Application of Iron Oxide Nanoparticles for Removal of Heavy Metals from Waste Water- A Review

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ABSTRACT

Waste water is generally the byproduct of different manufacturing, commercial and domestic processes which contains various contaminants in the form of heavy metals, pathogens and suspended particulates. The major contributors that are responsible for the presence of such contaminants in the natural water bodies are rapid industrial growth, overpopulation and consequent expansion, weathering as well as natural disasters. Industries are the main sources for the release of heavy metals into the water resources. The toxicity and ill effects of heavy metals like Cd, Cr, As, Pb, Hg, Ni, Cu, Co, Cd, Ag, As, Mo, Sr etc. are highly hazardous for the biological ecosystem concerning humans, animals and plants. Accumulation of heavy metals at each trophic level of the food web is quite detrimental to the health of living beings and also adversely affects the ecosystem and environment. With the passage of time, a large number of methods for the removal of heavy metals from waste water has been fabricated but their usages lack advantages in terms of cost, productivity and ease of operation.

In the present research scenario, adsorption by nano-particles has been proposed as a pioneering treatment method for the purification of waste water. It has a unique property in comparison with bulk materials. Nanomaterials have been proposed as a proficient, cost-effective and environment friendly alternative to the conventional waste water treatment processes.

Iron oxide nanomaterials have wide applications due to their novel properties and functions. As far as nanoscale dimension is concerned, adsorption technology is viewed as the most reliable technique for the removal of heavy metal ions. Iron oxide nanomaterials are regarded as very effective medium of separation to facilitate the removal of toxic metals from waste water since they are well-known for their distinct properties such as high surface area to mass ratio, high adsorption capacity, good

selectivity, and super paramagnetism. Through modification of surface with suitable functional groups, iron oxide nanomaterials help in decontamination of waste water. They have special advantages in terms of simplicity of design/operation, low cost, highly sensitivity to toxic pollutant, flexibility, least toxicity and also reusable with maximum efficiency. The present review highlights the prospective application of iron oxide nanomaterials in waste water treatment.

INTRODUCTION

The valuable resource for the human civilization is water and it is the most vital substance for the support and existence of life on earth. The prime goal of the human society is access to clean and affordable water which is a major challenge all over the world in current scenario. All over the world, 70-billion-gallon waste water is produced by different industrial activities. The spread over of a wide range of contaminated water mixed with natural water like surface and ground water has become a critical issue all over the world. The contaminant materials that are present in waste water are organic and inorganic pollutants, heavy metals and many other complex compounds [1-2]. The hydroxides, oxides, silicates, sulfides contain the colloidal and particulate forms of metals, which get adsorbed to clay, silica or organic matter. Human exposure to toxic metals may cause various types of infections and diseases. The effects of these toxic metals are quite deadly when found above the acceptance limit [3-7]. Over the years, this topic became the priority and a challenge to the researchers to find innovative economical approaches in order to purify the waste water discharged from the industries.

Water pollution is increasing worldwide due to rapid industrial growth and expansion, overpopulation as well as domestic and agricultural activities. Heavy metals pollution is becoming one of the most serious environmental problems globally. The toxic metal ions like Hg(II), Cr(III), Cr(IV), Pb(II), Co(II), Cu(II), Ni(II), Cd(II), Ag(I), As(V) and As(III) when contaminated with fresh water poses a severe threat not only to the environment but also to the public health. Removal of metals from waste water is principally achieved by the application of several processes such as adsorption, precipitation, electroplating, chemical coagulation, ion-exchange, photo-catalytic oxidation, filtration, flotation, bioremediation, membrane separation, electro-kinetics etc. Reverse osmosis uses a semi-permeable membrane surface that allows only certain molecules to pass through it. Complexation and chelation is also applied for purification of water from heavy metals. The coordination bond is formed with many metals by transferring electron to reach their stability. Each method has been found to be limited for cost effective, operational method, energy requirement, complexity of the process and efficiency.

Recently, an advanced treatment method for the purification of waste water has been developed on the basis of adsorption by nanoparticles. Nanoscience is one of the advanced research areas in modern science where we can use nanomaterials which are efficient, cost-effective and environment friendly alternative to the conventional waste water treatment processes.

Nanotechnology has brought out a tremendous revolution in the field of advanced research and engineering. [1, 7]. The size range of nanoparticles used is 1-100 nanometre. It has a unique property in comparison with the bulk materials [8-9]. Different kinds of nanoparticles such as magnetic nanoparticles, carbon nano-tubes, silver-impregnated cyclodextrin, nanocomposites, nanostructured iron zeolite, carbon-iron nanoparticles, photocatalytic titania nanoparticles, nanofiltration membrane and functionalized silica nanoparticles are used for removal of heavy metals, sediments, chemical effluents, charged particles, bacteria and other microorganisms from waste water. The iron oxide nanomaterials have a wide range of applications. It needs to be studied in greater details considering each and every aspect. This review highlights and throws some light on the important properties and characteristics of iron oxide nanomaterials and its application in the waste water treatment.

IRON OXIDE NANOMATERIALS

Magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite are different forms of iron oxides exist in nature[10]. Iron oxide nano-material has many applications due to its novel properties and functions. It has high surface area to volume ratio due to nano-size range of the particles and super paramagnetism [11-12]. It can be easily prepared by synthesis process and also has ability to control or manipulate matter on an atomic scale which provides unparallel versatility [13-14]. Being a low toxic material as well as having chemical inertness and biocompatibility, it has vast application in bio-technology area [15-16]. The unique properties of nano-iron oxide material in comparison with bulk materials are shown in Fig.1.

Preparation of nanomaterials play the key role in particle size distribution, morphology, magnetic properties and surface phenomena properties. Many researchers have focused to synthesis of iron oxide nanomaterials by physical and chemical processes in order to produce high quality nanoparticles. It has also been extended to produce super paramagnetic iron oxide nanoparticles as well as to exercise precise control of surface active sites by different techniques shown in Fig.2 [17].

The nano-particles have tendency to aggregate in aqueous medium. The presence of electrostatic and van der Waals interactions influenced the stability of colloidal nano-particles. Lot of works have been carried out to stabilize the iron oxide nano-particles by reducing the surface charge which limits the large-scale applications. The iron oxide nano-particles easily react with different organic functional groups. The use of stabilizer, electrostatic surfactants and steric polymers has been widely tested to facilitate the activity of nano-particles [18-20].

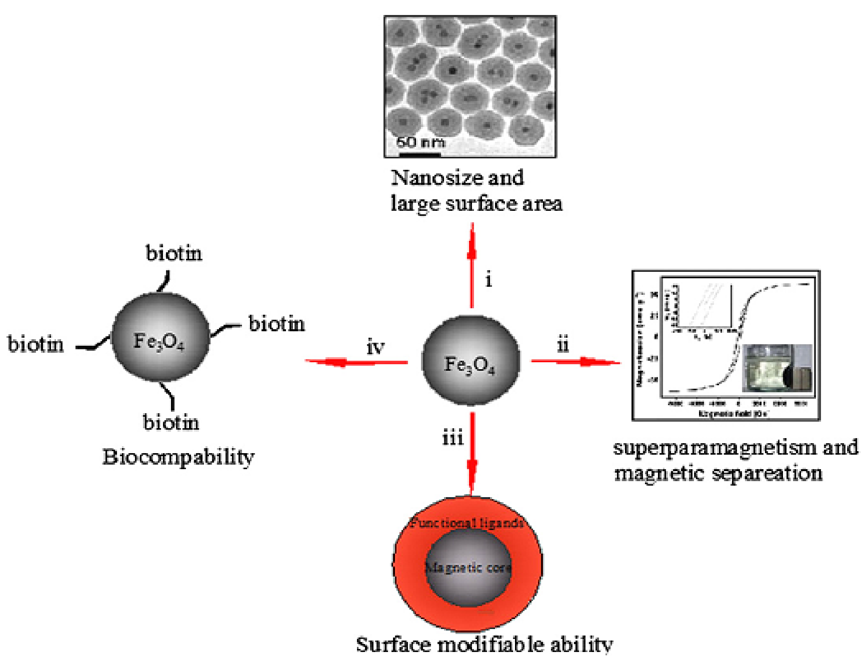

Fig.1 Important properties of iron oxide magnetic nano-particles for waste water treatment applications (Piao Xu et al.2012)

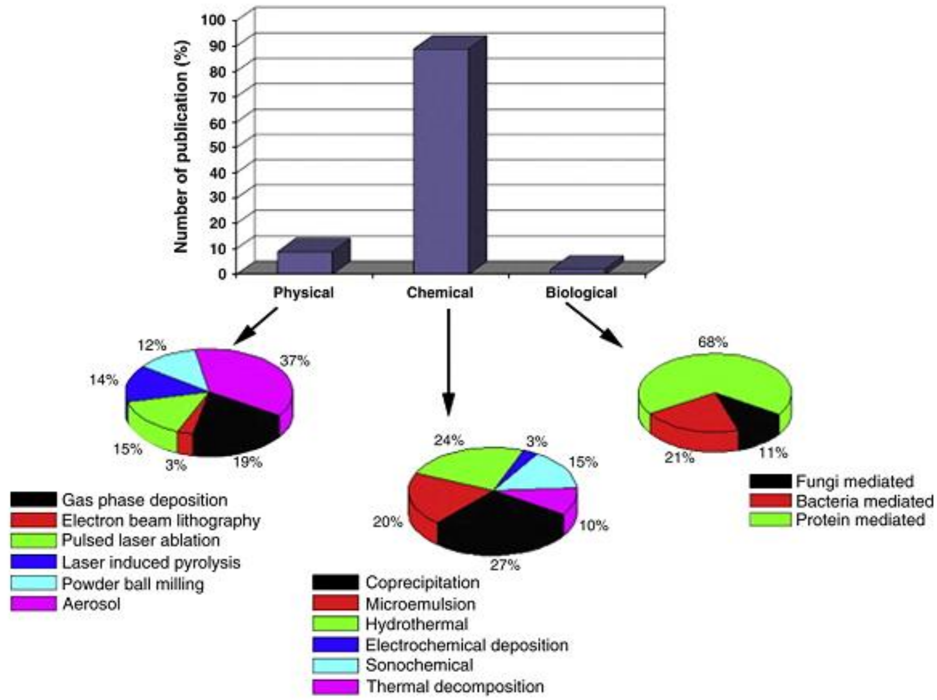

Fig.2 A comparison of published work on the synthesis of iron oxide nano-particles by three different routes (Mahmoudi eta al 2011 and Piao Xu et al.2012)

As shown in Fig.3, through surface modification with suitable functional groups such as phosphonic acids, carboxylic acids and amine, the stability of iron oxide colloid suspensions can be enhanced. The application of iron oxide is strongly associated with its intrinsic properties, which in turn depends on the preparation method and modified medium employed [21-22].

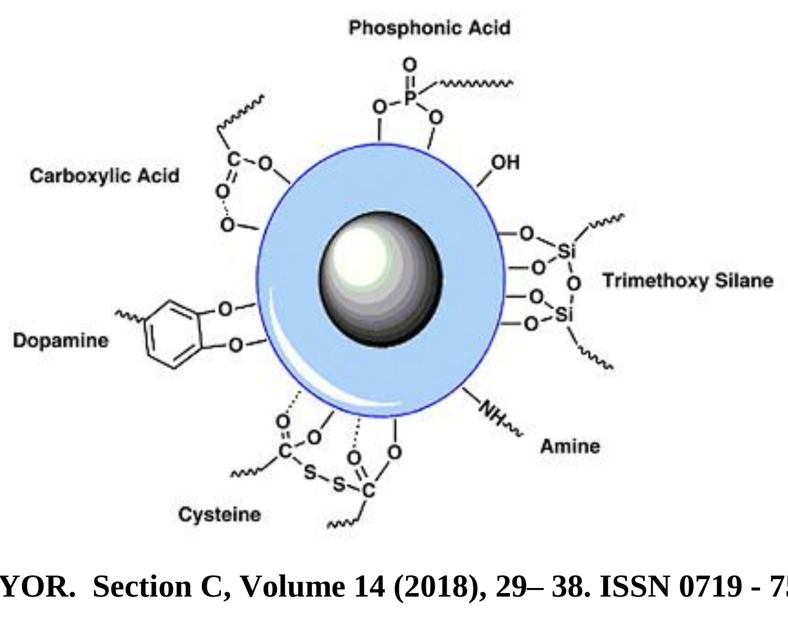

Fig.3 Surface modification of iron oxide nano-particles by different chemical functional groups (Dias et al., 2011and Piao Xu et al.2012)

EFFECT AND LIMITATION OF HEAVY METAL IONS

The industrial effluents and waste water discharged by the industries of electro plating, tanning, paint and pigment production as well as by the metallurgical industries contain chromium as a common contaminant which is generally found in the nature in two stable oxidation states, namely, Cr (III) and Cr (VI). Cr (III), being a vital micro nutrient, is essential for the metabolism of human beings and also for plants and animals whereas Cr (VI) is soluble and quite dangerous to the health of living beings. As far as natural water is concerned, chromium ions mainly occur in the form of chromate and cationic hydroxo complexes. Moreover, according to world health organization the recommended limits for concentration of chromium (VI) in potable water is 0.05 ppm.

Cadmium (II) is highly lethal and causes a number of severe and prolonged ailments and disorders such as renal damage, emphysema, hyper tension and skeletal malformation in fetus. 0.005 microgm/liter is the maximum permissible limit of cadmium concentration in drinking water.

The two common forms of arsenic are organic and inorganic. Being a known carcinogen, inorganic arsenic is acknowledged to cause various types of cancer. Thus, the maximum acceptable concentration for arsenic in drinking water is 10 ppb or 0.01mg/liter.

The compound form of mercury is more toxic than its elemental form. The brain and liver damage are caused by toxic organic compounds of mercury. Di-methyl mercury is most hazardous which is harmful to such an extent that even a few micro liters spilled on the skin can cause death. The acceptable limit of concentration of Hg in potable water is 0.001 mg/liter. As mercury is one of the persistent pollutants in wastewater its removal has a challenging task. It shows its most deadly form as the highly reactive mercury (II) salts [3], which are often converted by bacteria into a neurotoxic substance, methylmercury, which increases the health hazard for the humans and wildlife through the aquatic food chain [3].

The kidney damage, miscarriage, brain damage, impulsive behavior and hyper activity are associated with lead penetration to the human body through drinking of water, consumption of food and inhalation of air. Exposure to lead or its salts or even PbO_2 for a longer period of time can cause nephropathy. 0.01 mg/liter is the allowable concentration in drinking water.

WASTE WATER TREATMENT VIA IRON OXIDE NANO MATERIALS

In present scenario, a detailed study on iron oxide nanoparticles is being carried out in the field of separation technologies owing to its cost friendly synthesis, easy surface modification as well as its capability to control or manipulate materials on a nanoscale level which in turn is helpful for providing remarkable versatility in separation techniques [23]. The super paramagnetic iron oxide nanoparticles have noticeable characteristics which includes large surface area, surface modifiability, biocompatibility, low toxicity and chemical inertness. Due to these properties they are most suitable for adsorption technology essential for waste water treatment.

The most challenging job involves the proper selection of the best methods available and materials required for the waste water treatment which again depends on a number of parameters like meeting the quality standards, achievement of maximum efficiency as well as the cost [24]. Therefore, the following four factors must be considered for choosing the method to be employed for the treatment of waste water [24];

i. Treatment flexibility and final efficiency
ii. Reuse of treatment technology
iii. Environmental friendliness and security
iv. Less expenditure

Magnetism, being a unique physical property, autonomously helps in water purification by influencing the physical properties of contaminants in water. Combination of adsorption technology and magnetic separation technique has been widely employed in the fields of water treatment and environmental clean-up [25]. The iron oxide nanomaterials are quite promising for industrial scale waste water treatment due to their vast advantages like low cost, strong adsorption capacity, easy and effective separation and enhanced stability [26]. Adsorption is regarded as a conventional but efficient technique to remove toxic metal ions and bacterial pathogens from water which can be achieved with the help of magnetic nanoparticles.

SYNTHESIS OF NANO IRON OXIDE PARTICLES

Magnetic nanoparticles have been synthesized with different processes like physical, chemical and biological;

Physical Process

- Gas phase deposition
- Electro beam lithography
- Pulsed laser ablation
- Laser induced pyrolysis
- Planetary ball milling
- Solo-gel process

Chemical Process

- Co-precipitation
- Microemulsion
- Microwave assisted hydrothermal
- Electrochemical deposition
- Sonochemical
- Thermal decomposition

Biological Process

- Fungi mediated
- Bacteria mediated
- Protein mediated

Synthesized samples are characterized by different techniques;

- Dynamic light scattering measurements for particle size measurement
- UV–visible absorption spectroscopy to identify the presence of metal nanoparticles,
- Scanning Electron Microscopy (SEM) for the size and morphology of iron oxide nanoparticles
- The Atomic Absorption Spectroscopy (AAS) measurements for analysis of element
- Fourier Transform Infrared spectroscopy (FTIR) to identify the functional group

- TEM (Transmission electron microscope) for determination of iron oxide molecular structure
- X-ray Diffraction(XRD) to identify mineral phases
- XPS for detection of layer coating and functional group

ADSORPTION PROCESS IN WASTE WATER TREATMENT

Adsorption is defined as the deposition of molecular species onto the surface. The adsorbate adsorbs to the adsorbent through physical and chemical interactions.

Adsorption is generally used as a refining step to remove inorganic and organic pollutants from waste water during the treatment process. The limitations on the efficiency of conventional adsorbents commonly depends on the surface area or active sites, lack of selectivity and absorption kinetics. These limitations are overcome by iron oxide nanomaterials because of their extremely high specific surface area and associated sorption sites, surface chemistry, short intraparticle diffusion distance, tunable pore size, and finally being easily reusable. Inorganic shell and/or organic particles attaches themselves to the surface of the iron oxide nanoparticles resulting in surface modification. This modification of surface not only aids in stabilizing the nanoparticles but also prevents oxidation. It also increases the capacity of uptake of heavy metals during wastewater treatment by providing specific reaction sites or functional groups that are quite selective for ions uptake. The role of silica in the fabrication of coatings for magnetic nanoparticles in water remediation technology is quite significant and prominent as it screens the magnetic dipolar attraction among the nanoparticles as a result of which the magnetic nanoparticles are easily dispersed in the liquid media. The coating of silica also prevents the leaching of nanoparticles in an acidic environment. The activation of surface with various functional groups is easily achieved with the help of silica-coated magnetic nanoparticles due to presence of ample silanol groups on the silica layer. Thus, the coating of silica is considered to play an important role in water refinement process by facilitating nanomaterials with non-specific moieties, group specific or highly specific ligands. Removal of heavy metal is achieved by employing different types of functionalized groups through coating of chelating ligands on the magnetic nanoparticles' surface. (Sophie et.al., 2008; Jianghw et al., 2004; Jiang et al., 2009). Iron oxide nanosorbents in the size range of 2-20 nm are generally favorable for the metal ions to diffuse from the solution to the active sites (functional groups like -COOH, -NH2, -OH, -SH etc.) on the surface of the adsorbent (10-Figure 2). Heavy metals are adsorbed on to the surface of iron oxide nanomaterials after modification through a reaction mechanism which involves physiosorption (in the form of electrostatic and Vander walls interaction) as well as chemisorption (in the form of surface sites chemical binding and modified ligand combination or complex formation). As far as removal of heavy metals is concerned, this process not only proves to be cost friendly but also effective as it employs the application of external magnetic field for the separation of analytes which in turn is accompanied by easy regeneration process of magnetite nanoparticles for further usage.

MAJOR CHALLENGES IN LARGE SCALE APPLICATION

In spite of having unique advantages as nanosorbents for waste water treatment like ease of operation, super paramagnetism, flexibility, reusability, etc., the synthesis of iron oxide nanomaterials and its surface modification is quite essential for the wide application. The most challenging task is designing and synthesizing iron oxide nanoparticles especially super paramagnetic iron oxide because it requires adequate control of the reaction conditions so as to achieve a size distribution of narrow range, high dispersibility as well as a homogenous and uniform composition of the nanoparticles. The uses of iron oxide nanomaterials are highly dependent on the inherent properties which is associated with the preparation and modification methods. Emerging methods like biological and sonochemical methods still requires researches, studies and development through a wide angle and should also address different challenges to deliver efficient and specific magnetic nanomaterials. The stability of iron oxide nanomaterials along with its other properties like reactivity, selectivity and mobility is quite vital for the waste water treatment process. The adsorption of metals is generally affected by the different types of interactions among pollutants, types of pollutants and their respective concentrations in waste water. Introduction of a variety of functional groups on the surface of iron oxide nanoparticles can be achieved by tuning of surface modification in different mediums for a wide range of application and also an extensive research has to be carried out in this arena. As far as the materials employed for surface coating are concerned, the removal efficiency of heavy metals from waste water is quite dependent on factors responsible for the stability, biodegradability as well as on the surface chemistry.

BENEFIT OF WATER TREATMENT BY NANO IRON OXIDE MATERIALS

- Lower operational cost
- Lower energy cost
- Lower discharge and less waste water than reverse osmosis
- Reduction of total dissolved solids
- Reduction of pesticides and organic chemicals
- Reduction of heavy metals
- Reduction of nitrates and sulphates
- Reduction of colour
- Reduction of turbidity
- Softening the water
- Chemical free process
- Maintain required pH

CONCLUSION

Recent advancements in research and development in the field of nanomaterial science and technology and its applicability in wastewater treatment have made us to come to a conclusion that after achieving surface modification with various functional groups, iron oxide nanomaterials acquires unique physio-chemical properties such as easy, rapid and efficient separation by application of external magnetic field, chemical inertness, byproducts with less toxicity, biologically safe and biocompatible etc. and thus, now a trending potential research area .But it is important to take into account that the application of iron oxide nanomaterials are intensely associated with their inherent characteristics which in turn are dependent on the synthesis technique and modification medium. The most challenging and intriguing task is the design of iron oxide nanomaterials which requires appropriate control of reaction conditions in order to aid synthesis of particles with narrow size distribution, high level of monodispersity, homogenous composition, and high magnetic susceptibility. Factors such as stability, biocompatibility, biodegradability and surface chemistry should be considered during the selection of materials which are to be employed for surface coating in order to discreetly predict their nature and types of interactions with targeted contaminants. Though the nanotechnology method of waste water treatment has substituted the conventional process in a cost-effective and efficient ways, a lot of detailed studies and research work are still required to be carried out for absolute field applications.

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