doses of 10-100 mg/kg (i.p.) for 7 days twice daily, respectively. The signs of spontaneous abstinence syndrome in both studies were recorded 12 hours after the last dose of morphine for 30 minutes and quantified by the 'counted' and 'checked' signs. Ethanolic extract (EED) and methanolic fraction (MFD) of *Delphinium denudatum* was administered p.o. in different regimens: (a) 300 mg/kg (p.o.) of ethanolic extract or 200 mg/kg (p.o.) of methanolic fraction along with morphine twice daily for 4 days in moderately and 7 days in severely induced morphine dependence group. (b) Single dose of ethanolic extract 600 mg/kg (p.o.) or methanolic fraction of 400 mg/kg (p.o.) 10 hr after the last dose of morphine in both moderately and severely induced morphine dependence rats. Results: Administration of EED and MFD orally in both morphine dependent groups caused significant reduction in scores of 'counted' and 'checked' signs of morphine abstinence syndrome as compared to morphine control group. The reduction was observed more in regimen 'b' as compared to regimen 'a'. Conclusion: EED and MFD of *Delphinium denudatum* root significantly reduced the mean scores of various 'counted signs' and 'checked signs' of morphine withdrawal syndrome and could thus proved to be an alternative remedy in morphine de-addiction.

**Keywords:** *Delphinium denudatum*, Morphine sulphate, Morphine withdrawal syndrome, Morphine dependence.

**INTRODUCTION**

Morphine addiction is worst affected socio-economic problem worldwide. Its causes mild to severe dependence resulting into risky withdrawal and hence produces difficulties at the time of de-addiction. A number of therapeutic medicines have been described in indigenous system of medicine to overcome the addiction. *Delphinium denudatum* Wall of family Ranunculaceae is a medicinal herb used in Unani Medicine under the vernacular name *Jadwar*. The roots of Jadwar are reported in a variety of ailments such as paralysis, epilepsy, facial palsy, insanity, mania, hysteria, atony, migraine, numbness, tremors, infantile convulsions, anoxite poisoning, snake bite, scorpion sting, arthritis, cardiac weakness, palpitation, rheumatism, toothache. Nevertheless, its use in opium addiction is mentioned in classical literature. Earlier studies showed that ethanolic extract of *Delphinium denudatum* has potential to attenuate the withdrawal symptoms in morphine dependence. The present study is done to validate the earlier research work and to screen additionally the effect of methanolic fraction of *Delphinium denudatum* Wall.

**Materials and Methods**

**Plant Materials**

Roots of *Delphinium denudatum* Wall were obtained from the local market, Lucknow. These were identified and authenticated by Dr. (Mrs) Sumita Gar, Chief Scientist, Raw Plant Herbarium and Museum, National Institute of Science Communication and Information Resources (NCSIR), New Delhi.

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Acetylcholinesterase and Cytotoxic Activity of Chemical Constituents of *Clutia lanceolata* Leaves and its Molecular Docking Study

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**Abstract** Phytochemical investigations of the ethanolic extract of leaves of *Clutia lanceolata* (Family: Euphorbiaceae) resulted in the isolation of four compounds viz. 3,4-dihydroxy-2-methylbenzoic acid (1), 2,2'-dihydroxy-1,1'-binaphthyl (2), 1,3,8-trihydroxy-6-methylanthracene-9,10-dione (3) and 5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one (4). Although all the isolated compounds were known but this was the first report from this plant source. Their structures were established on the basis of chemical and physical evidences viz. elemental analysis, FT-IR, 1H-NMR, 13C-NMR and mass spectral analysis. Structure of compound 2 and 4 was further authenticated by single-crystal X-ray analysis and density functional theory calculations. The isolated compounds (1–4) were screened for AChE enzyme inhibition assay in which compound 3 and 4 were found to be more potent AChE inhibitor. Molecular docking study of potent AChE inhibitor was performed to find the probable binding mode of the compounds into the active site of receptor. Moreover, the isolated compounds were also screened for in vivo cytotoxicity by brine shrimp lethality assay.

**Graphical Abstract**

![Graphical Abstract](image_url)

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Article

Binding of a novel 12-E2-12 gemini surfactant to xanthine oxidase: Analysis involving tensiometric, spectroscopic, microscopic and molecular docking approach

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Abstract

Binding interaction of a synthesized biodegradable gemini surfactant, ethane-1, 2-diy1 bis(N, N-dimethyl-N-dodecylammoniumacetox) dichloride (12-E2-12), with bovine milk xanthine oxidase (XO) was studied using tensiometry, fluorescence spectroscopy, UV, CD, FT-IR, TEM and molecular docking. Tensiometry revealed lowering in surface tension (γ) and critical micelle concentration (CMC) of 12-E2-12 upon XO combination, suggesting a significant interaction between XO and 12-E2-12 (both in the bulk as well as at interface). Intrinsic fluorescence studies depict that 12-E2-12 quenches XO fluorescence intensity through static mechanism. The magnitude of binding parameters infers substantial and effective binding of 12-E2-12 to (XO). ANS and pyrene fluorescence demonstrate the exposure of aromatic residues (tyrosine/tryptophan) to a non-polar environment. UV, circular dichroism (CD) and FT-IR results delineate change in the secondary structure of the enzyme XO. Microscopic TEM micrographs confirm the disruption of enzyme structure at higher concentrations of 12-E2-12. Molecular docking results show that 12-E2-12 binds to XO in the vicinity of both hydrophobic and hydrophilic residues, inferring that binding is governed by both hydrophilic and hydrophobic forces. This study may be of significance in biomedical world to further interpret mechanistic treatment modes of diseases like gout and hyperuricemia. Moreover, this study provides deeper biophysical insight into surfactant-protein.
Effect of salt counterions on the physicochemical characteristics of novel green surfactant, ethane-1,2-diyl bis(\(N,N\)-dimethyl-\(N\)-tetradecylammoniumacetoxo) dichloride

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HIGHLIGHTS
- Effect of counterions on 14-E2-14 surfactant.
- Counterions refine physicochemical characteristics of 14-E2-14.
- It may help in designing green-surfactant-salt mixtures for industrial applications.

GRAPHICAL ABSTRACT

Inorganic counterions bind only electrostatically, inducing lesser effect on the physicochemical characteristics of 14-E2-14

Organic counterions, in addition, intercalate into polycrystalline layer of 14-E2-14, inducing appreciable effects on the physicochemical characteristics.

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ABSTRACT

In this research article we have examined the effect of chloride (Cl\(^{-}\)), sulphate (SO\(_{4}\)\(^{2-}\)), phosphate (PO\(_{4}\)\(^{3-}\)), anionate (\(\text{Am}^{-}\)) and tosylate (Tos\(^{-}\)) counterions on the physicochemical characteristics of green gemini surfactant, ethane-1,2-diyl bis(\(N,N\)-dimethyl-\(N\)-tetradecylammoniumacetoxo) dichloride (14-E2-14) through a multidimensional approach. Substantial changes were observed in the physicochemical parameters. Counterions were found to cause reduction in critical micelle concentration (CMC) and minimum area per head group (\(A_{cm}\)) of the 14-E2-14 gemini surfactant. However, increase in aggregation number (\(N_{a}\)) and surface excess concentration (\(C_{e}\)) of the 14-E2-14 surfactant was observed upon increasing the counterion concentrations. The Gibbs free energies of micellization (\(\Delta G_{mic}\)) and adsorption (\(\Delta G_{ads}\)) were found to be negative, indicating that 14-E2-14 micellization is spontaneous. The order of efficacy of counterions to influence the micellar characteristics was: \(\text{Am}^{-} > \text{Tos}^{-} > \text{PO}_{4}^{3-} > \text{SO}_{4}^{2-} > \text{Cl}^{-}\). Further, \(^{1}H\) NMR results demonstrated morphological transitions (spindle-to-rod) and newer phase formation. The UV-Vis and FT-IR results confirmed intercalation of organic counterions, \(\text{Am}^{-}\) and \(\text{Tos}^{-}\) into the polycrystalline layer of 14-E2-14 micelles. TEM micrographs reveal emergence of non-spherical micelles at higher counterion concentrations. This study could be significant to surfactant science arenas in tailoring green surfactants with desirable physicochemical characteristics, so that special-characteristic-tailored

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Bio-physicochemical analysis of ethylene oxide-linked diester-functionalized green cationic gemini surfactants†

Mohd. Akram,* Sana Anwar, Farah Ansari, Imtiyaz Ahmad Bhat and Kabir-ud-Din‡

A novel series of oxy-diester-functionalized gemini surfactants (Cn−E2O−Cm) was synthesized and the physicochemical parameters were evaluated by surface tension and steady-state fluorescence measurements. Negative values of Gibbs free energy change of adsorption and micellization indicate that adsorption and micellization of Cn−E2O−Cm gemini surfactants are spontaneous. These surfactants have lower Krafft points and thus better solubility. Besides, they exhibit excellent foam and microemulsion stability. Interestingly, these geminis show low cytolictoxity, as revealed by HCCp analysis. FT-IR spectra after alkaline treatment confirm their cleavable nature. Moreover, a fascinating feature of these geminis is their considerably high biodegradability. Thus, a comprehensive study of the synthesized gemini surfactants has been carried out that may be significant for potential applications in various fields, more specifically in biomedicine and cosmetics, where efficiency and safety are strictly connected.

Introduction

The discipline of surfactants has matured over the years, but there is still ample space for the synthesis of new surfactants with structural modifications in order to obtain desirable characteristics. In recent years, dimeric or gemini surfactants have drawn extensive attention of the scientific community, both at an academic as well as an industrial level, due to their fascinating properties over conventional (single tail/single head) surfactants. Gemini surfactants are a special class of surfactants that bear two hydrophobic chains and two polar head groups linked by a spacer. They are known to possess lower critical micelle concentration (CMC), better wetting, foaming, and dispersing properties. They offer promising applications in detergency, solubilization, soil remediation, gene transfection, enhanced oil recovery, environmental protection, antimicrobial activity, etc.† Hence, these surfactants are regarded as potentially the ‘next generation’ high quality surfactants.‡

Cationic gemini surfactants are gaining keen interest of researchers as the strategies for their synthesis are relatively simple.‡ Previous literature reports‡‡ have shown that majority of these surfactants are based on nitrogen carrying a positive charge and bio-quaternary ammonium halides which are designated as m−n−m. However, they are being limited by the environmental concern raised over their discharge after use into water bodies as industrial effluents and sewage.‡‡‡ Therefore, there is a dire requirement for synthesizing such novel surfactants that are not only efficient but are also extensively biodegradable. In addition, low cytolictoxity is very crucial for amphiphiles to be utilized as non-viral vehicle for drug delivery. One suitable approach to achieve this is to introduce polar or easily cleavable groups (such as ester, ethylene oxide, amide, carbonate, etc.) in the structure of surfactants.‡‡‡ Inspired by this, we wondered what new and diverse properties may appear if highly biocompatible diester groups along with polar ethylene oxide moieties are introduced together in the spacer. Although extensive literature is available‡‡‡ concerning synthesis and properties of gemini surfactants but to the best of our knowledge, there is no literature report addressing the comprehensive analysis involving synthesis, characterization, physicochemical and biological aspects of novel ethylene-oxide linked diester functionalized cationic gemini surfactants.

With the consideration of the above aspects, our research group has synthesized a novel series of quaternary ammonium based gemini surfactants containing flexible ester-linked (betaine type) ethylene oxide units as spacer. They are designated as Cn−E2O−Cm [where m (≥ 12, 14 and 16) is the number of carbon atoms in alkyl chains of cationic surfactants and E2O represents the ethylene oxide linked diester spacer]. As can be seen, the polar ester groups together with ethylene oxide moiety in the synthesized geminis have dramatically improved their self-assembling behavior along with other physicochemical properties.

The incorporation of betaine type ester groups into the spacer has been found to improve the biodegradability and

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Biophysical perspective of the binding of ester-functionalized gemini surfactants with catalase

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ABSTRACT

Interaction of surfactants with biomacromolecules is an essential subject of biophysical chemistry to address their diverse applications in industry, biomedical, and cosmetic domains. In this context, we have examined the binding interactions of three ester-functionalized surfactants (m-E2-m) with bovine liver catalase (BLC, 10 μM) by employing a multi-technique approach. The m-E2-m gemini quenches fluorescence intensity of BLC through static procedure. The binding ability of concerned gemini surfactants was found to be in the order 12-E2-12 > 16-E2-16 > 14-E2-14 > 10-E2-10. Quenching efficiency, as determined by $K_q$ values, was observed as 12-E2-12: $K_q = 1.0 \times 10^4$, 16-E2-16: $K_q = 3.0 \times 10^4$, and 14-E2-14: $K_q = 1.0 \times 10^4$. The negative $Q_{10}$ values ($Q_{10} = -0.268 \pm 0.001, -0.056 \pm 0.001, 0.06 \pm 0.001$) indicate spontaneous nature of m-E2-m-BLC interactions. UV-vis spectroscopy, circular dichroism (CD), and spectrofluorimetry ($T_1, T_2$) assessments indicate conformational changes in BLC upon m-E2-m conjugation. UV-vis spectroscopy further confirms the stability of BLC upon m-E2-m conjugation. Docking provides support to the fluorescence results, by predicting the hydrophobic site of m-E2-m surfactants near to aromatic residues (mainly Trp, Phe, and Tyr). Moreover, since surfactant-protein interactions have beneficial implications, therefore, this study can be significant for industrial and biomedical realms.

1. Introduction

Ever since surfactants were revealed as denaturants of biomacromolecules (especially proteins), protein-surfactant interactions unfolded the intellectual approach not only to understand protein folding/unfolding but, also to investigate their potential relevance in application perspective. Protein-surfactant interactions not only explore the functional properties of proteins but also are crucial in biological, industrial, pharmaceutical, and cosmetic systems [1-11]. Protein-surfactant interactions perturb the conformation, polarity and stability of former upon interaction with the latter [12-14]. Moreover, due to structural duality, proteins offer better tendency to interact with surfactants.

Gemini surfactants (Novel-age surfactants) were recently found to interact more effectively with proteins than the conventional surfactants; the reason being their unique properties (lower CMCs, lower Krafft points and strong hydrophobic micro-domains [14-17]). At the present time, cationic ester-bonded gemini (m-E2-m) are attracting immense attention than usual m-s-m type because of their remarkable nature: better biodegradability and lower toxicity. Presence of soft moieties (ester linkages) also gratifies environmental and legislative protocol and criterion.

Catalase, an anti-oxidant enzyme, found generally in aerobic organisms, is known to catalyse the decomposition of hydrogen peroxide into oxygen and water ($2H_2O_2 \rightarrow O_2 + 2H_2O$) and, therefore, is crucial in regulating oxidative stress [18]. Catalase is known to have relevance in apoptosis, aging, mutagenesis and many other diseases [19]. Its crystal structure reveals that it has four subunits and each subunit is composed of more than 500 amino and residues with porphyrin ring in the heme active site. Moreover, it has 24 tryptophan (surface) and 50 tyrosine (inner) residues. Catalase functional instability leads to accumulation of $H_2O_2$, consequently, oxidative damage to biomolecules [20].

Previous studies have shown the effect of various drugs on the catalase conformation [21-23]. However, to the best of our knowledge, no information is available about the influence of m-E2-m gemini surfactants on structural features of catalase. Therefore, studying interaction between m-E2-2H catalase with catalase seems suitable and appropriate both from application as well
Solution behaviour of an ester-functionalized gemini surfactant, ethane-1,2-diyl bis(N,N-dimethyl-N-dodecylammoniumacetoxy) dichloride in the presence of inorganic and organic salts

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Abstract

Herein, we have investigated the effect of inorganic and organic salts (NaCl, Na2SO4, Na3PO4, Na2CO3 and Na2SiO3) on the solution behaviour of a gemini surfactant, ethane-1,2-diyl bis(N,N-dimethyl-N-dodecylammoniumacetoxy) dichloride (12-EE-12), employing surface tensionometry, fluorescence. 1H NMR, TEM, UV-vis, and FT-IR. The surface tension measurements showed that all micellization characteristics were refined in the presence of salts with the order being Na2SiO3 > Na2CO3 > Na3PO4 > Na2SO4 > NaCl. Whereas fluorescence measurements were used to estimate the aggregation number (Na2) of the micelles. 1H NMR, TEM, UV-vis, and FT-IR results revealed morphological transition and new phase formation. This study in future could be useful for compilation of surfactant-salt mixtures for industrial applications.

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Introduction

Because of their wide use in industry and in daily life, study of surfactants and the related phenomena has been a subject of intensive research [1]. In the recent years a thriving maturity in the field is the emergence of dimeric or gemini surfactants. It was Menger [2] who coined the term "gemini surfactant" for the class of surfactant molecules bearing two hydrophilic (mostly tonic) groups and two tails per surfactant molecule linked by a spacer group of varying length/magnitude. Compared to single head-single tail conventional surfactants, double head-double tail gemini surfactants own a number of superior properties. These have far better surface-active properties and are, therefore, used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property, metal-encapped porphyrinase and vesicle formation, construction of high porosity materials, better solubility, better wetting and interesting viscoelastic properties [1–4]. Among the gemini surfactants, the m–s–m (m and s, respectively, represent the number of carbon atoms in alkyl tail and spacer of a gemini surfactant) guat (i.e., quaternary ammonium) gemini surfactants are most often used in studies to represent the class. However, despite their exceptional properties the quat guats are found to be toxic and non-cleavable [5–8]. This hampers their usage in broader spectrum and raises the need to design eco-friendly surfactants to obviate the environmental pressures and risks associated therein. In this context, in recent years, cleavable surfactants (i.e., surfactants having a weak bond deliberately included in the molecule) have attracted considerable attention [6]. An illustrative example of such “cleavable surfactants” is the surfactant family of esterquats — cationic surfactants with an ester bond inserted between the hydrocarbon tail or the quaternary ammonium head groups. Esterquats have replaced the conventional stable quats in many large-scale applications, such as fabric softeners, and for their easy degradation they are gaining increased attention. Moreover, introducing ethylene oxide (EO) groups in the surfactant moiety reduces the toxicity concerns. Further sophistications for end use to these green moieties are now-a-days added by using them with additives (like salts and proteins), significant for industrial and biomedical purposes [7–10].

Salts endorse micelle birth and/or growth by diminishing the electrostatic interaction between the head groups and thereby minimizing the effective area per head group. This is evidenced by a decrease in CMC and/or an increase of the micelle aggregation number [11]. Increase in salt concentration tends to transform the
Biophysical analysis of novel oxy-diester hybrid cationic gemini surfactants (\(C_m\)-E2O-C\(_m\)) with xanthine oxidase (XO)

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**Abstract**

Surfactant–protein/enzyme interactions have gained widespread interest in modern research due to their implications in various domains like pharmaceuticals, cosmetics, paints, biotechnology, etc. Thus, spectroscopic, microscopic and molecular modeling approaches have been employed to explore the interaction of a novel series of oxy-diester hybrid cationic gemini surfactants, \(2,2'\)-(oxydiethylene-1,2-diyl)bis(oxybis(7-alloyl-3,8-dimethyl-2-oxoanthranilinium)dichloride (\(C_12\)-E2O-C\(_12\), \(C_14\)-E2O-C\(_14\), \(C_16\)-E2O-C\(_16\)), with bovine milk xanthine oxidase (XO). Intrinsic fluorescence studies revealed that the concerned gemini surfactants quenched the XO fluorescence through static quenching mechanism. The trend for \(K_q\) values was \(C_12\)-E2O-C\(_12\) < \(C_14\)-E2O-C\(_14\) < \(C_16\)-E2O-C\(_16\) while the reverse trend was observed for \(K_q\) values \(C_12\)-E2O-C\(_12\) > \(C_14\)-E2O-C\(_14\) > \(C_16\)-E2O-C\(_16\). Negative \(\Delta G^0\) values confirmed the spontaneity of \(C_m\)-E2O-C\(_m\) + XO interactions. The results of other techniques (e.g., pyrene fluorescence, UV, CD and TEM) also indicated that the concerned gemini surfactants induce conformational changes in XO. Moreover, the actual binding site of \(C_m\)-E2O-C\(_m\) gemini surfactants into hydrophobic domains of XO was confirmed by molecular docking. This study elucidates the interaction mechanism of high performance gemini surfactants with XO which in general may be significant to compile the green amphiphilic systems, for industrial and pharmaceutical applications (more specifically to develop chemical entities for prevention and treatment of various diseases like gout, hyperuricemia, etc.).

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1. Introduction

The interaction of proteins with surfactants has been a subject of intensive study for several years because it has wide applications in industry, cosmetics, pharmaceutical and biological systems [1]. Such studies provide deeper understanding of the action of surfactants as denaturants and as solubilizing agents for proteins [2]. Usually, these interactions are regulated by the properties of surface active agents (surfactants) and, ionic surfactants, in general, cause protein denaturation being attributed to the binding of charged head groups of surfactants with oppositely charged sites on the protein surface, followed by unfolding and exposure of the interior hydrophobic patches [3,4]. Thus, these binding studies are significant for extracting more general view points for surfactant–protein interactions.

Xanthine oxidase (XO) is a prototypical member of the family of enzymes known as molybdenum hydroxylase [5,6]. XO, a key enzyme of purine metabolism, is a complex of molybdo flavoprotein. It is a homodimer of 290 kDa, comprising four redox centers: \(V_2\), a molybdenum cofactor (Mo-co, 85 kDa), one flavin adenine dinucleotide (FAD, 40 kDa) and two different iron–sulfur (Fe-S2, 20 kDa) centers per subunit [7–9]. XO catalyzes the oxidation of hypoxanthine to xanthine and then xanthine to uric acid. Increased concentration of uric acid in the blood plasma causes gout, hyperuricemia, and cardiovascular health issues [6,10,11]. Moreover, during catalysis, oxygen is converted to superoxide (\(O_2^-\)) or hydrogen peroxide (\(H_2O_2\)) [12–14]. These by-products may cause oxidative stress. Release of XO into the blood is accountable for severe liver damage [15]. Further, accumulation of xanthine in tissues causes multiple organ failure syndrome [15]. Due to these damaging consequences, scientists have an interest in devising such compounds that can alter/halt the enzyme activity or scavenge the free radical production [14,16,17].

Gemini surfactants represent a new category of surfactants made up of two identical or different amphiphilic moieties having the structure of conventional surfactants connected by a spacer at the level or in close vicinity to the head groups [18]. The study of gemini surfactants has gained widespread interest owing to their unusual solution and surface properties (10–100 times lower...
Glycidylmethacrylate based resin functionalized with graphene oxide for column preconcentration and trace determination of Cd(II) and Ni(II) in environmental and food samples†

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Abstract

A novel solid phase extractant was synthesized by the immobilization of graphene oxide onto a glycidylmethacrylate matrix via coupling through the diethylenetriamine spacer arm and explored for the development of a column method for the preconcentration and flame atomic absorption spectrometric determination of Ni(II) and Cd(II) in environmental and food samples. The sorbent was characterized by Fourier transform infrared spectroscopy, elemental analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray analysis and 13C NMR. The SPE method was optimized by varying experimental parameters such as pH, time, flow rate and elution.

https://pubs.rsc.org/en/content/articlelanding/2016/RA/c6ra15812f#!divAbstract
Copper selective self-sorting polymeric resin with mixed-mode functionality for column preconcentration and atomic absorption spectrometric determination

Aminul Islam,* Hilal Ahmad, Noush Zaidi and Suneeel Kumar

A new approach for the synthesis of a highly Cu(ii) selective mixed-mode solid phase extractant is proposed. In aqueous medium triethyleneetetramine (trienc) reacts with Dowex 50 resin and forms a self-assembled product. The self-sorting trienc molecules get attached by forming a hydrogen bond with the sulfonic acid groups of the resin, where nitrogen-containing functional groups flexibly change their orientation in order to selectively coordinate with Cu(ii) in a square-planar geometry. This enables the solid phase to behave in a manner similar to a free monomeric ligand in a liquid-liquid system. A column procedure for preconcentration/separation of Cu(ii) was developed optimizing various experimental variables which exhibits a low preconcentration limit (3.3 µg L⁻¹) and high sorption capacity (101.6 mg g⁻¹ of resin). An analytical method coupling column preconcentration procedure with flame atomic absorption spectrometry (FAAS) was validated analyzing standard reference materials and recovery of the spiked analyte. The proposed method was successfully applied for the preconcentration and determination of Cu(ii) in tap water, river waters, electroplating wastewater, and a tea sample.

Introduction

Copper is an essential element for many biological systems and a necessary micronutrient at very trace levels. However, it becomes toxic at higher levels due to its association with cell membranes, preventing the transport mechanism across the cell wall. Copper ions are components of more than 30 enzymes (in an organism), but long term exposure to high concentrations of copper leads to chronic toxicity. Functioning of copper in living organisms, and its deficiency or excess effects have been described in detail in numerous books, reports by the Agency for Toxic Substances and Disease Registry,¹ the International Copper Association² and the World Health Organisation.³ Aqueous systems are particularly more sensitive to copper exposure. Cu(n) concentration in fresh waters is typically about 0.5–50 µg L⁻¹. However, in industrial areas or also near to mines its concentration can increase several fold. Copper concentration in tap water is at the µg L⁻¹ level, but, when water is sampled from a copper-made installation system, the concentration of copper can reach a several mg L⁻¹ level just after opening the tap.⁴ Assessment and monitoring of Cu(n) content in the environment, food and drinking water is necessary due to its anthropogenic sources and the possibility of its accumulation in living systems.

The development of preconcentration techniques like solid phase extraction (SPE),⁵ liquid–liquid extraction,⁶ precipitation⁷ and cloud point extraction⁸ with selective separation potentiality for the accurate determination of metal ions from samples of complex matrices is frontier area of ongoing research in analytical chemistry. SPE using chelating resins enables accurate determination of trace metal ions using analytical techniques with less sensitivity such as atomic absorption spectrometry as well as sophisticated simultaneous, multi-element capability which usually suffers from interferences.⁹ Numerous chelating sorbents for sequestering of metal ions including polymeric resins,¹⁰ metal–organic framework,¹¹ graphene oxide sheets,¹² carbon nanotubes¹³ and monoliths¹⁴ are useful with certain shortcomings likely lack of selectivity, low sorption capacity, slower kinetics, and reusability of sorbent.¹⁵ Chelating resins tailored with a variety of organic ligands (smaller in size, containing hydrophilic groups and donor atoms) in order to have better accessibility of ligands, faster kinetics of metal ion sorption and higher metal–ligand stability constant. Such resins possess several advantages namely good sorption capacity with selectivity, mechanical and chemical stability, multiple quantitative sorption–desorption cycles with good reproducibility and high preconcentration factor.¹⁶,²⁵ However, the selectivity towards metal ions from the matrix containing other metal ions for the chelating resins possessing ligands with two or more
A graphene oxide decorated with triethylenetetramine-modified magnetite for separation of chromium species prior to their sequential speciation and determination via FAAS

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Abstract We describe a fast and sensitive method for sequential speciation and separation of chromium(VI) and chromium(III) using dispersive magnetic solid phase extraction prior to determination by FAAS. The sorbent (mf-GO) was obtained by functionalizing a graphene oxide decorated with magnetite which was modified with triethylenetetramine. The sorbent was characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray analysis, FTIR and elemental analysis. The use of mf-GO results in fast removal of chromium(VI) (10 min) and of Cr(III) (30 min). The sorption capacity is 16.4 mg g⁻¹ for Cr(VI) and 9.6 mg g⁻¹ for Cr(III). Effective chromium speciation is demonstrated by simply tuning the pH value of the solution. Following batch sorption, the particles can be magnetically separated. The method was validated under optimized conditions. Linear dynamic range of calibration plot extends from 5 to 100 µg L⁻¹, and their detection and quantification limits are 1.4 and 4.5 µg L⁻¹ for Cr(VI) and 1.6 and 5.2 µg L⁻¹ for Cr(III), respectively. Accuracy was established by analyzing the SRM JSS (513-4) chromium steel Standard Reference Material. Recoveries of (spiked) analyte range from 96 to 102%. The method was applied to speciate and quantify chromium in tannery wastewater, electroplating wastewater, and (spiked) river water.

Keywords Graphene oxide · Magnetic solid phase extraction · Chromium · Speciation · Flame atomic absorption spectrometry

Introduction

Chromium in ecosystem arises from its wide usage in chrome tanning, electroplating, printing industries, oxidative dyeing and cooling water towers [1, 2]. In a aqueous environment, chromium usually exists in trivalent Cr(III) and highly mobile toxic hexavalent Cr(VI) forms. Cr(VI) compounds can cause cancer, mutations and skin dermatitis and are being classified as carcinogen by the US Environmental Protection Agency (USEPA) and International Agency for Research on Cancer [3, 4]. The USEPA and World Health Organization has issued a maximum concentration of 100 and 50 µg L⁻¹ for total chromium and Cr(VI), respectively in drinking water [5, 6]. Commonly used atomic absorption and emission techniques for the direct determination of chromium can only yield total amount of chromium [7] and therefore, necessitated a multi-step sample preparation methods for the speciation of Cr(III) and Cr(VI) prior to their determination [8–10]. Preconcentration and speciation of chromium by solid phase extraction (SPE) using silver nano sorbent [11], carbon nanotubes [12], polymers [13], modified nano-particles [14] and gold nano clusters [15] offers many advantages such as high enrichment factor, complete recovery, rapid phase separation, and possible automation with different detection techniques. All these approaches are either based on the use of oxidizing/reducing agents for species inter-conversion or selective determination of an individual chromium species [Cr(III)/Cr(VI)], whereas speciation is achieved via subtraction of the concentration of the measured oxidized/reduced state from the total amount. However, the chemical conversion of metallic species can

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Recent developments in multicomponent synthesis of structurally diversified tetrahydropyridines

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Tetrahydropyridines (THPDs) have been recognized as a major constituent of naturally occurring alkaloids. Being heterocyclic nitrogenous compounds, they therefore display robust biological and pharmacological profiles. In this context, they are fascinating synthetic targets in synthetic chemistry and as a consequence of this their synthesis through simple and convenient tactics has emerged as an important and challenging task. To meet such challenge, multicomponent reactions (MCRs) are employed as an excellent tool for achieving compounds containing complex diversity in single step and production of their vast libraries. This review represents the advancement made in the field of multicomponent synthesis of THPDs and their derivatives of the last few years.

1. Introduction

In recent years, tetrahydropyridines (THPDs) have received massive attention as promising building blocks for numerous natural and synthetic molecules and have been acknowledged as the primary core structure of an extensive variety of biologically dynamic compounds especially nitrogen containing alkaloids. Alkaloids such as 1 (Fig. 1) isolated from Lettencaulis griffithii by Gan et al. exhibit moderate cytotoxicity against drug-sensitive and vincristine-resistant human KB cells. Recently Gan et al. isolated a new alkaloids 2 having THPD ring from Kopsia pachycephala showed in vitro growth inhibitory activity against human PC-3, HCT-116, MCF-7, and A549 cells.

Furthermore, alkaloid 3 isolated from Pandanus amaryllifolius is used as a flavor and in folk medicine in Southeast Asia. A newly discovered compound 4, fall under the category of bisbenzyltetrahydroisoquinoline alkaloids (BBIQAs) is a constituent of a Matis Par poison.

Apart from that, compounds containing THPD structural motif have found to possess biological as well as medicinal activities such as antimicrobial; anti-influenza; analgesic; hypoglycemic; muscle relaxant; nicotinic; cardiovascular; antihypertensive; antibacterial; antimalarial; anticancer; antioxidant; and anti-inflammatory activities etc. Some derivatives are also responsible for GABA (gamma-aminobutyric acid) inhibition.

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Synthesis of functionalized dihydro-2-oxypyrroles and tetrahydropyridines using 2,6-pyridinedicarboxylic acid as an efficient and mild organocatalyst

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Simple and efficient protocols have been developed for the synthesis of diversely functionalized dihydro-2-oxypyrroles and tetrahydropyridines. One-pot four-component reaction of dialkyl acetylenedicarboxylates, amines and formalddehyde in the presence of 2,6-pyridinedicarboxylic acid in methanol at room temperature provides dihydro-2-oxypyrroles. The combination of β-heteroesters, aromatic aldehydes and amines yielded tetrahydropyridine derivatives under the same reaction conditions. The salient features of these methods are mild reaction conditions, reduced reaction time, moderate to high yields, applicability to a broad range of substrates and no tedious column chromatographic separation.

Introduction

In organic chemistry, multicomponent reactions (MCRs) are a versatile strategy in which at least three components are combined together to generate diversely functionalized innovative molecules.¹ MCRs allow the formation of structurally diverse compounds from simple starting materials in one pot, and these have been proven to be green and efficient for the synthesis of heterocyclic compounds.² In addition, several advantages such as cost-effectiveness, superior atom economy, less time consumption, minimum waste disposal, and simple purification processes make them highly prominent in synthetic chemistry.³ ⁴ In recent years, MCRs have been used for the in situ generation of imines for the formation of various heterocycles, which have gained huge attention as promising reactive intermediates.⁵

2,6-Pyridinedicarboxylic acid (2,6-PDCA), also known as dipicolinic acid, is an organocatalyst and a weak protic acid having acidic hydrogens with pKa = 2.18 and pKa = 4.76. It can be believed that 2,6-PDCA activates the reacting substrate by proton donation as well as by H-bonding and therefore it is employed as an important catalyst in organic synthesis especially in MCRs. Several advantages such as its non-metallic nature, solubility, lower toxicity, cost-effectiveness, air stability and ready availability have made it a significantly suitable catalyst to carry out organic transformations. Literature revealed that 2,6-PDCA has been used as a bifunctional organocatalyst for hydrophosphonylation of aldehydes and ketones in water.⁶ Michael-type Friesel–Crafts reactions and acylation of aldehydes.⁷ Recently, M. Lal et al. have also shown its utility as an organocatalyst in the one-pot synthesis of 1,5-benzodiazepines.⁸ In addition, dipicolinic acid has also been explored widely as a ligand in metal–organic frameworks and some of them have been used as catalysts in organic syntheses.⁹ This information about 2,6-PDCA has prompted us to expand its catalytic application in one-pot MCR by synthesizing dihydro-2-oxypyrroles and tetrahydropyridines which are very important moieties in biological and medicinal chemistry.

Dihydro-2-oxopyrrole and its derivatives have been well recognized as crucial structural parts in various natural and unnatural products.¹⁰ They exhibit various biological activities such as anti-tumor,¹¹ herbicidal¹² and pesticidal activities.¹³ In addition, compounds containing the dihydro-2-oxopyrrole fragment such as Pl-091, a platelet aggregation inhibitor;¹⁴ EBPC, a highly specific alkoxy reductase inhibitor;¹⁵ (imidazolylphenyl)pyrrol-2-one, a cardiace cyclic AMP phosphodiesterase inhibitor;¹⁶ and VBOF-R, a vascular endothelial growth factor receptor¹⁷ have also been reported (Fig. 1). Due to the importance of dihydro-2-oxopyrrole derivatives, several efforts were made by chemists to synthesize these compounds. A number of methods have been reported by employing various catalytic systems such as molecular iodine,¹⁸ Al(H₂PO₄),¹⁹ sulfonic acid-modified polyethylene glycol 6000,¹⁰ ketoisomerase,¹⁰ sucrose,¹⁰ ylose,¹⁰ oxalic acid dihydrate,¹⁰ trityl chloride,¹⁰ [β-Bu,N][HSO₄],¹⁰ nano-Fe₂O₃,¹⁰ ZrCl₄,¹⁰ InCl₃,¹⁰ 1-methyl-2-oxopyrrolidinium hydrogen sulfate ([Hpyr][HSO₄]),¹⁰ Sn(OAc)₂·H₂O,¹⁰ (5)-camphorsulfonic acid,¹⁰ acetic acid,¹⁰ TiO₂ nanopowder,¹⁰ nano-ZnO,¹⁰ vitamin B12,¹⁰ ethylene-diammonium diformate (EDDF),¹⁰ and the DIO-66-SO₃H
Isolation of proton transfer complexes containing 4-picolinium as cation and pyridine-2,6-dicarboxylate complex as anion: crystallographic and spectral investigations, antioxidant activities and molecular docking studies†

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Three novel complexes with stoichiometry [4-pic-H][M(pda)]:2H2O (M = Cr (1), Fe (2) and Co (3); H2pda = pyridine-2,6-dicarboxylic acid and 4-pic = 4-picoline) have been prepared. The complexes (1–3) are characterized using elemental analysis, TGA, CV, FTIR, ESI mass, 1H & 13C NMR, EPR, UV-Visible, fluorescence, magnetic and X-ray studies. Spectral data ascertained the bonding modes and the geometry of the complexes. Single crystal X-ray data of (2) and (3) revealed the formation of proton transfer complexes in which a proton is transferred from the H2pda moiety to the pyridine nitrogen of 4-pic. Thermal and ESI mass data confirmed the proposed stoichiometry of the complexes. Cyclic voltammetric (CV) studies confirm the formation of M2+M3+ quasi-reversible redox couples in solution. The antioxidant activity of (3) assessed using DPPH and hydrogen peroxide assays has suggested that the present compounds may be used as potent antioxidants. Molecular docking studies performed for (2) and (3) reveal that the present complexes can efficiently bind with DNA receptor with free energy of binding (ΔG) values of –53.4 (2) and –276.8 kcal mol–1 (3). The molecular docking studies indicated a higher binding ability of (2) to DNA compared to that of (3).

1. Introduction

The coordinating nature and type of ligands with specific symmetry are key factors to the structures and properties of the final products. Functionalized polycarboxylic acids are among the multidentate ligands which can yield a number of mono and poly metallic coordination complexes. Pyridine-2,6-dicarboxylic acid (H2pda) has played a key role participating in interesting coordination chemistry.1,2 The reasons for this interest are the ability of H2pda to give stable chelates with different versatile flexible [N, O, O] coordination modes with metal ions, the great affinity to form strong hydrogen bonds and its biological activities.3,4 H2pda is a planar ligand with a rigid 120° angle between the central pyridine ring and the two carboxylate groups, and therefore could potentially provide various coordination modes to form both discrete and consecutive metal complexes under appropriate synthesis conditions.

The most important reactions of H2pda are proton transfer in acid/base systems with specific interactions such as hydrogen bonding. Their acid-base/proton transfer reactions are important in inorganic chemistry.5,6 Polycarboxylic acids are most probably used as building blocks for construction of metal coordination complexes by the proton transfer processes. The binding of two or more carboxylic groups in different angles allow the creation of 1D (long chain), 2D (sheet) or 3D (cage) structure.7,8 Non covalent interaction is backbone of supra molecular and molecular recognition chemistry. Non covalent interactions help to build molecular clusters while a covalent interaction is to form classical molecules.9 Non covalent molecular clusters affect the properties of the subsystem, and these changes are important for the detection of cluster formation. The stronger non-covalent interaction causes larger changes in the properties of the subsystem.10,11 Many proton transfer complexes have been prepared using H2pda and other ligand like propanol amine.12 However the chemistry of proton transfer complexes of H2pda with a heterocyclic moiety has not been reported to the best of our knowledge. We have used H2pda and 4-picoline (4-pic) in our system. H2pda behaves as a proton donor and 4-picoline acts as a proton acceptor, which is interacting by van der Waals force as H-bonding. Since such proton transfer complexes also exhibited biological (like SOD)
Synthesis, Spectral Characterization, X-ray and Magnetic Studies of Oxo-bridged Tetranuclear Coordination Polymers of Cobalt

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Abstract Two novel tetranuclear clusters have been crystallized out by the reaction of Co(NO3)2-6H2O with triethanolamine (H3tea) in the presence of α-diamine chelator (1,10-phenanthroline or 2,2′-bipyridine). The clusters were characterized by FTIR, 1H- and 13C-NMR, TGA, cyclic voltammetry, X-ray crystallographic, EPR and magnetic studies. Spectral and single crystal X-ray data revealed the molecular stoichiometry as [Co3II·Co3III(H3tea)2·(phen)4·2NO3·4H2O (1)] and [Co3II·Co3III(H3tea)2·(bipy)4·2NO3·4H2O (2)] (Phen = 1,10-phenanthroline and Bipy = 2,2′-bipyridine). Magnetic studies and X-ray crystallography confirmed the presence of mixed valence [Co3II·Co3III] state of metal ions. The clusters contain a defect dicubane core containing four cobalt ions. Cyclic voltammograms ascertain the presence of a quasi-reversible redox couple in solution.

Keywords Triethanolamine · Tetranuclear clusters · Defect dicubane · Crystal structure · Magnetic studies

1 Introduction

One of the current challenges in inorganic chemistry is the synthesis and characterization of new molecular 3d metal polynuclear clusters at moderate oxidation states [1]. Reasons for this are the aesthetic beauty that develops as the high nuclearity of the clusters increases and the complexity of their molecular structures become apparent. From a more practical viewpoint, such large clusters can represent an alternative, 'bottom-up' route to nanoscale particles complementary to the traditional 'top-down' approach [2, 3]. Tetranuclearity can be considered a common and representative class of high-nuclearity 3d-metal clusters showing interesting properties spanning from catalysis [4], and magnetism to modelling biochemical reactions [5]. A class of polynuclear metal–oxygen cluster complexes have unique chemical and physical properties with potential applications such as optics and medical chemistry. Various coordination motifs have been described in the literature, in which the most important M₄ cores are butterfly, incomplete cubane, cubane, defect dicubane topologies (Scheme 1) [6]. Cubane-like clusters, found in a variety of transition metal complexes, exhibit interesting magnetic exchange properties and under certain circumstances act as SMMs. In biology, such systems are well known; [7] e.g. the Fe₃S₄ cubane units are present in the structure of a ferredoxin protein and act as electron transfer agents [8]. The heteronuclear cubane Mn₃CaO₄ is present at the active site of the oxygen-evolving centre (OEC) of photosystem II, and the Fe₃MoS₄ has been identified at the active site of nitrogenase [9]. Cubane-like structures are favored in iron, manganese and vanadium hydroxo- and/or alkoxo-bridged chemistry, while in cobalt systems relatively limited especially the mixed valence CoIII/CoII compounds are reported [10]. Aliphatic amino alcohols belong to a group of ligands that are widely used for the construction of tetranuclear molecular complexes, including heterometallic ones, which are of continuous interest in modern chemistry [11]. The geometrical flexibility of aliphatic amino alcohols, their polydentate nature and ability to show a variety of coordination modes stipulate their
Synthesis, spectrophotometric and thermodynamic studies of charge transfer complex of 5,6-dimethylbenzimidazole with chloranilic acid at various temperatures in acetonitrile and methanol solvents

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Molecular charge transfer (CT) complex of donor 5,6-dimethylbenzimidazole with acceptor chloranilic acid was synthesized in methanol. Spectrophotometric study was performed in different solvents at different temperatures within the range of 25–45 °C. J–J stochiometry was determined by Benesi-Hildebrand plots. Various important thermodynamic parameters such as formation constant (Kf), molar extinction coefficient (εmax), energy of interaction (Eint), ionization potential (Ip), resonance energy (Er), free energy (ΔG), resonance energy (ΔR) oscillator strength (f), transition dipole moment (μt), enthalpy (ΔH) and entropy (ΔS) were determined using UV-visible spectrophotometry in different solvents at different temperatures and temperature dependencies of thermodynamic parameters were also studied. FTIR, 1H NMR and ESR-MAS spectroscopic techniques were used to ascertain the structure of new CT complex. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) determined the stability of CT complex with temperature. CT complex was formed by proton transfer from chloranilic acid to 5,6-dimethylbenzimidazole showing O–H–N2° bonding.

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I. Introduction

Charge transfer (CT) complexes are an electron donor-electron acceptor association which formed through intermolecular electronic charge-transfer transition. Formation of CT complex using organic species is accompanied by hydrogen transfer or electron transfer between donor and acceptor moieties [1–10]. Charge transfer interaction forms weak bonds [11,12] between donor and acceptor. The formation of CT complexes between n- and n-donors with n- and n-acceptors has been investigated [13–15]. CT complexes play an important role in human life due to their various physical and biological properties. CT complexes are used as potential high efficiency non-linear optical materials [16], photo-catalysts [17] electrical conductor [18–23] and as potential materials in organic semi-conductors [24–27] and others [28–32]. CT complexes are also used in pharmaceutical [33,34] and in many biological systems [35–36]. N- Heterocyclic compounds were used as efficient donors in the preparation of CT complexes with different p-benzoquinone derivatives [38–41]. Imidazole and its derivatives were found to have a broad scope of biological activity [42]. They were found to be essential in the biosynthesis of purine nucleotides and long-chain fatty acids [43]. The benzimidazole molecule is present in a great variety of pharmaceutical compounds with anthelmintic action and other applications. These compounds exhibit fluorescence, which often depends on the substituents on the benzimidazole ring and the solvents [44]. Alkyl derivatives of benzimidazole are used for inhibition of influenza virus multiplication [45]. Now days complexes of benzimidazole derivatives have pulled attention due to their amazing properties. 5,6-dimethylbenzimidazole (DMBI) is an important molecule in biology and pharmaceutical. 5,6-dimethylbenzimidazole is useful to construct complexes due to its following characteristics: (a) benzimidazole ligands contain both the imidazole ring and a larger conjugated n-system, capable of acting as hydrogen bond donor and for n-n stacking interaction to stabilize the supramolecular assembly; (b) nitrogen atoms of benzimidazole have strong coordination ability; (c) it acts as axial ligand for cobalt in vitamin B12 [46–49]. Quinones are prevalent motifs in various natural products, which are associated with diverse biological activities. Along with electron acceptor properties, chloranilic acid (CHA) exhibits acidic properties leading to formation of hydrogen bonds. Charge transfer complexes of chloranilic acid are studied with lennoxofloxacin, fleroxacin, ciploxacin, norfloxacin and with various donors [50–54]. Belonging to benzquinones, chloranilic acid can be treated as a component of supramolecular synthons in crystal engineering [55] and is interesting from the point of view of the electron transfer processes including biological systems [56–58].

In this article charge transfer complexes of 5,6-dimethylbenzimidazole (DMBI) with chloranilic acid (CHA) has been studied. The CT complex of

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PHOTOCHEMICAL ELECTRON TRANSFER REACTIONS OF TALOTREXIN

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Abstract
Talotrexin is an antifolate drug with promising antitumor activity. The present study deals with the photodegradation of talotrexin. An aqueous solution of talotrexin was irradiated under aerobic as well as in anaerobic condition with UVA light in a photochemical reactor. Progress of the reaction was monitored by thin layer chromatography. At the end of three major photoproducts were isolated as 2, 4-diaminopteridine-6-carboxylic acid (2), 2, 4-diamino-6-(hydroxymethyl)pteridine (4) and 2-(4-(4-aminoazobenzami)-4-carboxy butyl)carbamoyl)benzoic acid (3) by eluting with chloroform-petrol on silica column.

Key words: Talotrexin, electron transfer, photodegradation, phototoxicity.

Introduction
The dated interest of photochemists in the properties of the electronically excited states of compounds of pharmaceutical use has been rapidly increasing during the last decade [1,2]. The sensitivity of several drugs to ambient light, particularly in the spectral regions of UVA (320-400 nm) and UVB (290-320 nm) [3,4] may pose risks in their use because electronic photoexcitation can lead to their simple degradation and then to a simple decrease in their pharmaceutical efficiency, and also to the formation of side products that can have toxic effects [5,6]. The interaction of drugs with UVA and UVB radiations is usually responsible for a series of photosensitizing effects, i.e. phototoxicity, photoallergy, photomutagenesis and photocarcinogenesis [7,8]. Photoinduced electron transfer (PET) is the branch of photochemistry that exploits the ability of certain photoexcited molecules to act as strong oxidizing or reducing species, and induce a permanent chemical change in a ground state molecule through an electron transfer mechanism [9]. Photoinduced electron transfer (PET) processes have attracted growing interest in the last decade and many reactions such as cycloadditions, cycloreversions, oxygenations and photodegradation of drugs have been documented [10]. Photoinduced electron-transfer reactions are one of the most elementary chemical processes and plays important roles in many photosensitization phenomena [11]. The primary event in any photosensitization process is the absorption of a photon, and the following free radical (via electron transfer) and singlet oxygen generation (through energy transfer) by photo-excited drug molecules may appear to be the principal intermediate species in the photooxidative process [12]. Thus to assess potential drug phototoxicity, it is critical to determine the mechanism of drug photo degradation. Folic acid antagonists, often called antifolates, are cytotoxic drugs [13] used as antineoplastic [14], antimicrobial [15], anti-inflammatory [16] and immune-suppressive agents [17]. Antifolates are compounds commonly used to treat various forms of cancer such as breast cancer, head and neck cancer, bladder cancer, acute lymphoblastic leukemia, non-Hodgkin's lymphoma, chronic myelogenous and osteogenic sarcoma [18]. They are also being used in the treatment of non-cancerous diseases such as malaria [19], bacterial infections [20], psoriasis and rheumatoid arthritis [21]. They act as antitumor agents by suppressing the effects of folic acid and its derivatives on cellular processes [22]. Although it is a very useful but it can produce photosensitizing disorders such as photomutagenic, photocarcinogenic and photoallergy [23]. Nearly 50 years after their first use as anticancer agents, the antifolates remain a diverse and growing class of drugs with great promise and potential for improving our ability to treat a broad range of human diseases. Talotrexin (PT-523, N-(alpha)-(4-amino-4-deoxypteroyl - N (delta) -dihydrophenylalanyl L-ornithine)) is a newer antifolate and potent inhibitor of DFR. It combines characteristics of both the classical and nonclassical antifolates [24]. It has demonstrated enhanced antitumor activity in a broad spectrum of cancer models by targeting the enzyme DFR to prevent DNA synthesis in tumor cells and inhibit tumor growth [25]. Preclinical studies suggest that talotrexin, as compared to methotrexate, the most widely used antifolate, enters into cells up to 10 times more efficiently and demonstrates 10- to 100-fold more potency in overcoming polyglutamation, a well-established mechanism of antifolate resistance [26]. Several antifolate drugs are known to demonstrate phototoxicity [27]. Interest in the photocactivity of talotrexin arises from the clinical and pharmacological reports of toxic effects associated with the use of this drug [28].

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Molecular Mechanisms of Drug Photodegradation and Photosensitization

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Abstract: Drug-induced photosensitivity of the skin is drawing increasing attention. In past few decades, photosensitivity has been reported with an array of drugs, and is now recognized as a noteworthy medical problem by clinicians, regulatory authorities and pharmaceutical industry. The photosensitivity is of two types i.e., phototoxicity and photoallergy. Phototoxic disorders have a high incidence, whereas photoallergic reactions are much less frequent in human population. Several hundred substances, chemicals, or drugs may invoke phototoxic and photoallergic reactions. In order to avoid photosensitive reactions, it is essential to understand the mechanisms behind the photosensitizing properties of such substances before these drugs are introduced in clinical settings. Photosensitization is inter-related to photobiological reaction, through the knowledge of which the photosensitivity of a drug can be anticipated. This review highlights the current research status on photosensitizing drugs and its correlation to phototoxicity. Different mechanisms of photodegradation of phthalocyanine drugs have also been discussed.

Keywords: Drug, phototoxicity, photodegradation, photosensitization, photoallergy.

INTRODUCTION

A plethora of substances, chemicals, or drugs are known to induce photosensitive skin reactions. Photosensitivity is an adverse cutaneous reaction that results when a certain chemical or drug is applied topically or taken systematically at the same time when a person is exposed to ultraviolet radiations (UVR) or visible light. Photosensitivity reactions can occur in persons of any age but are more frequent in adults than children, possibly because adults are usually exposed to more medications and topical agents. Moreover, the degree of photosensitivity varies greatly among individuals. Several factors such as quantity and location of the chemical or drug on the skin, thickness of the horny layer, degree of melanin pigmentation, immunological status of the affected person, and quantity, spectrum and penetrating of the actinic radiation may influence the features of photosensitivity reactions. Phototoxic reactions may be more specifically categorized as phototoxic or photoallergic in nature [1].

PHOTOTOXIC REACTIONS

In phototoxic reactions, the drug may become activated by exposure to sunlight and cause damage to the skin. The skin's appearance resembles sunburn, and the process is generally acute (has a fast onset). Ultraviolet A (UV-A) radiation (320-400 nm) is most commonly associated with phototoxicity, but ultraviolet B (UV-B) radiation (290-320 nm) and visible light may also contribute to this reaction [2]. A phototoxic reaction typically dissipates once the drug is discontinued or has been cleared from the body. Phototoxicity is a form of photosensitivity that does not depend on an immunological response but is the result of release of energy by photosensitizing agents, causing potentially long term damage to the skin. Phototoxic reactions are dose dependent and will occur in almost any one who takes or applies an adequate amount of the offending agent and is exposed to UVB after topical application. However, the dose necessary to induce such a reaction is different for different individuals. Phototoxic reactions can appear on first exposure to the agent and demonstrate no cross-sensitivity to chemically related agents [3].

PHOTOALLERGIC REACTIONS

Photoallergy is a form of photosensitivity that is immunologically mediated. In photoallergic reactions, the ultraviolet exposure changes the structure of the drug so that it is recognized as an invader by the body's immune system. The immune system initiates an allergic response and causes inflammation of the skin in the sun-exposed areas. These usually resemble eczema and are generally chronic (long lasting). Many drugs in this family are topical agents. This type of photosensitivity may recur after sun exposure even after the drug has cleared from the system. Photoallergic reactions develop only in sensitized persons and are not dose dependent, although a sensitized person is likely to get a stronger reaction at a much higher dose [4].
Synthesis, crystal structures and spectral characterization of Cu(II) and Mn(II) complexes of 4-hydroxy-3-methoxybenzaldehyde: antioxidant properties and molecular docking studies

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ABSTRACT

[Cu(L)₂(H₂O)₂] (1) and [Mn(L)₂(H₂O)₂] (2) (HL = 4-hydroxy-3-methoxybenzaldehyde) were synthesized and characterized using elemental, spectral (FTIR, ESI-MS, UV-visible, fluorescence and EPR), thermal, cyclic voltammetric, powder, and single crystal X-ray crystallographic studies. Spectral and X-ray data ascertained the structural features, bonding modes of ligand and distorted octahedral geometry around the metal ions. Cyclic voltammetric studies confirmed the formation of a quasi reversible redox couple in solution. Crystal structure analysis of 1 and 2 reveal the presence of non-covalent interactions, resulting in a 1-D polymeric chain. Antioxidant properties (using DPPH and hydrogen peroxide assay) and molecular docking studies (using 1BNA) are also examined. The binding free energies (calculated from docked models), -270 (1) and -295 kJ mol⁻¹ (2), suggest that the complexes reasonably bind to DNA, and the DNA-binding affinity of 2 is stronger than that of 1.

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Synthesis, crystal structures and spectral characterization of Cu(II) and Mn(II) complexes of 4-hydroxy-3-methoxybenzaldehyde: antioxidant properties and molecular docking studies

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Structurally well-characterized new multinuclear Cu(II) and Zn(II) clusters: X-ray crystallography, theoretical studies, and applications in catalysis†

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Two new trinuclear Cu(II) and dinuclear Zn(II) clusters are crystallized out by reacting the metal salts with the triethanolamine (H3tea) ligand in the presence of benzoic acid (H-ba). The complexes are characterized by elemental, thermal, magnetic, spectral (FTIR, UV-Visible, EPR, and photoluminescence) and single crystal X-ray studies. Single crystal X-ray crystallography reveals the composition of the complexes to be [Cu3(H2tea)3(ba)2(NO3)2] (1) and [Zn2(H2tea)2(ba)2H2O] (2). FTIR ascertains the binding modes of H3tea−, ba− and NO3−. Triethanolamine binds in both the complexes in the monanionic (H2tea−) mode. ba− is present as an anchoring auxiliary to generate d1- and trinuclear clusters. The Cu(II) ion is present as a distorted octahedral center in the Cu3 complex (1), while the two Zn(II) ions in 2 have been reported for the first time to possess distorted octahedral as well as tetrahedral geometry in the same molecule. The intriguing features of the non-covalent supramolecular interactions have been investigated and supported theoretically by using Hirshfeld surface analysis and ab initio methods. The solid state photoluminescence (PL) spectra of 1 and 2 disclose the luminescence property of the complexes. Due to the closed or nearly closed shell configuration (d0 or d1), the present complexes are screened for catalytic properties in the hydrocarboxylation of alkanes and cycloalkanes. The catalytic activity data are indicative of the potential catalytic properties of 1 and 2.

Introduction

The design of polynuclear transition-metal complexes bearing unique structural features has become a challenge in the past decade due to their broad applications such as in catalysis, biocatalysis, materials science and medicinal chemistry. The reason for the wide utility of the high-nucleity metal complexes is their complex molecular structures, topology and electronic versatility. Though several transition metal ions yield polynuclear clusters, special emphasis has always been given to Cu(II) and Zn(II) chemistry.1

The chemistry of polynuclear copper complexes is a topic of great scientific interest due to its relevance to many areas, including bioinorganic chemistry and materials science. Copper complexes have recently attracted increasing attention as alternative O2 reduction catalysts. Among the numerous copper-containing enzymes such as hemocyanin, cytochrome c oxidase, and nitrous oxide reductase, few molecules play critical roles in biology and are responsible for activation and transformation of small molecules.2 Besides copper, the coordination chemistry of d10 systems like zinc(II) complexes has also attracted much attention owing to their versatile role in various metalloenzymes like carbonic anhydrase. Zn(II) complexes have been proven better enzymatic mimics in recent years. Especially the polynuclear zinc complexes are explored as efficient catalysts, e.g. the zinc cluster is used in the direct conversion of ester, carboxylic acids and lactones to oxazolines.3 Simultaneously, Cu(II) catalysts have been reported in the literature to catalyse a number of organic reactions.4 In designing polynuclear clusters of Cu(II) and Zn(II) metal ions, it is important to select the ligands which decide the structural topology and nuclearity of the resulting clusters.5

Flexible amino-polycarboxylic ligands are recognized as useful ligands in coordination chemistry and related areas, and have the ability to show a variety of coordination modes being broadly used for the preparation of diverse materials based on mono- and especially polynuclear metal complexes.6

Amino-acid derived ligands are useful in the synthesis of polynuclear coordination clusters by cleaving to one metal centre and bridging other metal centres through the alkoxide arms.
Effect of tartrazine dye on micellisation of cationic surfactants: conductometric, spectrophotometric, and tensiometric studies

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The interactions between anionic dye (tartrazine) and cationic surfactants (dodecyldimethylammonium bromide and cetyltrimethylammonium bromide) have been studied by conductometric, spectrophotometric, and tensiometric techniques. The conductance and surface tension of dodecyldimethylammonium bromide and cetyltrimethylammonium bromide in pure water as well as in aqueous tartrazine when plotted with surfactant concentration gave values of the critical micelle concentration at different temperatures. As well as increasing the length of the carbon chain of surfactants, the presence of tartrazine reduces the critical micelle concentration. From specific conductivity data, the counterion dissociation constant, standard free energy, enthalpy entropy of micellisation, surface excess concentration, surface tension at critical micelle concentration, maximum area per molecule, surface pressure at critical micelle concentration, and Gibbs energy of adsorption were evaluated. Spectroscopic studies reveal that the binding of dye to micelles brings a bathochromic shift in dye absorption spectra that indicates dye-surfactant interaction.

Introduction

Surfactants contribute to dyeing by wetting, levelling, or dispersing the low-solubility dyes, which in turn is helpful for industrial applications [1]. Tartrazine, also known as CI Acid Yellow 23 and CI Food Yellow 4, is a synthetic yellow-coloured monoazo pyrazolone dye having an aromatic ring and three functional groups that are capable of being ionised to negative centres (Figure 1). It is commercially used as an additive for colouring custards, ice pops, beverages, pastries, cookies, preserves, etc., as it can produce different colours and is inexpensive [2]. It helps in the dyeing of textile fibres such as wool and silk. Tartrazine is added to restore the appearance of natural colour post-processing or even to confer or enhance colour to food substances [3].

Surfactants consist of both a polar hydrophilic head group and a non-polar hydrophobic tail in their molecules, and hence are amphiphilic in nature. These amphiphiles are not only important for industrial applications and interesting from the physicochemical viewpoint but also fundamental to life because living tissues and cells are made up of colloids comprising a wide variety of amphiphilic [4]. The amphiphilic structure of surfactants is responsible for their tendency to form, in aqueous solution, thermodynamically stable molecular aggregates called micelles. Micellisation occurs above a narrow concentration range, known as the critical micelle concentration (CMC), below which surfactant molecules are predominantly dispersed as monomers [5−7]. Micellisation is important for interfacial phenomena, such as detergency, solubilisation, and surface or interface tension reduction, which do not directly involve micelles [5,8,9].

Both dyes and surfactants find wide industrial uses, and hence it is essential to understand the nature of the interactions between them. Among various dye-surfactant mixtures, oppositely charged systems have been studied widely compared with others because of their benefits in understanding the contributions of both electrostatic and hydrophobic interactions [10−12] also prevailing in biological systems. These investigations have shown the formation of dye-surfactant ion pairs and salts [10,12,14], induced dye aggregates, dye-rich micelles, and surfactant-rich micelles with stabilised dye monomers [10,12,13,15] for oppositely charged systems. Analyses of dye-surfactant interaction in aqueous solution provide knowledge about the thermodynamics and kinetics of the dyeing process, and how surfactants operate as levelling agents [16]. Experimental techniques normally used to study these interactions are spectroscopy [10−15], potentiometry [17−20], tensiometry [10,12,15,21,22], and conductivity [10,12,15,23,24]. Among the various available dyes, tartrazine dye was preferred for the present study on account of its extensive use in various pharmaceutical formulations and its wide use as a food colorant; studies on its interaction with surfactants are few [10,25]. A literature survey indicates that study of the micellisation behaviour of dodecyldimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB) in aqueous tartrazine has been scarcely reported using conductometric, tensiometric, and UV−vis spectroscopic measurements. The structures of tartrazine, DTAB, and CTAB are shown in Figure 1.

In the present work, conductivity, UV−vis spectrophotometry, and tensiometry techniques were used to study the interaction of CTAB and DTAB with tartrazine in aqueous solutions at different temperatures. All these methods are helpful in detecting micellar growth because of their high sensitivity and the reproducibility of data. In addition, UV−vis spectrophotometry represents a rapid, simple, cheap, and reliable method for determining colorants such as tartrazine dye [3], and hence interactions of tartrazine dye with DTAB and CTAB were investigated by UV−vis spectroscopy to complement the results obtained by


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In vitro DNA binding profile of enantiomeric dinuclear Cu(II)/Ni(II) complexes derived from L-/D-histidine–terephthaldehyde reduced Schiff base as potential chemotherapeutic agents

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ABSTRACT

New chiral reduced Schiff base ligands, 1L and 1D derived from L-/D-histidine and terephthaldehyde, and their Cu(II) and Ni(II) dinuclear complexes 1L & 2L (a and b) were synthesized and thoroughly characterized by various spectroscopic techniques. Comparative binding profile of both L- and enantiomeric Cu(II) and Ni(II) complexes with ct-DNA was studied by employing optical and spectroscopic techniques to evaluate their enantiopreference selectivity towards molecular target DNA and thereby explore their relative chemotherapeutic potential. Quantitative assessment of DNA binding propensity was ascertained by calculating \( K_s \), \( K_d \) and \( K_{diss} \), values of 1L & 2L (a and b) which demonstrated higher binding affinity of L-enantiomeric Cu(II) complex, 1L and followed the order as 1L > 1D > 2L > 2D. Scanning electron microscopy (SEM) was used to analyze the morphological changes of the DNA condensates in presence of complexes 1L and 1D. The SEM micrographs condensates revealed morphological transitions and formation of different structural features implicating the condensation process between the complexes and biomolecule occurred to form compact massive structures. The gel electrophoretic assay of complex 1L was carried out with pBR322 plasmid DNA which revealed an efficient cleaving ability of the complex via oxidative pathway with the involvement of singlet oxygen (\( \text{O}_2^* \)) and the superoxide anion (\( \text{O}_2^- \)) radicals as the ROS responsible the cleavage reactions. Molecular docking studies of 1L (a and b) with DNA revealed selective recognition of C-C residues of the narrow minor groove of the DNA duplex and complex 1L demonstrated binding affinity towards DNA ascertained from its higher binding energy values. Furthermore, the cytotoxic assessment of 1L was examined on a panel of cancer cell lines of different histological origin employing SRB assay which revealed remarkably good cytotoxic activity towards HeLa, HeLa and MCF7 cancer cell lines.

L. Introduction

Cisplatin is the most phenomenal metal based anticancer drug that has been successfully utilized for the treatment of solid malignancies, in particular for testicular cancers with the overall cure rate exceeding 90% [1]. However, the clinical use of cisplatin has been impeded by severe systemic toxicity and inherent/intrinsic resistance [2]. Consequently, these drawbacks have stimulated an extensive research on combinatorial tailor complexes that could exhibit improved clinical efficacy, circumvent the drug resistance and broaden the therapeutic window against different cancer phenotypes [3,4].

Transition metal complexes due to their unique electronic, spectroscopic signatures and multitude of coordination geometries often result in specific interactions with DNA and different mechanism of cytotoxic action [5]. Transition metal ions engulfs with antisumor activity when combined with diverse ligand scaffolds, such as Schiff bases, peptide motifs, and other chelating ligand groups have shown to improve the efficacy of cancer treatment modalities [6-8]. Therefore, a rational drug design strategy should be based on incorporating biocompatible metal ions (late 3d-metal ions preferably Co(II), Cu(II) and Zn(II)) in a chiral bioactive ligand pharmaphore which can lead to a highly organized and enantioselective environment at the active site on molecular level. Among 3d-metal ions, copper is an essential bioelement and is important for the functioning of several metalloenzymes and proteins [9,10].

The altered metabolism of cancerous cells and the differential response between normal and tumor cells to copper are the basis for the development of antitumor copper chemotherapeutics. It has been documented that elevated serum copper concentrations correlate well with tumor progression, and recurrence in a variety of human cancers viz., Hodgkin's lymphoma, sarcoma, cervix, prostate, liver, lung, brain, and breast cancers [11,12].
Thiophene-containing thiolato dimers, oxygen inserted Cu(II) complex, crystal structures, molecular docking and theoretical studies

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Neurodegenerative diseases linked to misfolded proteins and their therapeutic approaches: A review*

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ABSTRACT

Neurodegenerative diseases, such as Alzheimer's, Parkinson's, Creutzfeldt-Jacob, Huntington's diseases and amyotrophic lateral sclerosis, are mainly characterized by the massive deposition of misfolded protein aggregates consequent to aberrant production or overexpression of specific proteins. The development of new therapies for the treatment of neurodegenerative pathophysiologies currently stands at a crossroads. This presents an opportunity to transition future drug discovery efforts to target disease modification, an area in which much still remains unknown. In this review we examine recent progress in the area of neurodegenerative drug discovery, focusing on some of the most common targets.

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I. Introduction

Neurons are the building blocks of the nervous system which includes the brain and spinal cord. Neurons normally don't reproduce or replace themselves, so when they become damaged or die they cannot be replaced by the body. Neurodegenerative disease is an umbrella term for a range of conditions (progressive loss of structure or function of neurons) which primarily affect the neurons in the human brain, including death of neurons. Many neurodegenerative diseases including amyotrophic lateral sclerosis, Parkinson's, Alzheimer's, Huntington's, Prion disease, Motor neuron diseases (MND), Spinocerebellar ataxia (SCA), and Spinal muscular atrophy (SMA) occur as a result of neurodegenerative processes. Such diseases are incurable, resulting in progressive degeneration and/or death of neuron cells [1a]. This causes problems with movement (called ataxias), or mental functioning (called dementia). Neurodegeneration can be found in many different levels of neuronal circuitry ranging from molecular to systemic. Damage to the membranes of organelles by monomeric or oligomeric proteins could also contribute to these diseases. α-Synuclein can damage membranes by inducing membrane curvature [1b]. There is strong evidence that mitochondrial dysfunction and oxidative stress play a causal role in neurodegenerative disease pathogenesis, including in four of the more well known diseases Alzheimer's, Parkinson's, Huntington's, and Amyotrophic lateral sclerosis [1c]. In addition, axonal swelling and spheroids have been observed in many different neurodegenerative diseases. This suggests that defective axons are not only present in diseased neurons, but also that they may cause certain pathological insult due to accumulation of organelles. The greatest risk factor for neurodegenerative diseases is aging. Many of these diseases are late-onset, meaning there is some factor that changes as a person ages for each disease [1d]. Mitochondrial DNA mutations as well as oxidative stress both contribute to aging [1c]. One constant factor is that in each disease, neurons gradually lose function as the disease progresses with age.

There are many parallels between different neurodegenerative disorders including syringomyelia, protein assemblies, as well as induced cell death [1e]. Proteins are large, exquisitely folded molecules that play essential and diverse roles in all living organisms. Proteins must achieve and retain a specific 3-dimensional conformation in order to function properly. If protein folding is disrupted, proteins can display sticky surfaces and aggregate through several stages eventually assembling into fibers and such nonfunctional protein aggregates can be toxic. Protein misfolding is a particularly insidious contributor to human disease [1f]. Several neurodegenerative...
Binding of a novel 12-E2-12 gemini surfactant to xanthine oxidase: Analysis involving tensiometric, spectroscopic, microscopic and molecular docking approach

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ABSTRACT

Binding interaction of a synthesized biodegradable gemini surfactant, ethane-1,2-diyl bis(N,N-dimethyl-N-(dodecylammonium)carboxylic) dichloride (12-E2-12), with bovine milk xanthine oxidase (XO) was studied using tensiometry, fluorescence spectroscopy, UV, CD, FT-IR, TEM and molecular docking. Tensiometry revealed lowering in surface tension (γ) and critical micelle concentration (CMC) of 12-E2-12 upon XO combination suggesting a significant interaction between XO and 12-E2-12 (both in the bulk as well as at interface). Intrinsic fluorescence studies depict that 12-E2-12 quenches XO fluorescence intensity through static mechanism. The magnitude of binding parameters infers substantial and effective binding of 12-E2-12 to (XO). ANS and pyrene fluorescence demonstrate the exposure of aromatic residues (tryptophan/cysteine) to a non-polar environment. UV, circular dichromism (CD) and FT-IR results delineate change in the secondary structure of the enzyme XO. Microscopic TEM micrographs confirm the disruption of enzyme structure at higher concentrations of 12-E2-12. Molecular docking results show that 12-E2-12 binds to XO in the vicinity of both hydrophilic and hydrophobic residues, inferring that binding is governed by both hydrophilic and hydrophobic forces. This study may be of significance in biomedical world to further interpret mechanistic treatment modes of diseases like gout and hyperuricemia. Moreover, this study provides deeper biophysical insight into surfactant–protein interactions.

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1. Introduction

Proteins, being vital constituents of life, have ability to bind a wide variety of ligands viz., metal ions, surfactants, drugs and so on (1–10). In the recent times, protein–surfactant interactions are extensively investigated owing to their numerous technical applications in the fields of pharmaceuticals, cosmetics, paints, coatings and biochemical reactions (11–14). Further, these interactions are crucial to unfold surfactants as solubilizing, denaturing and renaturing agents for proteins (15,16). In particular, globular proteins, because of their ability to catalyze biochemical reactions, and to form molecular aggregates (17), are frequently used as functional ingredients in healthcare and pharmaceutical products.

Xanthine oxidase is an essential enzyme in purine metabolism. Its structural architecture involves three parts: N-terminal domain containing two iron-sulfur centers (Fe/S I and Fe/S II), a central flavin adenine dinucleotide (FAD) domain, and a C-terminal molybdenum-binding domain bearing the four redox centers aligned in an almost linear fashion (15–19). In biological systems, it governs various processes like conversion of hypoxanthine to xanthine and xanthine to uric acid. The excessive accumulation of uric acid in the parts of living organisms is responsible for clinical inadequacies viz., gout (16), hyperuricemia, and generation of reactive oxygen species (17–19). Due to these clinical flaws it has received a considerable interest among scientists. Numerous compounds were designed and tested to change the conformation of XO to mitigate these ill consequences but, biodegradable amphiphile “12-E2-12” was not tested so far, therefore, it seems relevant and appropriate to study the XO–12-E2-12 interaction.

The literature regarding protein–surfactant interaction reveals that most of the studies are focused on protein single chain/conventional surfactants like cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-100 and so on (20–22). Recent investigations have shown the employment of dimeric or gemini surfactants owing to their superior properties than the conventional ones. These dimeric surfactants have two tails and two head groups connected by a spacer. They have low Krafft
Reflection of the Physicochemical Characteristics of 1-(2-pyridylazo)-2-naphthol on the Pre-concentration of Trace Heavy Metals

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ABSTRACT

1-(2-pyridylazo)-2-naphthol (PAN) is a heterocyclic azo compound that forms inner, mostly reddish colored, water-insoluble chelates with many transition metal ions with metal ion–ligand ratios of 1:1 or 1:2. PAN is rather unselective but it does not form complexes with the alkali and alkaline earth metals, Ge, V, Al, Sc, and Ti. Numerous reported techniques of pre-concentration have been considered for analyzing the role of PAN on the physicochemical outcome of the procedures. PAN has been used as a chelating precipitant, flocculant, auxiliary complexing agent, as a ligand for anchoring on other supports with the purpose of introducing chelating property as well as selectivity. The role of PAN in the different techniques of pre-concentration, namely co-precipitation, membrane filtration, micro-extraction, cloud point extraction, and solid phase extraction, has been investigated. PAN influences the optimum experimental parameters, namely pH, concentration, time, amount, tolerance limit, etc.

KEYWORDS

1-(2-pyridylazo)-2-naphthol; heavy metal; pre-concentration; chelating agent

Introduction

The presence of trace metal ions at very low concentration level poses a serious challenge to the detectability of various sophisticated analytical instruments (Islam et al., 2013). Hence, the enhancement of the concentration before analysis, technically termed as pre-concentration, is carried out so that the instrument is fed with a sample containing detectable level of concentration of metal ions. In order to contain the pollution of wastewater by hazardous heavy metal, a wide range of technologies such as chemical precipitation, coagulation/flocculation, immiextraction, ion exchange, solid phase extraction and membrane filtration have come up for the removal of heavy metal from wastewater. The chemical precipitation methods, namely hydroxide precipitation and sulfide precipitation, have been substituted with chelating precipitants to precipitate heavy metals from aqueous medium (Ferreira et al., 2007). In one of the approaches for solid phase extraction of trace and toxic metal ions, functional groups are attached (physically and/or chemically) to the insoluble polymeric matrix to give chelating supports that are stable in aqueous phase leading to better regenerability. In liquid-phase synthesis, chelating agents have the potential of inhibiting the condensation reactions. The characteristic metal specificity and selectivity of the chelating agents make them a good selective flocculants.

In chelating agents, the presence of a variety of donor atoms, such as sulfur, nitrogen, oxygen and phosphorus make them very useful in several applications. The chemical behavior of donor atoms reflects the properties of the chelating agents. In the absence of any steric strain, a complex formed by chelating ligand becomes more stable with the number of participating donor atoms (Martell and Hancock, 1996). Among chelating ligands, the azo dyes have attracted attention by virtue of its capacity to form mostly neutral and hydrophobic complexes with different transition metals. Its basic structure is $\text{Ar}-\text{N} = \text{N}-\text{Ar}^*$, where $\text{Ar}$ and $\text{Ar}^*$ designate any aromatic groups. These dyes are considered as tridentate ligands and form chelates with metal ions through oxygen atom of the ortho-hydroxyl group, nitrogen atom from pyridine, and one of nitrogen atom of azo group, giving two 5-membered chelate rings. Azo dyes are divided into two groups: pyridylazo dyes with a PAN-type chelating structure and thiazolylazo with a (1-(2-thiazolylazo)-2-naphthol) TAN-type chelating structure. They form complexes with ions of small size carrying a large positive charge, such as titanium group (similar to salt-forming reagents) and with ions of heavy metals and transition elements with nearly full d-shells (like other nitrogen-donor chelating agents) (Anderson and Nickless, 1967). The most frequently used pyridylazo dyes for analytical purpose are: PAN, 2-(5-bromo-2-pyridylazo)-5-diethyldiaminophenol (5-Br-PADAP), and 4-(2-pyridylazo) resorcinol (PAR). PAN is the most frequently used pyridylazo ligand compared to others and deserves special attention.

PAN was introduced into chemistry by Cheng and Bray (1955) in 1955 and since then, it has found wide application in different areas of analytical chemistry due to the fact that it forms inner, mostly reddish colored, water-insoluble chelates with many transition metal ions with metal ion–ligand ratios of 1:1 or 1:2. The complexes of heavy metals form under slightly acid, neutral or alkaline conditions and their stability is greatly affected by the

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SPE coupled to AAS trace determination of Cd(II) and Zn(II) in food samples using amine functionalized GMA-MMA-EGDMA terpolymer: Isotherm and kinetic studies

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ABSTRACT
An ethylene-diamine functionalized glycidyl methacrylate (GMA) based terpolymeric chelating resin was synthesized for the separation and preconcentration of Cd(II) and Zn(II) by SPE from bread, rice and fruit juice prior to FAAS determination. The resin was characterized by FT-IR, TGA/DTA, SEM, BET analysis and EDS. Synthesized resin shows a good capacity of 53.95 mg g$^{-1}$ for Cd(II) and 24.18 mg g$^{-1}$ for Zn(II) at pH 8.0. Five isotherm equilibrium models were studied to explain the sorption phenomenon out of which Langmuir, Dubinin–Radushkevich, Scatchard and Temkin models were found to be the best fitted. The limit of detection (LOD) and limit of quantification (LOQ) were observed to be 1.5 and 5.1 μg L$^{-1}$ for Cd and 1.2 and 4.1 μg L$^{-1}$ for Zn. The reliability of the method was investigated by the analysis of CRM and the recovery of analytes from various spiked food samples.

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1 Introduction
As the global population rises and economies in many regions grow remarkably, industrial production is also predicted to increase. Hence, the level of environmental pollution especially water pollution is increasing considerably. The sources of water pollution are mainly metal extraction, smelting, electroplating, tannery, galvanizing, paper and paint industry (Rashed & Cam, 2002). The discharge of toxic waste material into the water bodies results serious effect on human health and environmental ecosystem via their entry in food chain. The primary source of cadmium exposure in non-smokers adults and children is food. In soils and water bodies cadmium is accumulated under certain environmental conditions which results increased risk of future exposure through food (Singh & Ansari, 2007).

In the priority list of Agency for Toxic Substances and Disease Registry (ATSDR), Cd is at rank 7 and Zn at 75 (ATSDR, 2013). Cadmium even at low concentration limit cause harmful effect like kidney damage, renal disorder, high blood pressure, bone fracture, and destruction of red blood cells (Hu, 2005). Although, Zn comes into the category of essential trace element, at higher concentration it causes nausea vomiting and hematemesis (Frohnire, 1990). Thus, removals of heavy metal ions before its discharge into the environment and monitoring of these toxic metals in industrial effluent, biological samples and food stuff are of prime concern.

Techniques such as ion exchange (Amin, Abd Elwahab, & El-Ashoubli, 2015; Nabi & Ahmeduddin, 2009), cloud point extraction (CPE) (Sokollahi, Ghader, Hosseini, Khajari, & Soylak, 2008), solvent extraction (Jha et al., 2014), coprecipitation (Kanjurawa & Bhus, 2008), extraction involving deep eutectic solvent (DES) (Dai, Wickamp, Veigouche, & Hae Chol, 2013; Kumar, Pari, & Praveen, 2015) and ionic liquids (ILs) (Levina et al., 2016) and solid phase extraction (SPE) (Dai, Gupta, & Das, 2012; Islam, Ahmad, & Laskar, 2012; Tabassum & Tahir, 2014) were proved to be efficient for the removal, separation and preconcentration prior to determination of toxic metal ions. However, ion exchange lacks selectivity since metal ion uptake involves only ion exchange mechanism and ion exchanger offers less versatility to chemical modification. The limitation of CPE is relatively low partition coefficients of metals. Solvent extraction suffers from the use of large volumes of carcinogenic organic solvent, emulsion formation by the mutual solubility of aqueous and organic phases and analyte loss during multi-step extraction. The low cost and biodegradable DES, allow selective extraction of mainly biological macromolecules. However, the high viscosity and solid state at room temperature restrict their application as extraction solvents. The disadvantages with ILs are due to the high toxicity and high cost of the synthesis of some of their ingredients (Dai et al., 2013). SPE has been turned out to be an economical and eco-friendly approach because of its advantages like ease of separation, regeneration, reproducible quantitative sorption and elution, low consumption of non toxic solvents, high selectivity resulting in
Glycidoxyxemethacrylate based resin functionalized with graphene oxide for column preconcentration and trace determination of Cd(II) and Ni(II) in environmental and food samples

Aminul Islam* and Suneel Kumar

A novel solid phase extractant was synthesized by the immobilization of graphene oxide onto a glycidoxyxemethacrylate matrix via coupling through the diethyleneetriamine spacer arm and explored for the development of a column method for the preconcentration and flame atomic absorption spectrometric determination of Ni(II) and Cd(II) in environmental and food samples. The sorbent was characterized by Fourier transform infrared spectroscopy, elemental analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray analysis and 1H NMR. The SPE method was optimized by varying experimental parameters such as pH, time, flow rate and elution. Under the optimized conditions the sorbent shows preconcentration factors of 180, 160 and detection limits of 0.23 and 0.06 μg L⁻¹ for Ni(II) and Cd(II), respectively. The absence of systematic and constant errors in the developed method was confirmed by analysis of a Standard Reference Material and recovery experiments 99.5% recovery with <5% RSD after spiking of a known amount of analyte in real samples.

1. Introduction

Graphene oxide (GO) is a well-established two-dimensional single-layered sp²-hybridized carbon compound derived from graphite by chemical oxidation. In solid phase extraction (SPE) and preconcentration of metal ions, GO is used due to its large specific surface area leading to high sorption capacity and the hydrophilic functional groups like epoxy (–COC), hydroxyl (–OH), carboxyl (–COOH) and carboxyl (–COOH) present on the edges and basal plane of GO form chelates with the metal ions and show fast metal ion uptake. Direct use of GO in SPE becomes challenging, particularly when the sheet size ranges in the nanoscale, due to unfavorable phase separation and recycling of GO. Recently published data show the use of GO in the separation and preconcentration of metal ions by dispersive solid phase extraction (DSPE), dispersive magnetic solid phase extraction (DMSPE) and cloud point extraction (CPE). However, these methods have several drawbacks e.g. dispersive mode filtration of GO leads to its aggregation because of strong van der waals interactions and π-π stacking between GO sheets which can significantly affect the efficiency and reusability and needs sonication for redisperision of GO.

During filtration there is a possibility of escape of GO which is simplified by the use of DMSPE. In CPE, the regeneration of GO is not possible since the analyte along with GO shurry is introduced into atomic spectrometer for analyte determination and gets degraded during atomization. Moreover, in all the three methods, application of large sample volume is restricted for metal ion preconcentration. Direct use of GO in SPE cartridge/column creates back pressure and needs a high pressure peristaltic pump which may results in GO escaping. In order to simplify these problems GO can be immobilized onto a solid support material for column application, providing enough flow rate for large sample volume without a use of high-pressure peristaltic pump. These solids not only play a role of support but also enhance the hydrophilicity due to the presence of functional groups and provide spacer arms. The introduction of spacer arm between the solid supports and GO is a new approach by virtue of which GO behaves in a manner similar to DSPE as well as free monomeric ligand in homogenous system for longer spacer arms and forms complexes with metal ions. In this work, we have synthesized a novel GO-baest solid phase extractant by the coupling of GO with glycidoxyxemethacrylate polymer beads via diethyleneetriamine spacer arm for the separation and preconcentration of metal ions. The polymer bound GO sheets restricts aggregation and leaching from column compared to direct use of GO and can be reused for several sorption elution cycle in SPE.
Synthesis and Structural Transformation of $0.7(\text{Ag}_{x}\text{Cd}_{1-x})0.3(\text{Ag}_{x}\text{Cu}_{1-x})$ of Fast-Ion Conductor ($x = 0.2, 0.4, 0.6$ and $0.8$ Mol. Wt. %)

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ABSTRACT

Some novel fast ionic solids in the mixed system were made to prepare $0.7(\text{Ag}_{x}\text{Cd}_{1-x})0.3(\text{Ag}_{x}\text{Cu}_{1-x})$ where $x = 0.2, 0.4, 0.6$ and $0.8$ mol. wt. % respectively by solid state reaction and quenching them at particular temperature. Powdered samples of different compositions containing a mol. wt. % of $(\text{Ag}_{x}\text{Cu}_{1-x})$ were synthesized by solid state reactions, using $(\text{Ag}_{x}\text{Cd}_{1-x})$ ternary halides as hosts. Powder specimens of these compositions were analyzed using differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA). Fourier transmission infrared spectra (FTIR) and x-ray powder diffraction (XRD) techniques. In host system, Ag and Cu substitution appears to stabilize the high-temperature, hexagonal structure to temperature well in excess of 450 K, associated correspondingly with the melting of the $(\text{Ag}^{+}\text{Cu}^{+})$ sublattice and with the storage of iodide/cadmium sublattices.

1. Introduction

In recent years one can see an upsurge in the interest of researchers in solid state fast ion conductors such as A$_{2}$B$_{X}$ etc. They present a large group of A$_{2}$B$_{X}$ compounds [1, 2]. Such fast ion conductors (i.e., A$_{2}$B$_{X}$) reveal attractive conductivity properties and represents meta-stable state fast ionic conductors [3]. This also arouses interest in their application for chemical sensors [3]. Due to their wide applications in solid state batteries and fuel cells, large numbers of researchers are working on their transport properties [4]. The design of electric batteries and potential optical devices requires an understanding of the role of the electronic structure in super ionic conductors [5]. One of the important aspects in understanding super ionic solids is the motion of mobile ions [5]. Several attempts have been made to synthesise new fast ionic solids suitable for electrochemical applications because of their high ionic conductivities at ambient temperatures, while characterizing the role in the development of new materials [5]. The new materials are linked by their high ionic conductivities; they display a wide variety of behavior in both the critical region and in the fast ion state [6]. Two routes can lead to improved solid fast ionic conductors, a search for new compounds and structures sustaining high level of ionic conductivity or a modification of existing compounds by heterogeneous or homogeneous doping [6]. Heterogeneous doping, on the contrary, involves mixing with a second phase with very limited solid solubility and for motion of defect concentration profiles in the proximity of interface, the deviation from local-electrical neutrality (space charge) is a consequence of point defect equilibria at interfaces [7]. A number of solids fast ionic conductors undergo solid phase transition to a high temperature phase accompanied by a sharp jump in ionic conductivity by a factor of about 10$^3$ as well as a structural change [8]. Many fast ionic compounds (including those belonging to the A$_{2}$B$_{X}$ group $(A = \text{Ag}$ and Cu, B = Cd and H, X = I)) are usually obtained by means of ceramic technology [12-13]. Chemical substitution in recent years to modify either the magnitude of ionic conductivity or the transition temperature separating super ionic and coherent phases in various solid electrolytes [14]. Present work is based on the study of some nominal compositions of $0.7(\text{Ag}_{x}\text{Cd}_{1-x})0.3(\text{Ag}_{x}\text{Cu}_{1-x})$ where $x = 0.2, 0.4, 0.6$ and $0.8$ mol. wt. % respectively using the differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), Fourier transmission infrared spectra (FTIR) and x-ray powder diffraction (XRD) techniques. In host system, Ag and Cu substitution appears to stabilize the high-temperature, hexagonal structure to temperature well in excess of 450 K, associated correspondingly with the melting of the $(\text{Ag}^{+}\text{Cu}^{+})$ sublattice and with the storage of iodide/cadmium sublattices.

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[Prof. S. Tabassum]

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New phthalimide-appended Schiff bases: Studies of DNA binding, molecular docking and antioxidant activities

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Abstract
Herein, we investigated new phthalimide-based Schiff base molecules as promising DNA-binding and free radical scavenging agents. Physicochemical properties of these molecules were demonstrated on the basis of elemental analysis, ultraviolet-visible (UV-Vis), infra-red (IR), 1H and 13C nuclear magnetic resonance (NMR) spectroscopy. All spectral data are in agreement well with the proposed Schiff base framework. The DNA-binding potential of synthesized compounds were investigated by means of UV-visible, fluorescence, iodide quenching, circular dichroism, viscosity and thermal denaturation studies. The intrinsic binding constants (Ka) were calculated from absorption studies were found to be 1.1 × 107 and 1.0 × 106 M-1 for compounds 2a and 2b suggesting that compound 2a binding abilities with DNA were stronger than the compound 2b. Our studies showed that the presented compounds interact with DNA through groove binding. Molecular docking studies were carried out to predict the binding between Ct-DNA and test compounds. Interestingly, in silico predictions were corroborated with in vitro DNA-binding conclusions. Furthermore, the title compounds displayed remarkable antioxidant activity compared with reference standard.

KEYWORDS
antioxidant, DNA binding, molecular docking, Schiff base

1 INTRODUCTION

Over the past decades, investigation on interaction between DNA and drug molecules has been fascinated incredible attention in clinical medicine due to the importance of DNA as an important target for many anticancer drugs. DNA is an essential cellular receptor that takes part in a broad range of physiological processes such as protein synthesis, mutagenesis and gene expression. As is known, many anticancer drugs exert their activity by interacting with DNA at particular sites, thus changing the replication of DNA and preventing the expansion of tumor cells. Several techniques have been reported to determine the DNA-binding capacities of small molecules including ultraviolet-visible spectroscopy, fluorescence spectroscopy, circular dichroism, nuclear magnetic resonance (NMR), electrochemistry, mass spectrometry and hydrodynamic measurements. At this time, molecular docking studies have emerged as an essential technique that has been widely used in modern drug designing to predict the interaction mode between small molecules and receptors.

Phthalimide analogues have been extensively studied as anticancer agents owing to their potential as DNA groove binders. Since phthalimide resembles natural purines in their structure they compete for binding to pyrimidine nucleotide bases of DNA. The planar ring system and hydrophobicity of phthalimide are principally responsible for its interaction with DNA. The absorption of phthalimide is better separated from that of DNA (250–275 nm). The aptness of phthalimides for the emergence of DNA-binding agents is further provoked by their capacity to form hydrophobic and hydrogen bonding interactions with nucleic acids as they possess \(N\)-H and \(C=O\) functionalities. Phthalimide Schiff base conjugates have also been proved to exhibit good DNA-binding ability by interacting at minor and major grooves. In addition to their pharmacological importance, phthalimides have also been reported to possess different applications in organic synthesis include single electron transfer acceptors, protecting groups and organo-catalysts.

Antioxidants are a significant group of pharmaceutics used to reduce the cellular oxidative stress by interacting and detoxifying free...
Design, Structural Characterization and Catalytic Activity of Incomplete Dicubane Clusters of N-Substituted Diethanolamines

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Abstract A series of four new clusters with cationic unit [Co₄(μ₃-OH)(Rdea)₂(L-L)₃]₄⁺ [R = -CH₃ (1 and 2) or -CH₂CH₂CH₂CH₃ (3 and 4), L-L = 1,10-phenanthroline or 2,2’-bipyridine] is designed and characterized by elemental, spectroscopic (FTIR, ESI MS, UV–visible), thermal, electrochemical, magnetic, SEM, EDX, PXRD and single crystal X-ray crystallographic techniques. Spectral and single crystal X-ray studies reveal the complexes 1–4 are tetranuclear clusters where the primary aminoalcohol derivative ligand is present in dianionic form i.e., Medea²⁻ or "Budea"²⁻. It is confirmed from the magnetic and bond valence summation data that the four cobalt ions are present in mixed valent states (Co₂²⁺-Co₃³⁺), which is further corroborated from the Co–O and Co–N bond lengths in X-ray structure. The bridging two hydroxide ions consolidate the tetranuclear clusters by bonding with three neighboring metal ions and a rare incomplete dicubane core is formed in all the complexes. A supramolecular framework is generated by H-bonding, π–π, CH–π, and H···H interactions. Presence of N-alkyl group and N-heterocyclic chelator facilitates the generation of these non covalent interactions thus stabilizing the framework. Of all the complexes reported here, 1 is found most efficient catalyst for the cobalt-catalyzed aerobic oxidation of neat ethylbenzene and p-xylene.

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Developing waste biorefinery in Makkah: A way forward to convert urban waste into renewable energy

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d Highlights

• Waste biorefinery is proposed to convert waste in Makkah into renewable energy.
• Total revenue of 758 million SAR can be achieved from waste biorefinery.
• 1.55 million barrels of oil and 11.2 million MCF of natural gas can be saved.
• Reduction in global warming potential of 1.15 million MtCO2 eq. can be achieved.

Abstract

The city of Makkah in the Kingdom of Saudi Arabia (KSA) hosts millions of Muslim worshippers every year. As a consequence, the municipal solid waste (MSW) quantities become enormous. City landfills receive about 2.4 thousand tons of MSW every day, whilst during the months of fasting (Ramadan) and Pilgrimage (Hajj), these quantities become 3.1 and 4.6 thousand tons per day respectively. Currently, there is no waste-based biorefinery or waste-to-energy (WTE) facility existing in KSA to treat different fractions of MSW as a source of renewable energy production and a solution to landfill waste problems. Therefore, the waste-based biorefinery, if developed in Makkah city, including WTE technologies such as anaerobic digestion (AD), transesterification, pyrolysis and refuse derived fuel (RDF) can be able to treat around 87.8% of the total MSW. The remaining 12.2% of MSW fraction can be recycled. The waste-based biorefinery, along with the recycling approach, can generate savings of about 87.6 million Saudi Arabian Riyal (SAR) from carbon credits. Similarly, a total net revenue of 758 million SAR can be generated from landfill diversion (330.4 million SAR) and electricity generation (288.5 million SAR). Moreover, 1.55 million barrels of oil and 11.2 million MCF of natural gas can be saved with a cost savings of 485.5 million SAR. Collectively, the waste-based biorefinery and recycling can reduce the global warming potential (GWP) of 1.15 million MtCO2 eq.© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Muslim Pilgrimage to the Kingdom of Saudi Arabia (KSA) is one of the oldest and largest religious gatherings in the world [1].

Abbreviations: AD, anaerobic digestion; CH4, methane; GHG, greenhouse gas; HHV, high heating value; IPCC, Intergovernmental Panel on Climate Change; KSA, Kingdom of Saudi Arabia; LCA, life cycle assessment; MPW, municipal plastic waste; MSW, municipal solid waste; OMSW, organic fraction of municipal solid waste; RDF, refuse derived fuel; SAR, Saudi Arabian Riyal; VAP, value-added product; WTE, waste-to-energy.

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Millions of Muslims from all over the world gather every year in KSA to perform worship at Al-Haram (Holy Mosques in Makkah and Medina) and Al-Masba'h (Mina, Arafat and Muzdalifah). The area of Al-Haram mosque in Makkah, including indoor and outdoor prayer space, is around 356,800 square meters. More than 2 million Muslims can worship at a time, especially during the Ramadan (9th month of the Islamic lunar calendar) and Hajj (12th month of the Islamic lunar calendar) [2]. The number of pilgrims visiting KSA has been significantly increased over the past few decades, with an annual rate of 1.15% from 1993–2014 (Fig. 1) due to expansion in the Holy Mosques, improved
Marinobacter lipolyticus from Red Sea for lipase production and modulation of silver nanomaterials for anti-candidal activities

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Abstract: In this study, the bacterial strain CEES 33 was isolated from the coastal area of the Red Sea, Jeddah, Kingdom of Saudi Arabia. The bacterium isolate was identified and characterized by using biochemical and molecular methods. The isolate CEES 33 has been recognized as Gram-negative rod shaped and orange pigmented spherical colonies. It also demonstrated a positive result for nitrate reduction, oxidase, catalase, citrate utilization, lipase and exopolysaccharide production. Strain CEES 33 was characterized at the molecular level by partial 16S rRNA sequencing and it has been identified as Marinobacter lipolyticus (EMBL/NCBI A53275.1). The lipolytic activity of the isolate was also observed 2.105 mkat/ml-1. Furthermore, the bacterial aqueous extract was used for green synthesis of silver nanoparticles (AgNPs), which was further confirmed by UV-visible spectra (430 nm), XRD and SEM analysis. Moreover, the biological functional group that involved in AgNPs synthesis was confirmed by FTIR spectra. The biological activities of AgNPs were also investigated, which showed a significant growth inhibition of Candida albicans with 16 ± 2 mm zone of inhibition at 10 µg dose/well. Therefore, bacterium Marinobacter lipolyticus might be used in future for lipase production and nanoparticles fabrication for biomedical application, to control fungal diseases caused by C. albicans.

1 Introduction

Screening of halophiles and thermophiles is an important step for discovery of thermostable proteins and enzymes. Marine-derived microorganisms of the Red Sea are stable at hyper-saline and thermophilic conditions because they have unique thermostable enzymes and proteins. These thermostable microbial contents can be extracted to be used for a number of biotechnological applications at high temperature and hyper-saline conditions [1, 2]. Moreover, lipase (EC 3.1.1.3) is one of the most important thermostable enzymes that could be extracted from marine-derived microbial isolates of the Red Sea. Recently, lipase activity has gained more attention because of its catalytic reaction that depends on water availability, and it also has the ability to synthesise and hydrolyse esters of long chain fatty acid [3]. There is a growing demand for using thermostable lipases for production of cosmetics, detergents and agro-industries [4, 5]. In addition, lipase can be used in various biotechnological applications such as bio-polymer/bio-diesel production, synthesis of fine chemicals for cosmetic ingredients and medically important drug production [6, 7]. A number of thermostable microorganisms that are able to produce thermostable enzymes, particularly lipase, have been isolated from several wild organisms [8-10]. Interestingly, some scientists genetically modified the organisms in order to express lipases for a huge production and wider applications [11, 12]. Screening methods for potential lipase-producing bacteria are still in progress with various activities, isolation, identification and characterisation of extracellular hydrolytic enzymes producing marine-bacteria have shown optimum enzymatic activities at hyper-saline and thermostable condition, which opens a new avenue for research and technology development. Most of halophiles are able to tolerate a wide range of salt concentrations and these bacterial cell metabolisms are regulated by specific enzymes and factors, which in turn will support the microorganisms to adapt and survive under extreme conditions [13]. A huge number of bacterial isolates derived from different sources has been reported with positive lipolytic activity [14, 15]; however, marine microbial diversity of the Red Sea with lipolytic activity remains largely unexplored. Furthermore, bacterial extract has also been used for silver nanomaterials synthesis through bottom up bio-fabrication process. This approach was cheap, eco-friendly, and effective in controlling pathogenic organisms. There is an urgent need to develop novel strategies of synthetic control of nanoparticles to generate nanocrystals that possess well-controlled surfaces, size, morphology and composition, and without hazardous material generation to be used for biomedical, optical and electronic applications. However, this objective is still a major challenge for the researchers to overcome [16, 17]. Therefore, understanding the importance of developing innovative techniques for nanomaterials synthesis would result in less detrimental effects to human health and the ecosystem. In addition, a number of researchers and institutional bodies are increasing the focus to search for novel bacteria and develop innovative materials that can be used for new drug development. Recently, the research field of nanomaterials has received a great attention due to development of newly synthesised nanomaterials of well-defined size and shape. Previous studies have observed some natural properties of nanoparticles such as high surface to volume ratios when their size is reduced [18, 19]. Several methods for nanomaterials synthesis have been reported in different studies such as sol-gel, ignition, pyro-synthesis and many other physical-chemical methods. However, the researchers have faced some limitations to use these methods because they cost a lot and not eco-friendly [20-23]. Therefore, there is a growing demand to develop innovative methods for nanomaterials synthesis to produce more environmentally safe and inexpensive nanoparticles. This will help to improve the development of nanomaterials based drugs to be used for different biomedical applications [24]. In this regard, applying nanomaterials with novel biological activities that have

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Microbial electrolysis cells for hydrogen production and urban wastewater treatment: A case study of Saudi Arabia

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HIGHLIGHTS

- KSA is the world’s third largest per capita waste water user country.
- 1.77 (domestic), 0.38 (industrial) billion m$^3$ year wastewater is generated in KSA.
- 612, 767 MW electricity can be produced for years 2025, 2035 from wastewater by MEC.
- Net 308, 637 MW electricity for years 2025 and 2035 can be added to national grid.
- MEC technology can achieve 25.6% of KSA 3G W electricity from waste target by 2035.

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ABSTRACT

This paper reviews the status of microbial electrolysis cells (MEC) as a means for hydrogen (H$_2$) production and urban wastewater treatment method. A case study of the Kingdom of Saudi Arabia (KSA) under MEC concept was developed. KSA is the world’s third largest per capita water user country with many lakes and rivers. Every year, around 1.77 and 0.38 billion m$^3$ of domestic and industrial wastewater is generated, respectively. The KSA government is seeking sustainable solutions for wastewater treatment and waste-to-energy (WTE) production to bridge the ever increasing water and energy demand-supply gap. However, there is no WTE facility exists to convert the wastewater into energy. Moreover, the potential of wastewater is not examined as an energy recovery substrate. This study, for the first time, estimated that a total electricity of 434 MW can be produced in 2015 from the KSA’s wastewater if MEC technology is employed. Similarly, an estimated total electricity of 612 and 767 MWe can be produced for the years 2025 and 2035 from the domestic and industrial wastewater by using MEC technology. A surplus electricity of 308 and 637 MWe for the years 2025 and 2035 respectively can be added to the national grid after fulfilling the energy requirement of MEC wastewater treatment plants. Collectively, MEC will contribute 20.48 and 25.68% share of the KSA government’s WTE target of 3 GW by 2025 and 2035 respectively. A number of challenges in MEC such as ohmic and concentration losses, saturation kinetics and competing reactions that lower the H$_2$ production are discussed with their potential solutions including, the improvements in MEC design and the use of appropriate electrolytes, antibiotics and air or oxygen.

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1. Introduction

Today, the world is facing the challenges of energy crisis and clean water shortage. In 2005, the global energy consumption was 460 quadrillion BTUs (British thermal units) that is expected to increase by 57% till 2030 [1]. Currently, the fossil fuels are the most exploited energy sources (up to 80%) in the world that are not only depleting the natural resources, but also damaging the environment and changing our climate [2]. Since last two decades,
Reflection of the Physiochemical Characteristics of 1-(2-pyridylazo)-2-naphthol on the Pre-concentration of Trace Heavy Metals

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\textbf{ABSTRACT}

1-(2-pyridylazo)-2-naphthol (PAN) is a heterocyclic azo compound that forms inner, mostly reddish colored, water-insoluble chelates with many transition metal ions with metal ion–ligand ratios of 1:1 or 1:2. PAN is rather unselective, but it does not form complexes with the alkali and alkaline-earth metals, Ge(IV), As, Se, and Te. Numerous reported techniques of pre-concentration have been considered for analyzing the role of PAN on the physiochemical outcome of the procedures. PAN has been used as a chelating precipitant, flocculant, auxiliary complexing agent, as a ligand for anchoring on other supports with the purpose of introducing chelating property as well as selectivity. The role of PAN in the different techniques of pre-concentration, namely co-precipitation, membrane filtration, micro-extraction, cloud point extraction, and solid phase extraction, has been investigated. PAN influences the optimum experimental parameters, namely pH, temperature, time, amount, tolerance limit, etc.

\textbf{KEYWORDS}

1-(2-pyridylazo)-2-naphthol; heavy metals; pre-concentration; chelating agent

\textbf{Introduction}

The presence of trace metal ions at very low concentration level poses a serious challenge to the detectability of various sophisticated analytical instruments (Islam et al., 2013). Hence, the enhancement of the concentration before analysis, technically termed as pre-concentration, is carried out so that the instrument is fed with a sample containing detectable level of concentration of metal ions. In order to contain the pollution of wastewater by hazardous heavy metal, a wide range of technologies such as chemical precipitation, coagulation/flocculation, micro-extraction, ion exchange, solid phase extraction and membrane filtration have come up for the removal of heavy metals from wastewater. The chemical precipitation methods, namely hydroxide precipitation and sulfide precipitation, have been substituted with chelating precipitants to precipitate heavy metals from aqueous medium (Ferreira et al., 2007). In one of the approaches for solid phase extraction of trace and toxic metal ions, functional groups are attached (physically and/or chemically) to the insoluble polymeric matrix to give chelating supports that are stable in aqueous phase leading to better regenerability. In liquid-phase synthesis, chelating agents have the potential of inhibiting the condensation reactions. The characteristic metal specificity and selectivity of the chelating agents make them a good selective flocculants.

In chelating agents, the presence of a variety of donor atoms, such as sulfur, nitrogen, oxygen and phosphorus make them very useful in several applications. The chemical behavior of donor atoms reflects the properties of the chelating agents. In the absence of any steric strain, a complex formed by chelating ligand becomes more stable with the number of participating donor atoms (Martell and Hancock, 1996). Among chelating ligands, the azo dyes have attracted attention by virtue of its capacity to form mostly neutral and hydrophobic complexes with different transition metals. Its basic structure is Ar−N=N−Ar′, where Ar and Ar′ designate any aromatic groups. These dyes are considered as tridentate ligands and form chelates with metal ions through oxygen atom of the ortho-hydroxyl group, nitrogen atom from pyridine, and one of nitrogen atoms of azo group, giving two 5-membered chelate rings. Azo dyes are divided into two groups: pyridalazo-dyes with a PAN-type chelating structure and thiazolylazo with a (1-(2-thiazolylazo)-2-naphthol) TAN-type chelating structure. They form complexes with ions of small size carrying a large positive charge, such as titanium group (similar to salt-forming reagents) and with ions of heavy metals and transition elements with nearly full d-shells (like other nitrogen-donor chelating agents) (Anderson and Nickless, 1967). The most frequently used pyridalazo dyes for analytical purpose are: PAN, 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (5-Br-PADAP), and 4-(2-pyridylazo) resorcinol (PAR). PAN is the most frequently used pyridalazo ligand compared to others and deserves special attention.

PAN was introduced into chemistry by Cheng and Bray (1955) in 1955 and since then, it has found wide application in different areas of analytical chemistry due to the fact that it forms inner, mostly reddish colored, water-insoluble chelates with many transition metal ions with metal ion–ligand ratios of 1:1 or 1:2. The complexes of heavy metals form under slightly acid, neutral or alkaline conditions and their stability is greatly affected by the