NANO CERIA: AN ADSORBENT FOR THE REMOVAL OF TOXIC ELEMENT

A

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CERTIFICATE – I

This is to certify that the thesis entitled, “Nano Ceria: An Adsorbent For The Removal Of Toxic Element” submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in **CHEMISTRY** to the Orissa University of Agriculture and Technology, Bhubaneswar, is a faithful record of bonafide research work carried out by **ARPITA PATRA , Adm No: 09-CHEM/18** under my guidance and supervision and that no part of thesis has been submitted for any degree or diploma or published in any form.

It is further certified that the help and sources of information availed of during the course of study have been duly acknowledged.

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CERTIFICATE – II

This is to certify that the thesis entitled, **“Nano Ceria An Adsorbent For The Removal Of Toxic Element”**submitted by **ARPITA PATRA** to the Orissa University of Agriculture and Technology, Bhubaneswar, in partial fulfillment of the requirements for the degree of master of science in chemistry, has been approved by the students’ advisory committee after an oral examination on the same in collaboration with an External Examiner.

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At the end, I bow down my head to the Almighty whose Omnipresence has always guided and helped me to overcome all odds and inconvenience.

Place: Bhubaneswar

Date: Signature

CONTENTS

ABBREVIATION

et al. – et alebi (and other)
etc. – et cetra
Fig – figure
pH – Negative logarithm of hydrogen ion concentration
ºC – Degree Celsius
XRD – X-ray Diffraction
TGA – Thermogravimetric Analysis
FTIR – Fourier-Transform Infrared Spectroscopy
SEM – Scanning Electron Microscope
XPS – X-ray Photoelectron spectroscopy
BET – Brunauer-Emmett-Teller
TEM – Transmission Electron Microscope
FE-SEM – Field-Emission Scanning Electron Microscope
EDS – Energy-Dispersive Spectroscopy
TPR – Temperature programmed reduction
TPD – Temperature programmed desorption

ABSTRACT

The Presence of toxic elements in aqueous solution is a cause of worldwide concern. In particular, the presence of metals such as arsenic, lead, cadmium, mercury, chromium can affect human health. These toxic metals are exposed to human and environment. The accumulation of these toxic metal ions causes serious health and environmental hazards. Hence it is a major concern in environment. Due to this concern, the significance of developing technology for removing toxic elements is increased. Adsorption based on the cerium dioxide (CeO_2) has been used to remove toxic elements such as arsenic, mercury, cadmium, lead and chromium. Ceria display high surface area, controlled porosity and redox property due to which it is widely popular for removal of toxic elements

This article reviews the various remediation methods of toxic elements with emphasis on the field of nano materials. The article discusses toxic contaminants in water and their impact on human health; the synthesis and adsorptive behavior of ceria based material including the role of morphology and surface area on the adsorption capacity, best fit adsorption isotherms, kinetic models, and possible mechanisms, regeneration of adsorbents and future perspective of using metal oxide such as cerium dioxide. The focus of the report is the generation of the cost-effective oxides of rare earth metal, cerium and their composite forms for the removal of toxic elements.

Chapter I

Introduction

INTRODUCTION

Environmental pollution is defined as the contamination of the physical and biological components in the earth/atmosphere system to such an extent that normal environmental process are adversely affected. Environmental problem is one of the most serious problems faced by our planet in the present day scenario. It causes irreversible changes in the environment. [1]

The agents causing pollution are called pollutants. A pollutant may cause long or short term damage by changing the growth rate of plant or animals species by interfering with human amenities, comfort and health. Pollutants towards which the environment has low absorptive capacity are called stock pollutants. Stock pollutants accumulate in the environment over time and can create a burden for future generations. Environmental pollutants have various adverse health effects from early life. Some of the most important harmful effects are perinatal disorders, allergy, malignancies, cardiovascular disorders, increase in stress oxidative, mental disorders and various other harmful effects. [2]

Pollution comes from both natural and human made sources. However globally human made pollutants from combustion, construction, mining, agriculture and warfare are increasingly significant in the air pollution equation. Motor vehicle emissions are one of the leading causes of air pollution. Principal stationary pollution includes chemical plants, coal fired power plants, oil refineries, petrochemical plants, nuclear waste disposal activity, large livestock farms (diary, cows, pigs etc.), PVC factories, metal production factories and other heavy industry. Agricultural air pollution comes from contemporary particles which include clear felling and burning of natural vegetation as well as spraying pesticides and herbicides. About 400milion metric tons of hazardous wastes are generated each year. Some of the more common soil contaminants are chlorinated hydrocarbons (CHF), heavy metals. Pollution can also be the consequence of a natural disaster. For example, hurricanes often involve water contamination from sewage and petrochemical spills from ruptured boats or automobiles. Some sources of pollution, such as nuclear power plants or oil tankers can produce widespread and potentiality hazardous releases when accidents occur. In case of noise pollution, the dominant source vehicle, producing about 90% of all unwanted noise worldwide. [3]

A pollutant generated in the effluent is classified as organic and inorganic pollutants which have a different level of toxic levels in it. Biological, physical and chemical methods are widely used in the treatment of organic pollutant [4]. But these methods are not suitable for the inorganic pollutants like heavy metals. Because of their qualities like solubility, oxidative, reduction characteristics, and complex formation, the heavy metal decomposition plays a major concern. The word heavy metal refers to the element which has a higher density and toxic even at low concentration.

Some of the toxic heavy metals like nickel, arsenic, chromium, zinc, copper, cadmium, cobalt, antimony etc. which induces the dangerous and toxic effects to the living environment [5,6,7]. Ionic forms of the metals like Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{2+}, and As^{3+} reacts with bio particles in the body to form toxic compounds which are crucial to isolate. Ligand and oxidation state plays a vital role in bioavailability of heavy metals. When the concentration of heavy metals is beyond the permissible limit, then the heavy metal is a toxic metal. The toxicity of the metal results in lowering the cerebral and nervous function, harm the blood content, lungs, kidneys and other organs, bring out weakness, memory loss, increase in allergies and increase in blood pressure in the human body. Cell death also takes place due to the formation of free radicals and these radicals are responsible for the oxidative stress. Due to these effects, health authorities are increasing worldwide and several regulatory bodies have adopted the permissible limits to the heavy metal discharge effluent.

CONTAMINANTS

Arsenic

Arsenic contamination in water takes place via several factors, some of which are arsenic leaching because of geological weathering of rocks, mining, release of industrial contaminants in the form of pesticides, dyes and paints, and processing ofminerals. It can have mutagenic, chronic neurotoxic and carcinogenic effects on humans over long-time exposure (Raichur and Panvekar 2002; Hokkanen et al. 2015) [8,9, 10]. The Environmental Protection Agency of United States has recommended permissible limit for arsenic in potable water to be less than 0.01 mg/L (Yamamura et al. 2003) [11].

Chromium

Chromium compounds find extensive use in metallurgical, chemical and refractory applications. Hexavalent chromium (Cr^{6+}) is identified as a potential mutagen and carcinogen. However, trivalent chrome is not toxic (Albadarin et al. 2013)[12]. Council of the European Union has put restrictions on the occurrence of Cr^{6+} to be lower than 0.05 mg/L (Recillas et al. 2010)[13].

Lead

Toxic lead (Pb^{2+}) is generally released in water stream by processes such as dyeing, petroleum industry, tannery, smelting, galvanization, mineral processing. The World Health

Organization limit for lead in potable water is 0.01 mg/L. The consumption of lead above safe levels can lead to attack on central nervous system and reproduction system. It can also adversely affect liver and kidneys (Huang and Pan 2016) [14].

Cadmium

The World Health Organization limit for cadmium (Cd^{2+}) presence in drinking water is 0.003 mg/L. The associated risks of exposure to cadmium include itai–itai disease and renal complications. It is produced mainly by battery industries and electroplating industries (Järup et al. 1998) [15].

Nickel

Nickel is hard and silver metal that has the atomic number of 28. It is the type of nonbiodegradable heavy metal found in wastewater. The industrial sources like printing, electroplating industries, silver refineries, battery manufacturing industries, alloy industries subject to the nickel metal [16, 17, 18, and 19]. The effects of nickel are a dry cough, chest pain, creates breathing problem, nausea, diarrhea, skin eruption, pulmonary fibrosis, renal edema etc. To avoid the certain health and environmental risks, an attractivetreatment methodology is needed to recover the nickel metal.

Mercury

The highly toxic heavy metal in the wastewater is mercury. Mercury exists in different forms like elemental mercury (Hg^0), mercurous ion ($Hg_2{}^{2+}$) and mercuric ion (Hg^{2+}) [20]. The mercury metal can transport in aquatic systems and accumulate in ecosystems [21, 22]. Dueto its availability in the environment, it creates various environmental problems. One of the mercury compounds like methyl mercury damages the enzyme sites and affects the protein synthesis [23]. Generally, the large amount of mercury is added in industries like paper and pulp, plastic industries, chloro-alkali industries, pharmaceutical industries oil refineries etc. [24, 25]. The possible consequences of mercury include damage to kidney, brain, reproductive and respiratory system. Therefore, the removal of mercury from the industrial effluent has recently gained a lot of attention by the researchers.

Researchers concentrated on developing the treatment techniques for the removal of the toxic elements[26]. Various techniques used for the removal of toxic elements are coagulation/flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical treatment, and adsorption. Among all the methods proposed for toxic elements removal adsorption stands out as a simple and efficient method.

ADSORPTION:

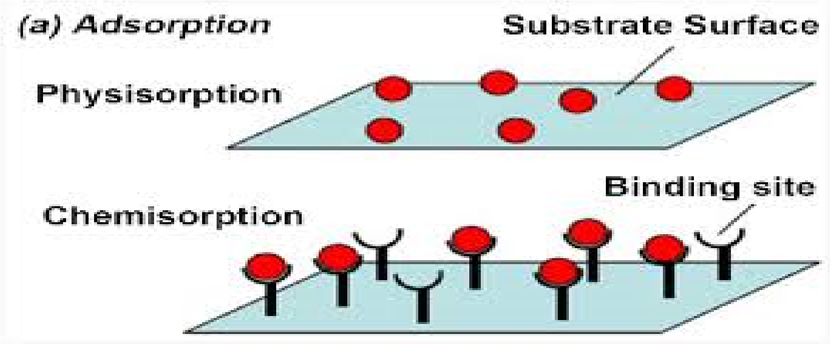
Nowadays the adsorption process is perceived as an admirable method to other technologies for the removal of toxic elements. The adsorption process is an alternate and assuring method to the traditional process for the purpose of lowering cost and most economic for heavy metal removal from the effluent. In the adsorption process, adsorbents can be recreated by desorption process because it is reversible technique and the regenerated adsorbent can be reused for several purposes. Several methods are available for the regeneration of adsorbent. Based on the regeneration, the adsorption is considered as an environmentally acceptable method. Adsorption technique is easy to use and doesn't produce toxic pollutants. High surface area, pore size distribution, functional groups, the polarity of adsorbent determines the efficiency of adsorption process.

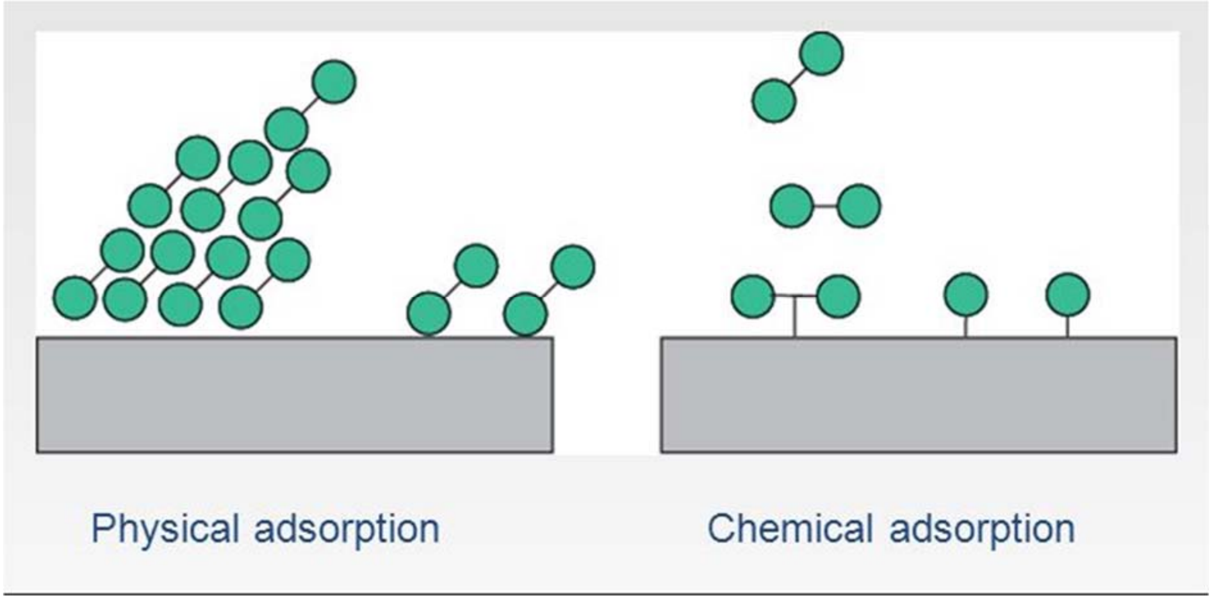
Adsorption is a process by which a solid holds molecules of a gas or liquid or solute as a thin film. It is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. It is the process which involves the accumulation of a substance in molecular species in higher concentration on the surface.

Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption process in which certain adsorbate are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. For adsorption process two components are required,

- Adsorbate: Substance which is deposited on the surface of another substance.
  For example; H_2, N_2 and O_2 gases.
- Adsorbent: Surface of a substance on which adsorbate absorbs. For example, Charcoal, Silica gels etc.

On the basis interaction of forces between adsorbate and adsorbent, adsorption is of two types:





- **Physisorption:**Physisorption is also known as physical adsorption and it is an exothermic process. Its adsorption enthalpy is low, nearly 20 to 40 kJ/mol.It is due to weak Van der Wall's forces between adsorbate and adsorbent.Physisorption lacks specificity because of the adsorbent in the given surface does not show any particular gas. It has reversible nature that is physisorption of gas by a solid can be reversed to a solid by a gas.

  Gas + solid = Solid/ Gas + Heat

  An example of physisorption is the adsorption of gases like hydrogen, nitrogen etc. at lower temperature on the surface of the adsorbent like charcoal.

  Physisorption depends on the surface area of the adsorbent. As the surface area increases, the extent of adsorption also increases. For example, finely divided metals and porous substances have a large surface area. So they are considered as good adsorbents. It also depends on nature of the adsorbate.

- **Chemisorption:** Chemisorption is also known as chemical adsorption. It is due to strong chemical forces of bonding type between adsorbate and adsorbent. Chemisorption has high specificity that is it is highly specific, and it takes place only if there is a chemical bonding between adsorbent and adsorbate. For example, involving the formation iron nitride on the surface when iron is heated in N_2 gas at 623K. Chemisorption has irreversible nature and it also favors high pressure. Its adsorption enthalpy is high nearly, 80 to 240 kJ/mol.Physisorption of gas adsorbed at a lower temperature may be converted into chemisorption at a higher temperature. Chemisorption depends on the surface area. As the surface area of the adsorbent increases, chemisorption also increases.

  An example of chemisorption is the adsorption of hydrogen, nitrogen etc. on the surface of adsorbent like ferrous catalyst at a high temperature.

Adsorption of a gas on a solid is a spontaneous exothermic reaction. Amount of heat liberated when a unit mass of a gas is absorbed on the surface is called **heat of adsorption**.

Adsorption isotherms

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of the adsorbent as a function of equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for description of adsorption data.

Freundlich Adsorption Isotherm:

Freundlich adsorption isotherm is obeyed by the adsorption where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

$X/m = K.p^{1/n}$, $\log x/m = 1/n \log p + \log k$

‘X’ represents the amount of gas adsorbed on the m gram of adsorbent

‘K’ and ‘n’ are adsorption constants

‘p’ is pressure, n always greater than one

A major drawback of Freundlich adsorption is that it fails at high pressure. It could not explain the multilayer adsorption process.

Langmuir Adsorption Isotherm:

The Langmuir adsorption model explains by assuming an adsorbate behaves as an ideal gas at isothermal conditions. According to the model, adsorption and desorption are reversible processes. This model is used to describe the equilibrium between adsorbate and adsorbent system, where adsorbate and adsorption is limited to one molecular layer at or before a relative pressure of unity is reached. Although the isotherm initially proposed by Langmuir in 1918 is generally suitable for describing chemisorption process when ionic or covalent bonds are formed between the adsorbent and adsorbate, the equation is obeyed in many systems with moderately low coverage and can be easily extended to describe the behavior of binary adsorption system. Langmuir further assumes that the fractional surface coverage $\emptyset$ is in direct proportion to the rate of desorption from the surface, and the adsorption and desorption rate are equal at equilibrium.

$k_a C_e (1 - \theta) = k_d \theta$

Where,

K_a is the respective rate constant for adsorption.

K_d is the respective rate constant for desorption.

The more usual from of the equation is described:

$\theta = q / q_m = bC_e / (1+b C_e)$

Where,

$b = k_a / k_d$

C_e is the equilibrium aqueous-phase concentration of the adsorbate (mg L-1)

$q_m$is the quantity of the adsorbate adsorbed in a single monolayer (mg L^{-1})

BET adsorption Isotherm

BET Theory put forward by Brunauer, Emmett, and Teller explained that multilayer formation is true picture of physisorption.

Activated Carbon

The efficiency of the activated carbon can be evolved by both high surface area and large pore size. Various researchers used activated carbon for the heavy metal removal from the waste water. Due to the deficiency of commercial activated carbon (AC), the cost of ac increases. Langmuir model best described the adsorption of activated carbon and led to maximum adsorption capacity of 27.53 mg/g at optimum dosage 2.0 mg/l. The kinetic studies showed that pseudo second order model best fitted with the adsorption. Recently a research was carried out in surface modification AC using an oxidation process which stimulates the adsorption efficiency in heavy metal removal.

Carbon Nanotube

Carbon nanotubes (CNT) are mostly considered in the toxic element removal process because of its great properties and its uses. The carbon nanotubes are made up of cylindrical graphite sheets folded into tube like structure. CNTs found to be the best adsorbent in waste water treatment because of its excellent mechanical properties and magnetic properties, high chemical and thermal stability. But the usage of CNTs has been reduced because of the strong accumulation of CNTs and their functional group shortage.

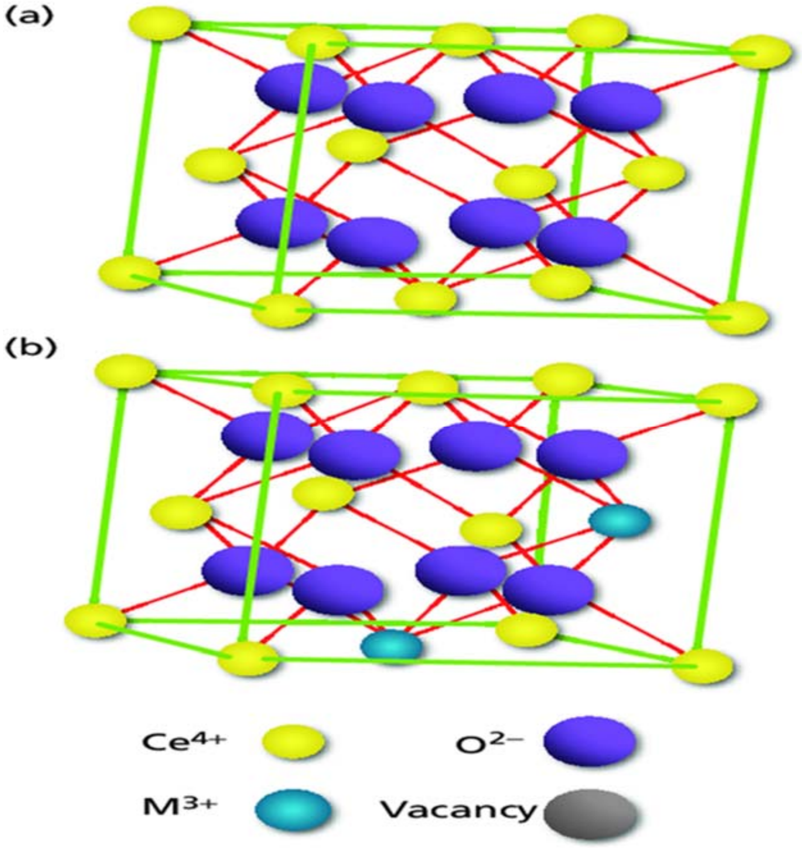
Biosorbent

Biosorption is the innovating technique in removal of toxic element from the effluent. This technique is considered to be an efficient and detoxification process in the elimination of heavy metal even at low concentration. Biosorption is a kind of adsorption process which consists of solid state (sorbents) and liquid state (solvent). Biosorpents are considered to be low cost adsorbents, feasible and can be obtained from various industries as a waste product. Due to the presence of functional groups like alcohols, aldehydes and ketones carboxylic acids, ether, phenolic groups enhance the adsorption activity towards the metal removal. The important factors affecting the potential of biomass in adsorption process are pH, temperature, adsorbent dosage, mutual concentration and contact time etc. The major phenomena in the bisorption process are adsorption, ion exchange, complexion and surface precipitation.

Cerium Dioxide

The use of metal oxide for treatment provides a low cost adsorption technology. Metal oxidescan include cerium dioxide, ferric dioxides, zinc dioxides and titanium dioxides. When sorption to heavy metals. In this article, the potential role of ceria and its composites with mainly other metal oxides materials for the removal of hazardous metal ions from water is reviewed. From the survey of the recent literature, it was found that hydrous ceria, ceria nanoparticles, ceria in various morphologies such as three-dimensional flower-type, hollow microspheres as well as nanospheres, nanorods, nanocubes and their combinations with graphene oxide, carbon nanotubes, silica, iron oxide, zirconia, tin oxide, manganese oxide and electrospun chitosan have been investigated in details for water purification. The target metal contaminants are arsenic, chromium, lead, mercury, cadmium, copper, nickel, vanadium, etc. Arsenic has been researched extensively compared toother metal ion contaminants. A brief of toxic effects of these contaminants on humans is provided. The core of the article deals with the synthesis strategies of cerium-based oxides as well as composites and adsorptive removal of metal ions and highlights mainly their adsorption capacity, mechanism of adsorption, isotherm model fit and kinetic model fit and regeneration of adsorbent materials for further use. Overall, a comprehensive outline of adsorption performance of ceria and its composites is provided.

CERIUM DIOXIDE STRUCTURE:-



Bulk cerium oxide has at least two stable stoichiometric, the dioxide(CeO_2) and dicerium oxide(Ce_2O_3) which is commonly referred as sesquioxide. At ambient conditions dioxide crystallises as CaF_2 (fluorite) structure in face centered cubic space group Fm3m with the lattice parameter of 5.411Å. In that structure cerium ions occupy the vertices and faces of cubic unit cell. Each Ce (IV) is coordinated with eight oxygen ions arranged in a perfect cube, while each oxygen ion is surrounded by four cerium ions in tetrahedral arrangements. This structure is often described as cubic close packing(ccp)of cerium with oxygen ions occupying all tetrahedral holes at elevated pressure (31GPa and room temperature)cerium dioxide undergoes phase transition from fluorite to cottunite structure type with orthorhombic space group Pnam.

Chapter II

Literature Review

LITREATURE REVIEW

1. Removal of mercury

R. Sharma & et al. studied on ceria nanoparticles (CeNps) entrapped in tamarind powder (Tm@CeNps) which were efficiently utilized for the simultaneous adsorption of aqueous mercury [Hg (II)] and aqueous lead [Pb (II)] [27]. The investigation was characterized by Brunner-Emmett-Teller (BET), XRD spectroscopy, X-ray photoelectron spectroscopy, FTIR and thermo gravimetric analysis. They used adsorption mechanism for adsorption of Hg (II) and Pb (II) by tamarind leaf composite. They studied that the mean free energy required for adsorption is lower than Pb (II), which means that the Hg (II) is easily adsorbed on Tm@CeNps. The use tamarind leaves opens a new class of adsorbent for the heavy metal ion removal, as the surface area of tamarind leaves is very high. The surface properties of adsorbents were analyzed by using N_2 adsorption-desorption isotherms with the use of the BET method. TGA and DGA analysis were carried out to the study of characteristics physical changes in the adsorbents.

Tian & et al. studied on activated carbon CeO_2 impregnated with cerium dioxide for removal of elemental mercury [28]. In this work, a novel CeO_2/AC (activated carbon impregnated with cerium dioxide) sorbent was studied with an attempt to produce economical & effective sorbent for capturing mercury. The properties of the sorbents were characterized BET, nitrogen adsorption & XRD technique. Low loaded samples have greater BET surface area & total pore volume than AC. The sample with higher loadings such as 5% CeO_2/AC has lower BET surface area & total pore volume than AC, 1% CeO_2/AC & 3% CeO_2/AC. The XRD patterns of CeO_2 show that CeO_2 is highly dispersed on the surface of the activated carbon when the CeO_2 loading was 3%. The results showed that CeO_2 impregnation particularly with 3wt% CeO_2 –impregnated greatly enhanced the AC adsorption ability for elemental mercury. The From the temperature effect test, we can also find that CeO_2/AC sorbent has poor anti-temperature performance. Therefore, future works should be concentrated on improving its ability of resisting high temperature by the chemical modification. The effect of flue gas components such as SO_2, NO and HCl on the Hg^0 removal efficiency of novel CeO_2/AC adsorbents should also be considered future research.

J. He et al. studied on high surface area ceria –titania materials & manganese oxide for both warm-gas mercury capture and low temperature selective catalytic reduction. The materials synthesized were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption, temperature programmed reduction (TPR), ammonia temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) [29]. Brunauer-Emmett-Teller surface area measurements suggested that increasing manganese loading reduced the surface area due to pore blockage. X-ray diffraction measurements showed that MnO_x is in an amorphous state on CeO_2-TiO_2 materials. X-ray photoelectron spectroscopy results indicate that the adsorbed mercury is present as both Hg^0 and Hg^{2+} on these ceria based materials. The XPS observations also suggest that the incorporation of titanium into the cubic lattice of ceria leads to the formation of more lattice oxygen atoms, leading to greater formation of Hg^{2+} on the CeO_2-TiO_2 support. Increasing manganese loading on the CeO_2-TiO_2 support increased mercury capacities at the same conditions. However, changing the bed temperature from 175 to 200^{oc} reduced the mercury adsorption. SO_2 inhibits Hg^0 adsorption on the MnO_x, but CeO_2- TiO_2 retains most of its Hg^0 capacity in the presence of 100 ppm SO_2. Simultaneous capture of Hg^0 and Hg^{2+} at 175^{oc} was obtained using CeO_2-TiO_2. These results suggest that the sulphur tolerant MnO_x/CeO_2-TiO_2 materials might be technically feasible warm-gas mercury adsorbents.

Q. Lv et al. studied on cerium modified semi coke for elemental mercury removal. In this study, raw semi-coke and a series of novel cerium (Ce) modified semi-cokes were synthesized and utilized for removing elemental mercury (Hg^0) from simulated flue gas [30]. The adsorption and reaction mechanism were discussed based on the characterization of the sorbents. The results shows that the sorbents performed best at the temperature of 150^{oc} and the optimal concentration of cerium nitrate solution was 0.2 mol l^{-1}. The introduction of O_2 enhanced the sorbents performance by oxidizing Hg^0 through Mars-Maessen mechanism. The most decisive component in simulated flue gas for mercury removal is NO, which participated in the formation of HgO and $Hg\ (NO_3)_2$ through Langmuir-Hinshelwood mechanism and Eley-Rideal mechanism. The Hg^0 removal efficiency decreased due to the addition of NH_3. However, the adverse influence could be ignorable considering the tiny amount of NH_3 in the vicinity of sorbents working zone. Besides, the modified semi-coke showed excellent resistant ability to SO_2. The results would be meaningful for developing the alternative low-cost mercury sorbent and understanding the elemental mercury removal mechanisms. The properties of sorbents depend to a large degree on the type of semi-coke. Thus, the sorbents derived from other type of semi-coke will be investigated in future.

D. Liu et al. investigated on the kinetic behavior of gas phase mercury sorption on ZSM-5 supported cerium and lanthanum based composites oxides in the temperature range of 120-240^{oc}[31]. The study was characterized by field emission scanning microscope. In the temperature range of 120-240^{oc}, cerium-based composite oxides perform better than lanthanum based composite oxides on Hg^0 sorption [32, 33]. Cerium oxide possess good oxygen defects leading to production of more surface lattice oxygen, which significantly improves the Hg^0 sorption performance attributed to the enhanced chemisorption ability. However, adding Cu or Mn into La_2O_3 lattice would reduce the Hg^0 sorption abilities of the lanthanum-based composite oxides owing to the formation of perovskite or perovskite like compounds with stable structures and less surface lattice oxygen. The Hg^0 removal efficiencies all first increase and then decease with incremental sorption temperatures. The optimal sorption temperatures for CeO_2-CuO/ZSM-5 and CeO_2-Mn_2O_3/ZSM-5 are 210^{oc} and 180^{oc} respectively, while the best sorption temperatures for La_2O_3-CuO/ZSM-5 and La_2O_3-Mn_2O_3/ZSM-5 are 210^{oc} and 150^{oc} relatively.

S. Mohajer studied on cerium dioxide nanoparticles for preconcentration of trace amounts Hg (II) ions from aqueous solution [34]. The analysis of mercury was performed by cold vapor atomic adsorption spectrometry. The characteristics of nanoparticles were assessed using X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. Experimental parameters influencing the extraction procedure recovery were thoroughly investigated. Under the optimized experimental conditions, the calibration curve was linear in the range of 0.035 to 0.8 µg/L of mercury. The method was validated by analysis of a certified reference material. The results showed no interfering effects from different foreign ions at the level studied and so the method can be used for determination of Hg (II) in various samples.

2.Removal of Arsenic

T.M. Arsic and et al. studied on carbon cryogel/ceria composite with 10wt% of ceria which was synthesized by mixing of ceria and carbon cryogel for the adsorption of arsenic (III) ions from aqueous solutions [35]. The sample was characterized by field emission scanning electron microscopy (FESEM), nitrogen adsorption and x-ray diffraction. Characterization by the FESEM showed that the homogenous distribution of ceria on the surface of the carbon cryogel was achieved. Nitrogen adsorption confirmed that the high specific surface area and porous structure of the material were preserved. XRD analysis confirmed the presence of ceria. In this study, adsorption kinetic, the effect of solution pH and arsenic concentration on removal rate were examined in batch system. Adsorption kinetics followed the pseudo-second order model. Adsorption dose experiments i.e. calculation of optimal ratio between the volume of the solution and mass of the adsorbent, showed that the optimal mass of theadsorbent was reduced 20 times, in comparison with cc. Adsorption isotherms confirmed that the amount of As(III) removed is slightly pH dependent and the shape of isotherms is the characteristics for the physical, multilayer adsorption. Experimentally obtained isotherms are best fitted by the application of BET isotherms for melting the liquid phase adsorption.

Q. Feng & et al. investigated on the adsorption and desorption behaviors of arsenic on ceria nanoparticles in aqueous solution [36]. Ceria nanoparticles used in the experiments were synthesized using a precipitation method. The surface area was characterized by nitrogen adsorption/desorption analysis of Brunauer-Emmett-Teller. The adsorption and desorption behavior was studied by using batch technique. The adsorption isotherm was fitted very well to both the Langmuir and Freundlich isotherm models. The thermodynamic parameters (ΔH^0, ΔS^0, & ΔG^0) for the adsorption of arsenic were determined at three different temperatures of 283, 303 and 323K. In this work, high adsorption capacity & reversible adsorption of arsenic suggests that ceria nanoparticles may influence the fate &behavior of arsenic in the environment. Thus, ceria nanoparticles with arsenic may exhibit synergistic effect when interacting with living organisms. The results indicate that studies dealing with the potential ecotoxicological effects of nanoparticles for the environment have to be designed in order to have the defined understanding between the nanoparticles and the adsorbed chemicals in the environment.

Yu & et al. studied on hydrous cerium oxide modified graphene nanoparticles composite (GNP HCO) to describe the key limitations of slow adsorption kinetics for arsenic removal [37]. The sample was characterized by FESEM, EDS, XPS & TEM technique to study the morphological & compositional information of the asynthesized adsorbent. The point of zero charge was estimated by pH drift method. The value of point zero charge (pH_{PZC}) of the adsorbent is determined to be approximately 6.0. The surface charge of the adsorbent is highly depends on pH. When the solution pH is above its pH_{PZC}, negative charges can be readily formed on the surface of the adsorbent, which is unfavorable for the uptake of anion because of the enhanced electrostatic repulsion between the adsorbent surface & the target anions. The experimental data was better described by the Langmuir isotherm model & the maximum adsorption capacities were 62.33 & 41.31 mg-As g^{-1} at pH 4.0 & 7.0 respectively, which are much higher than many modified carbon based adsorbents. XPS analysis indicated that the major chemical state of cerium element in the adsorbent was +IV & the hydroxyl group might be involved in the adsorption process.

R. Sawana et al. investigated on methodologies for arsenic removal from drinking water by using ceria modified activated carbon [38]. The CeO_2 powdered activated carbon (PAC-

CeO_2) is highly efficient as an adsorbent for arsenic removal from drinking water. It removes both As (III) and As (V) from water without any peroxidation process. The materials were characterized by X-ray diffraction technique, Zeta potential meter, BET surface measurements, X-ray photoelectron spectra, Raman spectra and FTIR spectra. In this case, the pseudo second order kinetics indicates that the arsenic adsorption on PAC-CeO_2 happens through chemisorption, which also been observed in FTIR study. After the arsenic adsorption experiments, the Ce-OH bending vibrations disappeared and a new vibration at 839cm^{-1} appeared which could be attributed to ν (As-OCe) bond. The FTIR studies indicate that substitution of OH groups by As from Ce-OH plays a major role in the adsorption process which could be explained through specific adsorption mechanism. The specific adsorption involves ligand exchange reaction where the anion displaces OH^- and/or H_2O from the surface.Since the surface change of the PAC-CeO_2 adsorbent was positive in the experimental pH range the columbic attraction between the positive surfaces and negative anions also played a role in giving the adsorbent a high removal capacity for both As(III) and As(V) across the pH ranges.

P.K Mishra et al. studied on cerium dioxide nanoparticles of size 3-5nm for adsorptive removal of arsenic species. CeO_2 nanoparticles with huge surface area (257 m^2 g^{-1}) and ultra-low bulk density (0.049 g ml^{-1}) were synthesized using one-pot aerogel process [39]. CeO_2 nanoparticles were characterized by TEM, SEM, XRD, N_2 adsorption, BET, and FTIR. The R-P model was best fitted on adsorption data & indicated the characteristics of monolayer adsorption over CeO_2 nanoparticles. Prepared CeO_2 was used to remove As (III) and As (V) from water at variable contaminant concentrations (25-100 ppm)& pH (3-10). CeO_2 nanoparticles indicated adsorption capacities of 71.9 and 36.8 mg g^{-1} against As (III) and As (V), respectively. The adsorption data best fitted with Redlich-Peterson model, depicting monolayer adsorption. The adsorption followed pseudo-second-order kinetics and intraparticle diffusion with three-step diffusion process.pH dependency studies indicated a down trend in adsorption capacity for the adsorption of As(V) over the pH range of 3-10. While in case of As (III), the change in pH could not make any significant effect on adsorption capacity of CeO_2 nanoparticles. Conclusively, CeO_2 nanoparticles were found promising for the fast and efficient removal of arsenic species from contaminated water.

Jing Chen et al. investigated on Ce-Mn binary oxide with a Ce/Mn molar ratio 3:1which was synthesized by a facile oxidation-coprecipitation method [40]. The sample was characterized by X-ray diffraction method, transmission electron microscope, Brunauer-Emmett-Teller method, FTIR technique. The synthetic Ce-Mn binary oxide is very effective for As (III) uptake and exhibits an obvious synergistic effect of Ce oxide and Mn oxide. The maximum sorption capacity of As (III) is 97.7 mg/g, which is competitive with most of reported sorbents. The As (III) uptake is achieved mainly through As (III) oxidation coupled with As (V) adsorption on the Ce-Mn binary oxide. The As (III) sorption is slightly affected by tested solution pH, ionic strength, dissolved organic matters and coexisting anions except for phosphate. The spent Ce-Mn binary oxide could be easily regenerated using NaOH solution for reuse. Due to its facile synthesis process, good arsenic removal performance and easy regeneration, the Ce-Mn binary oxide could be a promising sorbent for As (III) removal from contaminated water.

L. Zhang et al. studied on cerium modified chitosan (Ce-CNB) ultrafine nanobiosorbent for the removal of arsenic (III) from water [41]. The sample was characterized by FTIR, XRD, SEM, EDS, TEM, EMI and XPS analysis. Batch of adsorption experiments were performed to investigate the effects of various conditions on As (III) adsorption. The adsorption behaviors were well described by the Langmuir isotherm and the pseudo-second order kinetic model, with the maximum adsorption capacities of 57.5 mg g^{-1}. The adsorption mechanisms for As (III) were formed monodentate and bidentate complexes between hydroxyl groups and arsenite & partial As (III) oxidized to As (V) followed by simultaneously adsorbed on the surface of Ce-CNB. This novel nanocomposites can be reused while maintaining a high removal efficiency and can be applied to treat 5.8 L of As (III)- polluted water with the effluent concentration lower than the World Health Organization Standard, which suggests its great potential to remove As (III) from contaminated water.

3. Removal of Nickel

R. Murugan studied on CeO_2 and Ni-CeO_2 thin films with cubic fluorite structure were prepared by rf magnetron sputtering [42]. The sample was characterized by X-ray diffraction, UV-Visible and Photo Luminescence analysis. Vibrational and magnetic properties of the films were analyzed through Raman and VSM analyses. The results from XRD and Raman spectroscopy indicate that doped Ni species were dispersed on the ceria surface. Room temperature magnetic measurements reveal paramagnetic nature of pure CeO_2 thin films and ferromagnetic nature with reasonable saturation magnetization of Ni doped CeO_2thin films. It is believed that the ferromagnetic contributions exhibited in the M-H loops originate from the absorptive oxygen on the surface rather than the oxygen vacancies in the lattice.

Chang-Yan Cao et al. studied on ceria hollow nanospheres for heavy metal ion removal catalysis. Ceria hollow nanospheres composed of CeO_2nanocrystal were synthesized via a template-free and microwave assisted aqueous hydrothermal method [43]. This is a low-cost and environmentally benign method. The chemicals used are all environmentally benign materials (cerium nitrate, urea, and water). An Ostwald ripening mechanism coupled with a self-template, self-assembly process, in which amorphous solid spheres are converted to crystalline nanocrystal and the latter self-assemble into hollow structures, was proposed for the formation of the hollow structures. The products were characterized by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, high-resolution TEM, energy-dispersive X-ray analysis, X-ray photoelectron spectroscopy, and N_2 adsorption-desorption methods. These ceria hollow nanospheres show an excellent adsorption capacity for heavy metal ions, for example, 22.4 mg g-1 for As (V) and 15.4 mg g-1 for Cr (VI). These values are significantly higher than reported data from other ceria nanostructures. These ceria hollow nanospheres are also excellent supports for gold nanoparticles, forming an Au/CeO_2 composite catalyst. In CO oxidation, a 100% CO conversion was achieved at room temperature.

A.L. Santos et al. studied on silica- alumina compound impregnated with cerium, nickel and molybdenum oxides for removal of sulphur and nitrogen compounds from a hydro treated Brazilian diesel at 313K [44]. The sample was silica doped boehmite with an Al_2O_3/SiO_2 named as SIRAL & the sample was identified as SIRAL-C. The sample was characterized by infrared and X-ray diffraction method. The textural characteristics such as specific area (BET) & pore volume (BJH) were determined by N_2 adsorption/desorption isotherms at 77K. It was observed that the incorporation of metal oxides to led to an increase of the adsorptive capacities per specific area. The increase in nitrogen and sulphur uptake capacity was tentatively associated to acidic properties. However, the impregnation process also brought a reduction of the adsorbent surface. As a consequence, an increase of the total adsorption capacity in a mass basis was not observed. These results suggest that the impregnation process using the proposed oxides is a possible alternative, if the diminishing of the adsorbent surface will be controlled.

4. Removal of phosphate

Y. Su et al. studied on Cerium-zirconium binary oxide nanoparticles synthesized by solvothermal process for phosphate removal in batch studies. Through careful modulation of the Ce/Zr ratio, Ce/Zr binary oxide nanoparticles were created with different structure, crystal size, surface properties, and phosphate adsorption performance. It was found that $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles had the best phosphate adsorption performance among these Ce/Zr binary oxide nanoparticles, which could attributed to their desirable structure & properties. The phosphate adsorption capacity of $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles was determined at ~ 112.23 mg/g, the highest among various adsorbents reported in literature. The adsorption of phosphate onto $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles followed the inner-sphere complexing mechanism, and the surface –OH groups played the major role. Commonly coexisting anions showed no or moderate effect on the phosphate adsorption onto $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles, and little pH dependence was observed for their phosphate adsorption in the range from pH 2 to 6. After adsorption, phosphate adsorbed on these $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles could be easily desorbed by NaOH solution washing. Thus, $Ce_{0.8}Zr_{0.2}O_2$ nanoparticles may have the potential to be a promising adsorbent as the supplement to the biological process for the phosphate removal on small-scale treatment facilities or waste water with relatively low phosphate concentration.

Wei Gu et al. investigated on Ce-incorporated zinc ferrites ($ZnCe_xFe_{2-x}O_4$, x~ 0.48) to develop a stable and easily separable adsorbent for the efficient removal of phosphate from water [46]. The sample was investigated by X-ray diffraction method, Transmission electron micrograph, and Brunauer-Emmett-Teller, FTIR and N_2 adsorption-desorption method. Results indicated that, though introduction of Ce decreased saturation magnetization, the ferrites were magnetically separable with saturation magnetization exceeded 32.0 emu/g when $x \leq 0.12$. On the other hand, increasing Ce content greatly boosted the adsorptive capacity of phosphate, with Langmuir adsorption maxima increasing from 5.2 mg/g to 41.6 mg/g at 25^{oc} when x increased from zero to 0.48. However, P/Ce molar ratio was found to be the highest when x=0.12, enabling the most efficient use of Ce. The adsorption of phosphate was the most favorable within the middle pH range and the increase in both ionic strength and temperature enhanced adsorption. The material showed good affinity for phosphate in the presence of common anions. Experimental results also showed that NaOH or KOH were applicable for the purpose of adsorbent regeneration. In conclusion, Ce-incorporated zinc ferrite with the composition of $ZnCe_{0.12}Fe_{1.88}O_4$ has the potential for the removal of phosphate from water.

5. Removal of cadmium, lead, and chromium

Contreras and et al. studied on potential differences of the sorption capacity of CeO_2 nanoparticles with regard to cadmium (II), lead (II) & chromium (VI), dissolved in water, both in single systems (one metal in solution) as well as in multicomponent system (all three metals mixed together in solution) [47]. The study was performed at two different pHs (5 & 7), which are typical pHs found in environmental system. A factorial experimental design was used to obtain an empirical equation that can describe the sorption capacities as a function of the initial metal concentration, initial nanoparticle concentration & pH. The adsorption studies considered the metal concentration from 1mg l^{-1} to 10mg l^{-1} and nanoparticle concentration from 0.064g l^{-1} to 0.640g l^{-1}.The highest adsorption capacity was obtained in the removal of lead (II) (128.1 mg g^{-1}), followed by cadmium(II) (93.4 mg g-1) and finally chromium (VI) (34.4 mg g^{-1}). Data were fitted to a polynomial function obtaining the best reduced models. The type of system (single, multicomponent) did not affect sorption capacity, while pH affected the sorption of Cd and Cr, but not that of lead. CeO_2 Nps proved to be effective adsorbent in removing all the three heavy metals in multicomponent system, which opens a new window for their uses as sorbent materials in complex waters contaminated with mixture of heavy metals.

Chao Wang et al. investigated on cerium dioxide nanoparticles for removal of lead from contaminated water [48]. They investigated on the adsorption behavior of Pb^{2+} on sediments spiked with cerium dioxide nanoparticles at a weight ratio 5.0%. The results showed that the adsorption rates at three stages occurring during adsorption clearly increase for sediments contaminated with cerium dioxide nanoparticles. Moreover, the results obtained from the adsorption isotherms indicated that the Langmuir isotherm model best fits the isotherm data for both sediments and those contaminated with cerium dioxide nanoparticles. After spiking the sediments with cerium dioxide nanoparticles, the theoretical maximum monolayer adsorption capacity (Q_{max}) for Pb^{2+} increased from 4.433 to 4.995 mg/g and the Langmuir isotherm coefficient (KL) decreased from 8.813 to 7.730 L/g. The effects of cerium dioxide nanoparticles on the surface charge and pore surface properties affect the adsorption of several chemicals in sediments. The results showed that pH_{ZPC}, SBET, Sext and average pore size of sediments contaminated with cerium dioxide nanoparticles. Hence the strong adsorption capacity of CeO_2 Nps and the changes of sediment surface charge and pore surface properties caused by CeO_2 NPs are important factors affecting the adsorption behavior of Pb^{2+}. The potential risk of Pb^{2+} in aquatic environment may increase with CeO_2 Nps buried in sediments.

H. Sharifan et al. studied on physiochemical properties of cerium oxide nanoparticles for removal of Cadmium and arsenic [49]. This study measured the adsorption isotherms of Cd and As (III)/ As (V) onto 100 mg L^{-1} cerium oxide nanoparticles (CeO_2 Nps) both in presence and absence of synthetic root exudates (SRE) in batch reactors. The adsorption study was allowed to proceed for 48 hours to ensure equilibrium. Addition of SRE lowered the pH of the mixture from around 5.9 to 2.3. Both As and Cd displayed strong adsorption on CeO_2 Nps at pH 5.9. The adsorption was drastically reduced at pH 2.3 without SRE. The presence of SRE mitigated the pH effect, but the adsorption of As and Cd was invariably lower at pH 2.3 than at pH 5.9, irrespective of the SRE. The interaction of metalloids with CeO_2 Nps significantly increased the hydrodynamic size of some CeO_2 Nps to micrometer and significantly changed the zeta potential of these nanoparticles to the range of -10 to +10 mV. Different effects on CeO_2 Nps and these two metalloids on their plan uptake and accumulation, and demonstrated for the first time that co-existing heavy metalloids may significantly alter the fate and accumulation of ENPs in plants.

S. P. Mishra et al studied on hydrous ceric oxide for the efficient removal of cadmium ions from aqueous solution [50]. The sample was characterized by infrared and X-ray diffraction (XRD) technique. The adsorption of cadmium ions on hydrous ceric oxide has been studied as a function of concentrations (10^{-2}-10^{-7}), temperature (303-333 K) and pH (7.08-10.47) of adsorptive solution, applying radiotracer technique. The kinetics of adsorption was found to follow first order rate law with respect to the adsorptive concentration and agrees well with classical Freundlich isotherm. The effect of temperature on equilibrium adsorption values has been utilized to evaluate the change in standard thermodynamics quantities (viz. ΔH^o, ΔS^o and ΔG^o). The sorption process was found to be endothermic and irreversible in nature. Overall results suggest that the synthetic hydrous ceric oxide may be used for the removal of cadmium ions from aqueous industrial wastes and should be of help in environmental protection.

A.Al-Kinani investigated on Polyaniline-coated cerium oxide nanoparticles which were synthesized in alkaline media and applied for preconcentration of ultra-trace levels of cadmium (II) in different real samples followed by electrothermal atomic adsorption spectrometry [51]. Cerium oxide nanoparticles were synthesized by a microwave method and modified by poyaniline to produce Polyaniline-coated cerium oxide nanoparticles. Fourier-transform infrared spectroscopy and scanning electron microscopy were used to characterize the synthesized adsorbent. To optimize the critical experimental conditions; surface response methodology- Box-Behnken experimental design was used. On the basis of the results, pH 8.4, 10mg of poyaniline-coated cerium dioxide nanoparticles, 14.4min extraction time, and 4.3min desorption time were selected as the optimum conditions. Under the optimum conditions the calibration curve of cadmium (II) was linear in the range of 0.02-0.4 ng mL^{-1} with a correlation coefficient of 0.9976. The analysis of certified reference material shows very good agreement with the certified value. Finally, the proposed method was applied for the determination of ultra-trace levels of cadmium (II) in different water, rice, and tea samples.

A.R. Contreras studied on cerium dioxide (CeO_2), iron oxide (Fe_3O_4) and titanium oxide (TiO_2) were studied for the removal of dissolved cadmium from water at concentrations ranging from 25 to 350 mg/L [52]. Adsorption was the predominant mechanism for sequestration, and particularly efficient cadmium removal was demonstrated for Fe_3O_4 NPs. Experimental data were fitted to three different adsorption isotherm: Langmuir, Freundlich and Temkin. The best fit was obtained for the Freundlich isotherm ($R^2>0.96$ for all NPs). Adsorption was shown to follow pseudo second order kinetics ($R^2 \geq 0.91$ for all NPs). All three NPs showed some removal of cadmium in aqueous solution, but after 72hr of process, Fe_3O_4 NPs showed a higher capacity of cadmium adsorption (101.1 mg Cd/g NP) than CeO_2 Nps (49.1mg Cd/g NP) or TiO_2 Nps (12.2 mg Cd/g NP). These results demonstrate the potential use of this Nps to remove dissolved cadmium at high concentrations.

S. Mandal studied on cerium oxide Polyaniline composite for the removal efficiency of Cr (VI) from water [53]. The characterization of cerium oxide composite has been done by various physicochemical techniques followed by mechanistic explanation of Cr(VI) adsorption. The experimental design, parametric appraisal and prediction of the adsorption process are performed using response surface methodology (RSM-CCD) and artificial neural network (ANN) method, respectively. Adsorption studies with respect to various process variables such as dose, time, pH, temperature and initial concentration is carried. A second order predictive quadratic equation relating to removal percentage and important process variables was developed and adequacy of the model was checked. The kinetic studies revealed that the adsorption process followed pseudo-second order kinetics. The adsorption data were best fitted to Langmuir model. The adsorption capacity for Cr(VI) ions was 357 mg/g at pH 6. Based on the above findings it can be stated that the material cerium oxide Polyaniline composite can be efficient adsorbent material for the removal of Cr(VI) from water.

J.S. da Silva Neto et al. studied on cerium doped iron oxide nanoparticles for removal of chromium from aqueous solution [54]. The sample was characterized by X-ray diffraction (XRD), Infrared (IR), scanning electron microscopy, analysis of porosity and surface area (BET). The analysis of porosity and surface area were performed using the method of nitrogen physisorption. The hexavalent chromium adsorption tests were performed at acidic pH. Under these conditions, the surface charge of the iron oxides becomes positive due to the protonation of the surface hydroxyl groups, thus, creating an electrostatic attraction between the surface and the hexavalent chromium, which is present as oxyanion ($HCrO_4^-$) when hydrolyzed in water. The results showed that cerium doping is a favorable process to obtain iron oxides with textural characteristics. The results showed that all doped sample exhibited higher surface areas and smaller crystallite diameters. The best results on chromium removal was obtained for the 5% cerium doped sample, where it was possible to show that doping enhanced the removal power both due to the specific adsorption phenomenon and as a result of the photoreduction of Cr (VI) to Cr (III) desorption and precipitation. This favors the easy recovery of the adsorbent produced, which can be reused in new adsorption cycles.

F. Wang et al studied on fibrous mat of chitosan/polyvinyl alcohol (CS/PVOH/Ce) containing cerium (III) for the removal of chromium (VI) from aqueous solution [55]. The sample was prepared by electrospinning technique and used as a biosorbent. The chemical, structural and morphology characteristics of the fibrous mat are determined by Fourier infrared spectrum (FTIR), scanning electron microscopy, and X-ray diffraction (XRD) method. The adsorption kinetics studies of Cr (VI) on the CS/PVOH/Ce fibrous mat were performed based on pseudo-first order and pseudo-second order. The data indicated that the adsorption kinetics of Cr (VI) on the CS/PVOH/Ce fibrous mat followed the pseudo-second order. The equilibrium data have been analyzed using the Langmuir isotherm. It was found that data followed by Langmuir isotherms and the equilibrium adsorption capacities for Cr (VI) is 52.88 mg/g. The adsorption of Cr(VI) on the surface of the CS/PVOH/Ce fibrous mat is found to depend mainly on the pH of the solution. The adsorption of Cr(VI) in acidic pH is higher as compared to alkaline pH. The mechanism of adsorption of Cr (VI) on CS/PVOH/Ce fibrous mat can be explained in terms of a combination of electrostatic adsorption coupled with reduction. Meanwhile, the experiment result proves that the CS/PVOH/Ce fibrous mat is more efficient than bare chitosan. Thus, this system is promising as a filter that can get rid of Cr (VI) ions.

A.B. Albadarin et al. studied on hydrous cerium oxide (HCO) for the removal of hexavalent chromium from aqueous solution [56]. The sample was characterised by BET method, X-rat diffraction study and FTIR analysis. Simple batch experiments and 25 factorial experimental designs were employed to screen the variables affecting Cr(VI) removal efficiency. The effects of the process variables; solution pH, initial Cr(VI) concentration, temperature, adsorbent dose and ionic strength were examined. Analysis of variance demonstrated that Cr (VI) adsorption significantly increases with decreased solution pH, initial concentration and amount of adsorbent used (dose), but slightly decreased with an increase in temperature and ionic strength. The optimization study indicates 99% as the maximum removal at pH 2, 20^{oc}, 1.923 mM of metal concentration and a sorbent dose of 4g/dm^3. At these optimal conditions, Langmuir, Freundlich and Redlich-Peterson isotherm models were obtained. The maximum adsorption capacity of Cr (VI) adsorbed by HCO was 0.828 mmol/g, calculated by the Langmuir isotherm model. Desorption of chromium indicated that the HCO adsorbent can be regenerated using NAOH solution 0.1 M (up to 85%). The adsorption interactions between the surface sites of HCO and the Cr (VI) ions were found to be a combined effect of the both anion exchange and surface complexion with the formation of an inner-sphere complex. Hence, HCO nanoparticles are promising material for the efficient removal of toxic Cr (VI) from the waste water.

S.Jena studied on the Ceria nanopowder which was synthesized by using Cerium chloride and sulphuric acid at a pH of 7 to remove the chromate by Ceria nanopowder in batch mode [57]. The adsorbent is characterized by various analytical techniques like FTIR, SEM, XRD, BET and AAS. The percentage removal of hexavalent chromium was studied as a function of pH of the solution, contact time, dosage of adsorbent and reaction temperature. From SEM-EDAX report it is found that the material is nano fibre and do not have identifiable pores. From BET, the specific surface area of the material is not incorporated because the results of the analysis are awaited. The removal efficiency of the hexavalent chromium from water is done by using this material is conducted by varying the variable parameters like contact time, pH, amount of adsorbent and temperature and initial concentration. The hybrid material was found to have a maximum efficiency for the removal of hexavalent chromium with 86 to 88%, pH at 7, adsorbent dose of 0.07gm and temperature of 28±2^{o}C and initial concentration of 10 ppm. The structure of the material is confirmed by the FTIR data which shows the presence of metal-oxygen bonding. From all the above observations it may be concluded that the material is suitable to act as adsorbent for the removal chromium (VI) from water and also it requires a further study.

6. Removal of Uranium

K. Kuncham et al. investigated the factors influencing the adsorption behavior of uranium (VI) onto the ceria nanocrysatls like pH, dosage, time of contact and initial metal crystal .They used mechanism of adsorption based on the isothermal and kinetic studies [58]. A monolayer surface of adsorption capacity of 270mg/g involving adsorptive pore filling and electrostatic interactions was indicated. The ceria nanocrystals could be regenerated and reused without significant reduction of adsorption capacities. Nanosized cerium oxide was prepared by adopting a co-precipitation method using cerium nitrate. The synthesized ceria nanocrysatls were characterized by X-ray diffraction pattern, Brunauer-Emmett-Teller method, UV-Vis diffuse reflection spectra measurements, X-ray photoelectron spectroscopy. The ceria nanocrystals were synthesized using a template free and eco-friendly methodology and were successfully applied for the selective adsorption of U (VI) ions from aqueous solutions at a near neutral pH. The experimentally observed adsorption, results confirms the high efficiency of nanosized materials towards the remediation and preconcentration of the radio nuclide in presence of varying aqueous environments through multicycles. The experimental results in batch experiments were in good agreement with pseudo second order kinetic model. The empirical data of the variation of concentration of the metal ion fitted better with Langmuir adsorption isotherm compared to Freundlich adsorption isotherm. Hence above study for uranium adsorption using ceria nanocrystal is economical, selective and environment benign.

Chapter III

Conclusion

Conclusion

Removal of toxic elements from water is one of the important reasons to control the environment pollution problem. This paper reviewed the usable adsorption technologies for the removal of toxic elements from aqueous solution. In this paper, Ceria and its composites used for contaminant remediation in the recent years have been reviewed. The adsorption of contaminants to large extent by cost-effective and efficient ceria-based adsorbents offers better alternatives for existing adsorbents. The large surface area combined with ability to form ceria and composites in variable morphological properties makes them component adsorbents for treating toxic contaminants water. These studies suggested that the novel nanocomposites could be used as a potential efficient and good renewable adsorbent for the removal of toxic element from the polluted water. Future research should focus on developing less toxic, more efficient, cost-effective and increasingly reusable nanoadsorbents.

Chapter IV

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