



Nanoparticles as Adsorbent; A Positive Approach for Removal of Noxious Metal Ions: A Review

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Abstract: A number of potent adsorbents have been developed from carbon and oxide based nanoparticles for enhancing the adsorption capacity and removal capacity of hazardous impurities from the aqueous sources. The exclusive surface morphological, textural and structural properties of nanoparticles proved it an capable and excellent adsorbent which can be potentially helpful to eradicate a number of hazardous ecological issues and evils. Several oxide and carbon based nanomaterials were reported as adsorbents frequently in the literature for the removal of hazardous metal ions i.e., Ni²⁺, Cr³⁺, Cr⁶⁺, Cu²⁺, Cd²⁺, Co²⁺, Hg²⁺, Pb²⁺, As³⁺, As⁵⁺, Th⁴⁺, Eu³⁺, Sr²⁺, Zn²⁺ and U⁶⁺ from polluted aquatic sources.

Key words: Oxide nanomaterials, carbon nanotube, metal ions, adsorbents, adsorption, graphene oxide

INTRODUCTION

Rapid urbanization and industrialization of human civilization leads to the discharge of several hazardous contaminants and pollutants in to aquatic streams, these effluents contains toxic wastes such as metals, organic impurities, etc., which directly produces detrimental impact on the biotic resources (Kim and Aga, 2007; Khan *et al.*, 2008; Muchuweti *et al.*, 2006). The unmanageable discharge of pollutants and contaminants due to their severe toxicity and more carcinogenic nature as comparable to other water contaminants, metal ions can cause brutal health troubles for aquatic fauna as well as flora but it also troubles human health through the prevailing ecological food chain (Lundberg *et al.*, 2004; Phillips *et al.*, 2004; Wu *et al.*, 1999; Singh *et al.*, 2010). Thus, the instantaneous removal of these toxic pollutants from wastewater is a noticeable issue in the aerobic and aquatic world. A number of physical, chemical and biological methodologies have been developed to control these toxic contaminants successfully (Gupta and Suhas, 2009; Dean *et al.*, 1972; Demirbas, 2008; Stafiej and Pyszynska, 2007). Several analytical and removal techniques like

electrochemical oxidation and sensors (Gupta *et al.*, 2000, 2006, 2007a, b, c, 2011a), sorption, chemical coagulation, solvent extraction, bioremediation, photo catalytic degradation and adsorption were reported for the removal of lethal impurities from polluted water. However, adsorption process was reported to be the most suitable method because of its extremely high removal efficiency and economic consideration, additionally adsorption does not result in any secondary pollution by producing harmful substances during the process. Simple and cost effective adsorbents, such as; activated carbon (Acharya *et al.*, 2009), clay minerals (Zhao *et al.*, 1998), organic polymers (Mor *et al.*, 2007), metallic oxidants (Deng and Bai, 2004) and natural adsorbents such maize bran (Singh *et al.*, 2006) are known for their efficiency in the adsorption of chromium, several other previously developed adsorbents, such as; carbon nanotubes (Mahmoodian *et al.*, 2015; Saleh and Gupta, 2012a, b; Gupta *et al.*, 2011a, 2013a, b; Gupta and Saleh, 2013; Pahlavan *et al.*, 2014), multiwalled carbonnanotubes (Khani *et al.*, 2010; Ihsanullah *et al.*, 2015), nanoparticles and nanocomposites (Gupta *et al.*, 2011c, 2012a, b; Nekouei *et al.*, 2015; Ghaedi *et al.*, 2015), rubber tire (Gupta *et al.*, 2014a, b) and other low cost adsorbents

(Gupta *et al.*, 1998; 2011b) etc. are used for the removal of impurities from the polluted aqueous sources. Therefore, developing an efficient adsorbent now a days is of great concern and the center of attention for the different research groups, so that the developed adsorbent may lead to rapid removal and fast adsorption of toxic impurities within few minutes of application. Materials with the particle size in the range of 1-100 nm were defined as nanoparticles (Hua *et al.*, 2012), with novel size-and shape-dependent properties, nanomaterials have been extensively used over a decade (Patzke *et al.*, 2002).

Recently, the advancement of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems (Zare *et al.*, 2013; Sadeh *et al.*, 2014). As compared to conventional materials, nanostructure adsorbents have exhibited much higher efficiency and faster removal rate of pollutant from the wastewater (Rickerby and Morrison, 2007). A variety of efficient, cost-effective and eco friendly nanomaterials with unique functionalities have been developed for potential applications in detoxification of industrial effluents, groundwater, surface water and drinking water (Brumfiel, 2003; Theron *et al.*, 2008).

Applications of nanoparticles as adsorbents for high efficient removal of heavy metal ions from wastewater must satisfy the following criterions: (1) The nanosorbents themselves should be nontoxic, (2) The sorbents must show relatively high sorption capacities and selectivity even to the low concentration of pollutants, (3) The adsorbed pollutant could be removed from the surface of the nano adsorbent easily, (4) The sorbents could be infinitely recycled and (5) The process should be reversible so that we can get our adsorbent back; the nanoparticles studied in the removal of heavy metal ions from wastewater should show high adsorption capacity (Cloete, 2010; Savage and Diallo, 2005).

There are several techniques for the removal of loaded nanoparticles i.e., nanoparticle decorated or impregnated on the activated carbon from the water such as by filtration, flocculation, coagulation, centrifugation, sedimentation or magneto deposition, followed by acid treatment, extraction, combustion etc are used to separate the nanoparticle from the water.

Flocculation and removal of commercial nanoparticles with high electrolyte concentrations:

Sharma *et al.* (2009) performed a flocculation experiment for the removal of nanoparticle from the aqueous solution; they add 0.1 M MgCl₂ to 10 mg L⁻¹ nanoparticle suspensions yielded an ionic strength of 0.3 M at pH 8.1. In the presence of 0.1 M MgCl₂, the zeta potentials of all commercial nanoparticles had absolute values less than 10 mV, due to EDL compression or Mg²⁺ adsorption on

negatively charged particle surfaces (Sharma *et al.*, 2009). After 30 min of slow mixing, the sizes of all commercial nanoparticle aggregates increased by 0.25 μm or more. In the absence of MgCl₂, however, the size of Fe₂O₃ aggregates also increased rapidly, as compared with other metal oxide nanoparticles. Because, the initial nanoparticles were got aggregated in water, even in the absence of MgCl₂, 5-35% of the total original mass of nanoparticles settled out of the water within 1 h of sedimentation. Although, the addition of 0.1 M MgCl₂ led to further rapid flocculation of these nanoparticle aggregates, only 20-30% of the nanoparticles were removed after 30 min of slow mixing followed by 1 h of sedimentation. A simplified calculation of orthokinetic flocculation (Sharma *et al.*, 2009) on the basis of mono-dispersed suspensions shows that 2-6 h mixing time is required to reduce the number of nanoparticle aggregates by 50% under these experimental conditions. Although, the suspensions used in this research were poly-dispersed, the calculation results still provide insight into the mixing time required to remove particles. In the experiments, large aggregates of all nanoparticles were observed after 2-4 h of slow mixing. Accordingly, a relatively long mixing time may enhance the settling efficiency of nanoparticles in the presence of 0.1 M MgCl₂. After 8 h of mixing, sedimentation removed 40-80% of the nanoparticles. Increasing the mixing time to 24 h did not increase the removal significantly, however and 20% or more of the nanoparticles still remained in the settled water (Sharma *et al.*, 2009; Mandel *et al.*, 2012).

Removal of commercial nanoparticles by alum coagulation:

The ability of conventional water treatment processes to remove nanoparticle aggregates was evaluated using alum dosages of 20-60 mg L⁻¹, which were added to buffered nanopure water or tap water spiked with nanoparticles (pH 7.77, 0.01 M ionic strength). At an alum dosage of 20 mg L⁻¹, 20-80% of the commercial nanoparticles in nanopure water were removed by sedimentation (following coagulation and flocculation); further increment in the alum dosage did not improve removal significantly. At the same alum dosage, TiO₂ received as suspensions had lower removal efficiencies than TiO₂ received as powders because the former initially contained smaller aggregates (200 nm) in water than the latter (500 nm). Among the other four commercial nanoparticles, NiO aggregates in water have the largest size (750 nm) and therefore have higher removal efficiency. Although, the initial silica nanoparticle aggregates also have sizes around 740 nm, its removal efficiency is relatively low, which may be related to its low density. The presence of Natural Organic Matter

(NOM) in water has an important influence on the alum coagulation process. The NOM may consume part of the alum dosage because it can react or bind with aluminum ions. In Arizona (Tempe) tap water, the Total Organic Carbon (TOC) concentration is about 3 mg L⁻¹. Therefore, removal efficiencies of nanoparticles were found to be lower in tap water than in buffered nanopure water for the same alum dosage. Generally, good particle removal requires particle flocs to have low zeta potentials. After alum addition, nanoparticle flocs had negative zeta potentials from 10-25 mV in both buffered nanopure water and tap water. Dynamic Light Scattering (DLS) measurements showed that TiO₂ nanoparticle flocs having sizes up to 1000 nm remained in water after sedimentation. Other nanoparticle gave similar results. This indicated that, within the above zeta potential range, nanoparticle did not form settleable flocs completely, which resulted in the incomplete removal of nanoparticle by sedimentation. Although, the removal of commercial nanoparticles by alum coagulation and settling is difficult, membrane filtration is a promising technique because the nanoparticle are present aggregated form. After 0.45 mm filtration, all nanoparticle flocs larger than 500 nm were removed from water and only 1-8% of the total TiO₂ mass remained in the water regardless of alum dosage. However, 0.45 mm filtration was much less successful in removing lab-synthesized hematite than commercial nanoparticles. In the absence of alum, more than 80% of hematite nanoparticles remained in the permeate form because the hematite could be present in water as primary nanoparticles smaller than 100 nm (Crittenden *et al.*, 2005).

Salient approach of nanomaterials as adsorbent

Specific features of oxide and carbon based nanomaterials: Oxide and carbon based nano-adsorbents are most effectual and cost-effective for the rapid removal and recovery of metal ions from wastewater effluents due to their large surface area and optimal magnetic properties (Aillon *et al.*, 2009; Li and Zhang, 2009; Zhang *et al.*, 2013). They can be reused as adsorbent after magnetic separation for removing the noxious toxic contaminants (Chen and Mao, 2007). The surface modification of oxide and carbon based nano-adsorbents by the attachment of inorganic shells and organic molecules, stabilizes and prevents the oxidation of nanoparticles (Vollath, 2013; Zhang *et al.*, 2013). These surface functionalities provide active sites for the rapid uptake of specific/selective metal ions, which directly results in exponential enhancement of removal efficiency (Zhang *et al.*, 2013). Among some of the metal oxides, including ZnO and TiO₂, are reported in photocatalytic degradation of metallic contaminants and the adsorption

of heavy metals (Vollath, 2013; Tuzen and Soylak, 2007; Singh *et al.*, 2013; Curran *et al.*, 2006; Schwarzenbach *et al.*, 2005). In particular, these nanoparticles have gained much attention because of their high photosensitivity, higher absorption capacity, better quantum efficiency, nontoxicity and wide band-gap (Wang and Grady Jr., 1995; Bellona *et al.*, 2004). These nanoparticles with a high surface area and porosity exhibit a higher photocatalytic activity than their bulk counterparts by minimizing the distance between the sites of photon absorption and preventing the electron-hole (e⁻-h⁺) recombination (Kwon *et al.*, 2008; Bhatkhande *et al.*, 2002; Pelaez *et al.*, 2012; Hoffmann *et al.*, 1995). The photocatalytic activity plays a crucial role in the removal mechanism; it oxidizes or reduces the metal impurities present in the polluted water and results in the increased removal rate for the particular metal ion concentration (Abollino *et al.*, 2003; Saïen *et al.*, 2014). Photocatalytic transformation (e.g., using TiO₂ solutions) is strongly affected by the natural water constituents, such as organic and inorganic substances; nitrate and trace metals, which are a source of active oxygen species producing photosensitized reactions in test solution. A photocatalyst is activated when the irradiation energy is equal to or greater than the band gap, i.e., the energy difference between the valence and the conduction bands, the absorption of photons results in the excitation of electrons from the valence band to the conduction band leading to the formation of excited state conduction band electrons and positive valence band holes. The formed charges can either recombine to produce heat or can be used to reduce or oxidize the species present at the surface of nanoparticle (Wang *et al.*, 2015). In general, OH⁻ radicals are produced, because it is a strong oxidant, but are unselective hence leads to the formation of a variety of different oxidation products. Furthermore, formed electrons can react with O₂ to form O₂⁻ (Ozmen *et al.*, 2010; Zhong *et al.*, 2006; Hao *et al.*, 2010), these valence electron and radical may help in the conversion of more toxic forms of metal to less toxic forms so that the removal rate increases and detoxification of water takes place.

Also, numerous oxide and carbon based nanocomposite/hybrid materials have been developed for water purification; these are composed of two or more components and can exhibit the properties of multi component systems in the same material (Liu *et al.*, 2008; Lefevre *et al.*, 2008; Shen *et al.*, 2009; Hu *et al.*, 2005).

On the other hand, a critical in-depth analysis has revealed that the surface textural and morphological, active sites, structural features, curvature of sidewalls, π-conjugative structures are some of the physical

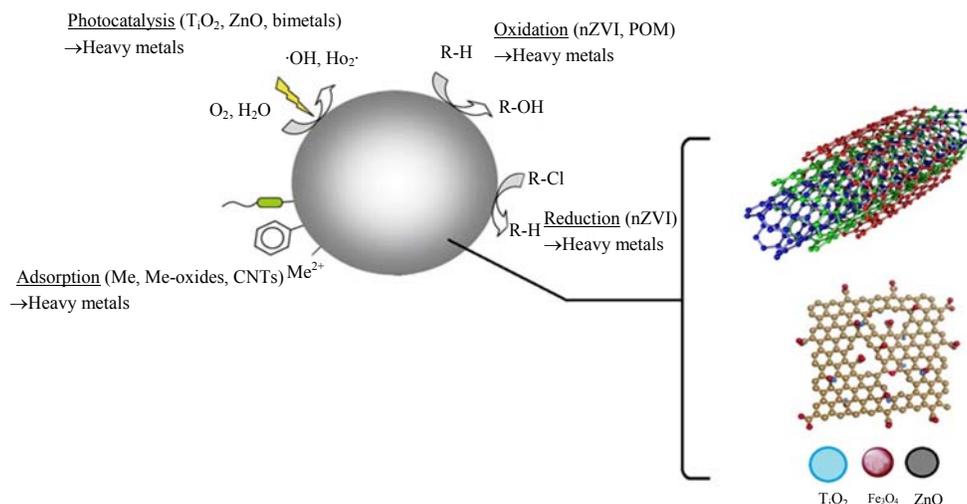


Fig. 1: Relevant processes for the removal of heavy metal ions, where ZVI stands for zerovalent ion and POM stands for polyoxymetalate

properties possessed by graphene and CNTs that have enabled them to exhibit enhanced adsorptive properties (Ray, 2010; Zhang *et al.*, 2013; Chen and Wang, 2006; Curran *et al.*, 2006; Wang and Grady Jr., 1995; Bellona *et al.*, 2004; Kwon *et al.*, 2008; Bhatkhande *et al.*, 2002; Hoffmann *et al.*, 1995) and their length ranges from nanometers to millimeters with diameters up to 100 nm and a large specific surface area, high porosity, hollow as well as layered structures. These unique properties of CNTs are due the cause of strong π - π electronic and hydrophobic interactions, which allow CNTs to interact with other molecules or atoms thereby making them a promising adsorbent material (Stafiej and Pyrzynska, 2007; Cloete, 2010; Al-Degs *et al.*, 2006).

Size exclusion: The rejection of metallic solutes by membrane filtration such as nanofiltration/reverse osmosis (NF/RO) is affected by different factors and parameters (Al-Degs *et al.*, 2006). For dissolved metallic pollutants key parameters are molecular weight (M_w), molecular size, acid dissociation constant (pK_a) and diffusion coefficients, while for membranes the factors are the molecular weight cut-off, pore size, surface charge and morphology and hydrophobicity/hydrophilicity (Aillon *et al.*, 2009; Zhang *et al.*, 2013; Singh *et al.*, 2013; Curran *et al.*, 2006; Wang and Grady Jr., 1995). Hydrophobic interactions are expected to play a major role for pollutants having higher octanol-water partition coefficient (K_{ow}) values, where as, highly polar and negatively charged compounds can add an electrostatic rejection with usually negatively charged nanofiltration

(NF) membranes (Ray, 2010; Zhou *et al.*, 2011; Zhang *et al.*, 2013). In addition, nanoparticles having specific disinfection properties will play a foremost role in reducing and preventing the biofouling of membranes, which is one of the major drawbacks of this technology.

Processes involved for the removal of heavy metal ions: Adsorption, redox reactions, photocatalytic transformation and size exclusion are processes, which can be enhanced or initiated by nanoparticles for the removal of hazardous heavy metal ions from wastewater (Fig. 1).

Adsorption on to nanoparticles depends on the adsorption coefficient K_d and recitation partitioning of a contaminant under equilibrium conditions (Hu *et al.*, 2010; Mehrizad *et al.*, 2011). However, as in most cases diffusion is rapid compared to the hydraulic retention times in water treatment and compared to the biological removal of most compounds, equilibrium can be assumed for solid-liquid partitioning (Shim *et al.*, 2001). Redox reactions are favored for persistent inorganic pollutants to initiate the transformation of the ionic structure. For metals it is well known that a change of the redox conditions has a major influence on its toxicity (Chen and Mao, 2007; Rao *et al.*, 2006; Aillon *et al.*, 2009; Ray, 2010).

Techniques involved for adsorption of heavy metal ions: To understand the mechanism of the adsorption of noxious metal ions by nanoparticles, the impact of the adsorption processes using different analytical techniques, i.e., infrared (IR) spectroscopy (Long and Yang, 2001;

Mauter and Elimelech, 2008), X-Ray Diffraction (XRD) (Di Natale *et al.*, 2008), X-ray Photoelectron Spectroscopy (XPS) (Selvi *et al.*, 2001) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy (Graydon *et al.*, 2009; Lee and Anderson, 2005) have been investigated. The basis of discussion include; physical adsorption (Selvi *et al.*, 2001), surface complexation (Vollath, 2013), ion exchange (Di Natale *et al.*, 2008), electrostatic interaction (Vollath, 2013) and hard/soft acid-base interaction (Vollath, 2013).

The impact of various effective parameters including pH of solution, ionic strength and coexisting matter have also been investigated (Patnukao *et al.*, 2008; Ewecharoen *et al.*, 2009). Through these studies, adsorption mechanisms were elucidated at the molecular level. Various functional groups like -COOH, -C = O and -OH were found to be introduced onto CNTs surfaces by acid or air oxidation. Such functional groups made CNTs more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar contaminants (Ewecharoen *et al.*, 2009; Iijima, 1991; Pyrzynska and Bystrzejewski, 2010).

Also, mechanisms of contaminant adsorption from wastewater by modified iron oxide nanoparticles include; surface sites binding (Li *et al.*, 2002a), magnetic selective adsorption (Li *et al.*, 2003a), electrostatic interaction (Li *et al.*, 2003b) and modified ligands combination (Gao *et al.*, 2009). The addition of novel modification functionalities and mediums to NPs can achieve high efficiency. For example, a novel magnetic nanosorbent (MNP-NH₂) has been developed by the covalent binding of 1, 6-hexanediamine on the surface of Fe₃O₄ nanoparticles for the removal of Cu²⁺ ions from aqueous solution (Gao *et al.*, 2009).

Generally in nanoparticles, the negatively-surface-charged nanoparticles form a chelate complex with metal ions above the pH of the point of zero charge (pH_{pzc}) (i.e., pH > pH_{pzc}). For example, the negatively-charged carboxylate ions (COO⁻) of carboxyl-functionalized nanoparticles have a strong coordinative affinity in forming chelate complexes towards metal ions (Mⁿ⁺) at pH > pH_{pzc}. The enhanced chelate forming tendency of carboxylate ions at higher pH values is expected, because at lower pH values the chelating sites were occupied with H⁺ (the chelating sites are neutral, i.e., -COOH) and were released at a higher pH, thereby lead to the origination of the desired chelate formation. Also, at lower pH values, H⁺ ions were adsorbed onto the surface of nanoparticles, leading to a net positive charge. A certain amount of metal ions can still be adsorbed by carboxyl-functionalized nanoparticles at pH < pH_{pzc}. This is perhaps due to the fact that ion exchange takes place at

pH < pH_{pzc}. Since, the affinity of metal ions to Fe₃O₄ is higher than that of H⁺ ions, metal ions can replace the adsorbed H⁺ ions from the Fe₃O₄ surface by an ion exchange mechanism (Di Natale *et al.*, 2008). The research group (Wang *et al.*, 2005) observed the adsorption of metal ions-particularly Cd²⁺ directly on the surface of Fe₃O₄ rather than on the coated organic moiety (humic acid). The adsorption of metal ions by ion exchange is relatively slow compared to surface complexation, since the organic molecules present on the surface of the nanoparticles may cause steric hindrance towards the adsorption of metal ions.

Generally, the degree of competition is dependent on the type and concentration of the competing ions, the number of surface sites and the affinity of the surface for the adsorbate. However, the adsorption process, followed by magnetic separation, leads to the rapid and inexpensive removal of metal ions.

Removal of heavy metal ions: For the rapid adsorption of heavy metals from aqueous systems, the most widely studied nanomaterials include activated carbon, carbon nanotubes, graphene, ferric oxides, manganese oxides, titanium oxides, magnesium oxides and zinc oxides. They are present in different forms, such as particles, tubes and others. Also, in the following sections, recent advances in heavy metal removal from water and wastewater by nanoparticles are presented and discussed in terms of their synthesis, characterization, application perspectives and their classification by the components of nanomaterials.

Oxide based nanomaterials: Nanomaterials formed by metal or metal oxides are the inorganic nanoparticles, which are broadly used for the removal of the hazardous metal ions. Nanosized metals or metal oxides include; ferric oxides (Xu *et al.*, 2008), manganese oxides (Feng *et al.*, 2012), titanium oxides (Gao *et al.*, 2008), magnesium oxides (Gupta *et al.*, 2011d) and zinc oxides (Tuzen and Soylak, 2007) possess high surface area and specific affinity for the adsorbate impurities. Metal oxides possess minimal environmental impact, low solubility and even do not lead to any secondary pollution; they have also been widely adopted as sorbents to remove heavy metals.

Fe₃O₄ nanoparticles: Iron is one of the most prevalent elements in the earth. The facileness of resource and ease in synthesis render nanosized ferric oxides to be low-cost adsorbents for noxious metal sorption. Since iron is eco friendly, nanosized ferric oxides can be pumped directly to contaminated sites with negligible risks of secondary contamination (Li *et al.*, 2003a, b). Most of the available literature reports the adsorption rate

and impact of different parameters on the removal efficiency of metal ions by Fe₃O₄ magnetic nanoparticles (Lefevre *et al.*, 2008; Luo *et al.*, 2010; Yavuz *et al.*, 2006). The adsorption efficiency of Ni²⁺, Cu²⁺, Cd²⁺ and Cr⁶⁺ ions by Fe₃O₄ nanoparticles is strongly dependent on pH, temperature, adsorbent dose and the incubation time. Further, (Shen *et al.*, 2009) had reported a higher removal efficiency of these metal ions at a 3.5 mg mL⁻¹ dose of nanoadsorbent at an optimum pH of 4. In comparison to bare Fe₃O₄ nanoparticles, surface functionalized Fe₃O₄ nanoparticles have been extensively used for the removal of heavy metal ions (Gupta *et al.*, 2014a; Feng *et al.*, 2010; Wang *et al.*, 2015, 2013b; Xu *et al.*, 2008; Yean *et al.*, 2005; Ozmen *et al.*, 2010; Ge *et al.*, 2012). In the mean time the removal of noxious metal ions from wastewater by using carboxyl-, amine- and thiol-functionalized Fe₃O₄ nanoparticles (succinic acid, ethylenediamine and 2, 3-dimercaptosuccinic acid, respectively). Depending upon the surface functionality (COOH, NH₂ or SH), these magnetic nano-adsorbents captured the metal ions either by forming chelate complexes by ion exchange process or else through electrostatic mechanism of removal and hydrogen bonding between the adsorbate and adsorbent molecule. It has been observed that these modified surface engineered Fe₃O₄ nanoparticles have a strong affinity for the simultaneous adsorption of Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Pb²⁺ and As³⁺ from wastewater. In addition, the adsorption process was found to be highly dependent on the adsorbent dose, surface functionality and pH of the reaction medium, which caused these nanoparticles to selectively adsorb noxious metal ions. An almost 100% removal rate of Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ ions from water was observed at pH>8 i.e., alkaline reaction medium is more sensible for the removal of these metal ions by these surface modified functionalized nanoparticles.

The removal efficiency of As³⁺ by carboxyl, amine and thiol-functionalized Fe₃O₄ was found to be 91, 95 and 97%, respectively, at optimum pH 8 (Gao *et al.*, 2008). The adsorption-desorption behavior of metal ions on amine-functionalized Fe₃O₄ showed an 85% desorption ratio in the first cycle, which indicates their excellent regeneration capacity for the further use of Fe₃O₄ functionalized nanoparticle. Warner *et al.* (2010) also prepared ethylenediamine tetraacetic acid-functionalized (EDTA) Fe₃O₄ nanomagnetic chelators (NMCs), which show a strong tendency towards the adsorption of Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺ and Pb²⁺ from wastewater (Warner *et al.*, 2010). The use of 3-aminopropyltriethoxysilane and glutaraldehyde-modified Fe₃O₄ nanoparticles for the removal of Cu²⁺ from water (Yean *et al.*, 2005) and effective removal of heavy metal ions (Cd²⁺, Zn²⁺, Pb²⁺

and Cu²⁺) from an aqueous solution using polymer modified magnetic nanoparticles (Ozmen *et al.*, 2010), they had reported a higher removal efficiency of metal ions in acidic pH 5.5 and a lower one in alkaline pH. Based on their results, they have suggested that the polymer-modified Fe₃O₄ was more efficient than non modified Fe₃O₄. The reported studies suggest that the functional groups present on the surface of magnetic nanoparticles provide a higher number of active sites as well as aqueous stability, which is essential for the successful adsorption of metal from aqueous solution. More specifically, these modified surface-engineered magnetic nanoparticles are highly effective, efficient, economically viable and reusable magnetic nanoadsorbents are used for the removal of metal ions from wastewater. Polymers with specific functionalities can be obtained by either synthesizing new monomers carrying the special groups capable of interacting with the target metal ions and polymerizing them into practically applicable shapes and forms or by converting some groups on existing polymers or copolymers with suitable reactants into desired forms either by chemical or radiation treatment. Radiation induced graft polymerization (RGIP) is one of the processes for the manufacturing of advanced polymeric materials by modifying widespread polymers (Visa *et al.*, 2009; Nasef and Guven, 2012). Radiation grafted adsorbents have been used usually for separation and wastewater treatment (Seko *et al.*, 2004, 2005; Shiraishi *et al.*, 2003; Kavakli *et al.*, 2005a, b). Several types of ion exchange matrices have been prepared by grafting monomers like acrylic acid, methacrylic acid, glycidyl methacrylate, dimethylaminoethylmethacrylate, acrylonitrile on trunk materials like polyethylene and polypropylene (Hegazy *et al.*, 1999; Kavakli *et al.*, 2007; Mukherjee and Gupta, 1985; Gupta and Chapiro, 1989).

Efficient polymers for the removal of metal impurities:

Numerous polymer materials have been applied to the removal of actinide species such as U, Pu, Np, Am and Cm (Kawai *et al.*, 2000; Geckeler and Volchek, 1996; Bayer *et al.*, 1985). Especially, studies on the removal of uranium from solution have attracted much attention from many researchers, since uranium is the most major actinide species in spent fuel. Various polymers including polyetherimide (PEI), polyisocyanodipeptide (PIAA), polyacrylic acid (PAA), polyurethane (PU) and Poly Vinyl Alcohol (PVA) were used to separate uranyl ions. Ultrafiltration technique, which needs an appropriate membrane of very small pore size was used in conjunction with such polymers for the effective treatment of uranium. Recently, functional polymer-based hybrid adsorbents have been developed to simplify separation process and further to apply to the stationary

phase for High Performance Liquid Chromatography (HPLC) (Guibal *et al.*, 1994; Barbette *et al.*, 2004; Venkatesan *et al.*, 2004; Bryant *et al.*, 2003; Chanda and Rempel, 1995; Leroy *et al.*, 2003). The hybrid adsorbents are composed of functional polymer materials to bind with uranyl ions and solid matrix (e.g., silica) as a substrate of polymers. Functional materials introduced, so far can be classified into organic molecules and polymers. The organic molecules have been covalently fixed to the surface of solid matrix, however, these adsorbents showed relatively poor uranium adsorption capacity. On the contrary, functional polymers, which have been introduced to the surface of solid matrix (e.g., silica or polymer resin) by simple coating process showed a good uranium adsorption capacity.

The polydopamine coating (PDA) thickness was measured by an indirect method, i.e., thermogravimetric analysis (TGA). Assuming homogeneous deposition of DA on the silica surface, PDA coating thickness on the silica surface (d) was obtained from the following equation:

$$\delta = \frac{d_p}{2} \left(1 - \sqrt{\frac{m_{\text{DOPA}}}{V_p \cdot m_s \cdot \rho_{\text{DOPA}}}} \right)$$

where, m_s is the mass of the Si1000 (in mg unit), d_p is the pore size of the silica (according to the data provided by Merck company $d_p = 100$ nm), V_p is the pore volume of the silica (0.16 cc g^{-1}), ρ_{DOPA} is the density of PDA (1.2 g mL^{-1}) and m_{DA} is the mass of PDA on the silica surface, which is determined by TGA according to the following equation:

$$m_{\text{DOPA}} / m_s = \frac{\text{Weight loss (\%)}}{100 - \text{Weight loss (\%)}}$$

Magnetic nanoparticles were also successfully used for the separation of metal ions from different sources. Use of rhodamine hydrazide modified Fe_3O_4 microspheres (Fe_3O_4 -R6G), as adsorbent for the selective detection and removal of mercury ions from different environmental samples, such as; tap water, lakewater (Linghu Lake, Anqing, China) and river water (Changjiang River, Anqing, China). Ge *et al.* (2012) found that $1.5 \times 10^{-7} \text{ mol L}^{-1}$ is the detection limit for Hg^{2+} and that $37.4 \text{ } \mu\text{mol g}^{-1}$ is the maximum adsorption of Hg^{2+} in a 3 mL sample with 5 mg Fe_3O_4 -R6G. The adsorption of Hg^{2+} onto Fe_3O_4 -R6G was confirmed with the shift in binding energy from X-ray Photoelectron Spectroscopy (XPS) analysis (Ge *et al.*, 2012). They also

studied the regeneration capability for up to three cycles and observed that it could reversibly bind with Hg ions repeatedly. The concise data in form of summary will be well elucidated from Table 1.

MnO nanoparticles: Nanosized manganese oxides (MnOs) exhibit an adsorptive performance superior to their bulk counterpart because of its polymorphic structures and higher specific surface area (Luo *et al.*, 2010). In the past decades, MnOs had been exploited (Denizli *et al.*, 2004; Wang *et al.*, 2011) for sorption of cationic or anionic pollutants from natural water sources, i.e., metal ions (Wang *et al.*, 2011), arsenate (Trivedi and Axe, 1999) and phosphate (Mishra and Vijaya, 2007). Such sorption processes significantly mediate the fate and mobility of the targeted pollutants in water (Takamatsu *et al.*, 1985; Kawashima *et al.*, 1986; Su *et al.*, 2010; Tripathy *et al.*, 2006). The widely studied MnOs for environmental concerns include; Hydrous Manganese Oxide (HMO) and nanoporous/nanotunnel manganese oxides.

Parida *et al.* (1981), Zaman *et al.* (2009), reported HMO could be prepared by adding $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ into NaClO solution (containing active chlorine). The precipitate was washed with HCl to remove excessive alkali, followed by rinsing with double-deionized water. The BET surface area was around $100.5 \text{ m}^2 \text{ g}^{-1}$. Gadde and Laitinen (1974) proposed another approach for HMO synthesis, i.e., adding manganese nitrate into alkaline sodium permanganate solution and re-dispersing the particles in sodium nitrate solution. The BET surface of the resultant HMOs was $359 \text{ m}^2 \text{ g}^{-1}$.

Heavy metal sorption onto HMOs, including Pb (II), Cd (II) and Zn (II), usually results in the inner-sphere complex formation mechanism and it can be described by an ion-exchange process. Divalent metals adsorption on HMO involves of two steps i.e., rapid adsorption of metal ions to the external surface followed by slow intraparticle diffusion along the micropore walls (Parida *et al.*, 1981). The adsorption can be represented by the Freundlich model more reasonably than the Langmuir model, implying that the active sites of HMO surface are heterogeneous for metal sorption. The HMO prefers metal sorption in the order of $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$, which might rest on the different softness of these metals (Fan *et al.*, 2005; Misono *et al.*, 1967). Compared to two commercial resins, D-001 and Amberlite IRC 748, HMO exhibits more selective sorption toward these heavy metal ions in the presence of Ca^{2+} at high concentration levels (Kawashima *et al.*, 1986). The concise data in form of summary will be well elucidated from Table 1.

Table 1: Data of maximum adsorption capacity of heavy metal ions with oxide based nanomaterials

Adsorbent	q_m	SA	RP	Conditions	Reference
Fe ₃ O ₄	As(V):16.56	178.48	45	pH: 2-13, contact time: 24 h C ₀ : 60, T: 298 K	Feng <i>et al.</i> (2012)
	As(III): 46.06				
NCMO	As(V): 18.653	116.96	98	pH: 7, contact time: 3 h, C ₀ : 5-40, T: 303 K	Gupta <i>et al.</i> (2011)
MgO	Cr(VI): 156	38	NA	pH: 4, C ₀ : 10	Gao <i>et al.</i> (2008)
CeO	As(V):22.4	72	NA	pH: 7, T: 298 K	Luo <i>et al.</i> (2010)
	Cr(VI): 15.4				
	Pb (II): 9.2				
Fe ₃ O ₄ -NCs	As (III): 165000 (mg kg ⁻¹)	300	99.2	Contact time: 24 h, C ₀ : 22	Yavuz <i>et al.</i> (2006)
	As (V): 190000 (mg kg ⁻¹)				
Fe ₃ O ₄	As (III):1532	98.8	NA	pH: 8, contact time: 2.5-5 min, C ₀ : 0.1 g L ⁻¹	Yean <i>et al.</i> (2005)
	As (V):622.7				
Fe ₃ O ₄ - NPs	Cu(II): 61.07	NA	80	pH: 4, contact time: 15 min, C ₀ : 0.2, T: 293 K	Ozmen <i>et al.</i> (2010)
	Cd(II): 29.6				
Polymer-modified Fe ₃ O ₄	Zn(II): 43.4	NA	85	pH: 5.5, C ₀ : 50, T: 298 K	Ge <i>et al.</i> (2012)
	Pb(II):166.1				
	Cu(II):126.9				
	Hg(II):37.4 μmol g ⁻¹				
Fe ₃ O ₄ -R6G	Pb(II):1.625 mmol g ⁻¹	NA	91.6	Contact time: 60 min, T:298 K	Wang <i>et al.</i> (2013a)
	Cd(II):1.376 mmol g ⁻¹				
HMO	Zn(II):1.002 mmol g ⁻¹	100.5	90	pH: 7, C ₀ : 0.8 and 0.4 mM, T: 298 K	Wang <i>et al.</i> (2011)
	Cd(II):2 mmol g ⁻¹				
HMO	Cd(II):0.2 mmol g ⁻¹	NA	98	pH: 6, C ₀ : 0.05 mmol L ⁻¹	Trivedi and Axe (1999)
	Cd(II):0.2 mmol g ⁻¹				
β-MnO ₂	Cu(II): 22	83.5	NA	pH: 7, C ₀ : 68.04, T: 303 K	Takamatsu <i>et al.</i> (1985)
FA-TiO ₂	Cd(II): 85	37.97	65	pH: 10, contact time: 120 min, T: 298 K	Visa <i>et al.</i> (2009)
	As(III):3.93				
TiO ₂ - NCs	As(V):4.05	329	NA	pH: 6, C ₀ : 365 and 306 mg L ⁻¹ , T: 291 K	Jing <i>et al.</i> (2009)
	Pb(II):401.14				
TiO ₂ - NPs	Cd(II):135.14	185.5	100	pH: 8, contact time: 120 min C ₀ : 500 μg L ⁻¹ , T: 298 K	Engates and Shipley (2011)
	Ni(II):114.94				
	Zn(II):15.3				
TiO ₂ - NPs	Cd(II):7.9	208	90	pH: 9, contact time: 30 min, C ₀ : 10 μg mL ⁻¹ , T:298 K	Liang <i>et al.</i> (2004)
	Cu(II):1600 mg g ⁻¹				
ZnO-NPs	Pb(II):160.7	147	94	pH: 6, contact time: 10 h, C ₀ : 1400, T: 298 K	Wang <i>et al.</i> (2010)
	Cd(II):147.25				
ZnO	Zn(II): 357	15.75	46.21	pH: 8, contact time: 90 min C ₀ : 100, T: 312.5 K	Kumar <i>et al.</i> (2013)
	Cd(II):387				
ZnO	Hg(II):714	NA	78	pH: 5.5, contact time: 2.5 min C ₀ : 600, T: 303 K	Sheela <i>et al.</i> (2012)
	Pb(II):6.7				
ZnO nanocomposite		NA	NA	Contact time: 12 h, T: 393 K	Ma <i>et al.</i> (2010)

NA: Not available, q: Maximum adsorption capacity (mg g⁻¹), SA: Surface area (m² g⁻¹), RP: Removal percentage (%), C₀: Initial concentration (mg L⁻¹), T: Temperature, NCs: Nanocrystals, NPs: Nanoparticles, Fe₃O₄-R6G: Rhodaminehydrazide modifying Fe₃O₄, HMO: Hydrous manganese dioxide, NCMO: Nanostructured cerium incorporated manganese oxide, MNO: Manganese dioxide, FA: Formic acid, ZnO: Zinc oxide, TiO₂: Titanium dioxide, Fe₃O₄: Ferric oxide, MgO: Magnesium oxide, CeO: Selenium oxide

TiO₂ nanoparticles: Titanium dioxide is another type of nanoparticles that has been widely used as a powerful and efficient adsorbent for the removal of Cr (VI), Cd (II) and Cu (II) (158), As (III) (Visa and Duta, 2013) and multiple metals (Pb, Cd, Cu, Zn and Ni) (160).

Parida *et al.* (1981) have examined the removal of Cr (VI) by TiO₂-immobilized mesoporous MCM-41. They found 91% absorption of Cr (VI) from a solution containing 100 mg L⁻¹ Cr (VI) metal ions in 80 min at pH ~5.5 and 323 K. Visa *et al.* (2009) and Visa and Duta (2013) developed a substrate by hydrothermal processing from fly ash coated with TiO₂ and investigated its influence on the adsorption capacity of heavy metal ions (Cu²⁺ and Cd²⁺) from synthetic wastewater. They observed that the removal efficiency of the fly ash-TiO₂ substrate is much higher for Cu²⁺ from

the solution. Jing *et al.* (2009) evaluated the simultaneous removal of As (V), As (III), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) in contaminated ground water. Luo *et al.* (2010) have also demonstrated the high absorption capacity, recovery and reuse of TiO₂ nanoparticles for the removal of As (III) from copper smelting industries effluents wastewater. They found a reduction of 59±79 μg L⁻¹ of As (III) at pH 7 after 21 successive treatment cycles using regenerated TiO₂ containing 3890±142 mg L⁻¹ As (III) in the polluted water. Jing *et al.* (2009) have studied absorption of single and multi-metal ions by TiO₂ nanoparticles and compared the results with those obtained by bulk particles. They have found a 100% removal efficiency of Pb, Cd and Ni ions at 0.1 g L⁻¹ within 120 min, which is five-times greater than the bulk particles at the same concentration.

They also observed the good photostability of TiO₂ nanoparticles after eight cycles at pH 8, whereas the bulk particles were exhausted after three cycles. A similar study conducted by Liang *et al.* (2004) reported on the adsorption capacity of Zn and Cd by nano-TiO₂ of size 10-50 nm were 15.3 and 7.9 mg g⁻¹, respectively, at pH = 9. Further, they observed that the presence of common cations and anions (100-5000 mg L⁻¹) has no significant influence on the adsorption of Zn²⁺ and Cd²⁺ ions. Hence, from the literature reported, it can conclude that the removal rate and adsorption capacity was found to be maxima in the optimum pH range of 5-9. The concise data in form of summary will be well elucidated from Table 1.

MgO nanoparticles: Numerous works have focused on the synthesis of nanosized magnesium oxides of various morphologies, such as; nanorods (Jing *et al.*, 2009; Engates and Shipley, 2011), fishbone fractal nanostructures induced (Liang *et al.*, 2004), by nanowires (Cao *et al.*, 2005; Mo *et al.*, 2005), nanobelts (Zhu *et al.*, 2001), nanotubes (Yin *et al.*, 2002) and three dimensional entities (Tang *et al.*, 2002; Klug and Dravid, 2002) and nanocubes (Li *et al.*, 2002b).

Gao *et al.* (2009) developed a facile method to fabricate MgO of different morphologies and investigated their influence on the adsorption capacity to pollutants. By changing the concentration of Mg²⁺ and HCO₃⁻, monoclinic Mg₅(CO₃)₄(OH)₂(H₂O)₄ with nanoflakes and flowerlike microspheres composed of flakes and hexagonal MgCO₃ were synthesized. After annealing at 650°C, four kinds of nano-MgO of mesoporous structures were obtained. It is a good example for the tunable synthesis of morphological nanoparticles by adjusting the components and the crystal phases of the precursors. The highly supersaturating of the reactant species is believed to be the driving force for the hierarchical growth. In the formation of nanostructure, it was well-known that the supersaturation ratio plays as, a key role in determining their microcosmic growth behavior. Supersaturation ratio was an important factor affecting the growth behavior of nanomaterial. When the Mg vapor reacted with oxygen to form MgO, the reaction was as follows:



The oxygen atom mainly originated from the oxygen molecule in the carrying gas. Its supply was kept constant during the whole reaction. The Mg vapor came from two sources; direct evaporation of metal Mg powder and indirect carbon thermal reduction reaction of MgO and carbon powder. As to the Mg vapour evaporated from Mg powder, the evaporating rate was defined by the

temperature. Under our experimental condition (reacting temperature: 1100°C), the evaporating rate was high and the supersaturation ratio of Mg would keep high. As the reaction proceeded, the Mg powder largely evaporated and was used up after some time. This point could be confirmed by the EDS result of residue after reaction. It indicated that there was no residual Mg powder in the source. As a result, the supply of Mg vapor evaporated from Mg powder would disappear in the latter reacting stage. So the supersaturation ratio of Mg supplied by the Mg powder was unstable during the whole reaction: a high supersaturation ratio at the initial stage and no contribution at the latter stage (Stankic *et al.*, 2005).

The novel structure of the microspheres improved the adsorption capability of MgO. The flowerlike mesoporous MgO microspheres also exhibited excellent adsorption capabilities to Cd (II) and Pb (II) (Li *et al.*, 2003b). It was noticed that at a contact time of 120 min, the concentration of Cd (II) and Pb (II) decreased from 100-0.007 and 0.05 mg L⁻¹, respectively, which are much lower than the Pollutant Dischargeable Standard in China (Cd (II)<0.01 mg L⁻¹, Pb (II)<0.1 mg L⁻¹) and a little higher than MCLs for drinking water established by the Environmental Protection Agency (EPA) of the United States (Cd (II)<0.005 mg L⁻¹, Pb (II)<0.015 mg L⁻¹). The concise data in form of summary will be well elucidated from Table 1.

ZnO nanoparticles: Zinc oxide is a promising candidate for the removal of contaminants and environmental remediation. It has many surface active sites for the adsorption of heavy metal ions from an aqueous solution. Further, ZnO nanoparticles with a porous micro/nanostructure provide an ample surface area for the adsorption of heavy metal ions from contaminated water. Recently, there have been reports on the adsorption of heavy metal ions using porous micro/nanostructured materials with different morphologies, such as; nano-assemblies, nano-plates, hierarchical ZnO nano-rods and microspheres with nano-sheets as absorbents (Tuzen and Soylak, 2007; Ge *et al.*, 2012; Yan *et al.*, 2008; Wang *et al.*, 2010; Kumar *et al.*, 2013).

Wang *et al.* (2010) demonstrated the higher efficiency of porous ZnO nano-plates and ZnO hollow microspheres with exposed porous nano-sheets in the removal of Cu (II) from contaminated water when compared with commercial ZnO. These nano-plates and microspheres showed an unsaturated adsorption capacity for Cu (II) ions, whereas that of commercial ZnO nano-powders is saturated at around 300 mg g⁻¹. They have attributed this enhanced adsorption of heavy metal ions to their unique micro/nanostructure. Singh *et al.* (2013) reported on the removal of various

toxic metal ions, such as Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} and As^{3+} from wastewater by porous ZnO nano-assemblies. It was reported that Hg^{2+} , Pb^{2+} and As^{3+} have a stronger attraction towards ZnO nano-assemblies due to their electropositive nature and hence, they exhibit better removal efficiency (63.5% Hg^{2+} , 100% Pb^{2+} and 100% As^{3+}). Kumar *et al.* (2013) have demonstrated the removal of Pb(II) and Cd(II) under different adsorbate concentrations, contact times, adsorbent dosages, pH values and temperature conditions from aqueous solutions by mesoporous hierarchical ZnO nano-rods. They observed the maximum adsorption capacities of Pb(II) and Cd(II) to be 160.7 and 147.25 mg g^{-1} , respectively and that the loading capacities of recycled ZnO nano-rods have two-thirds that of their original capacities. Similarly, Sheela *et al.* (2012) used ZnO nanoparticles of size 25 nm for the removal of Cd(II) and Hg (II) ions from an aqueous solution. They found a maximum adsorption capacity of 387 and 714 mg g^{-1} for Cd (II) and Hg (II) ions, respectively. In addition, Ma *et al.* (2010) reported a novel strategy to prepare ZnO/Pb Sheterostructured functional nanocomposites based on Pb^{2+} sorbed ZnO. The Pb^{2+} adsorption mainly exists in a form of lead oxide as well as a little lead sulfide. The diffraction peaks of 2 of PbS are appeared in 25.43, 30.10, 43.69, 53.02, 68.63, respectively. This is because some sulfur-containing source used for ZnO nanosheet preparation is still remaining. The PbS is a good photoelectron material in near-infrared band, so the combination with PbS may change the photoelectronic property of ZnO. The ZnO nanosheets adsorbing Pb^{2+} were put into a Telfon-lined stainless steel autoclave containing sulfur source to treat at 120°C for 12 h. The diffraction of PbS increased clearly after the hydrothermal treatment. Strong diffraction peaks of 2 of PbS were clearly appeared in 25.84, 43.08, 53.22, 62.34, 68.83 and 71.06. This indicates that it is feasible to remove toxic heavy metal ions utilizing the doping-effect of ZnO nanocomposite, while avoiding the secondary pollution during regeneration of conventional absorption treatments. They prepared ZnO nano-sheets via a hydrothermal approach, which exhibited a good sorption capacity for Pb^{2+} (6.7 mg g^{-1}) due to the presence of surface hydroxyl groups.

Carbon based nanomaterials: Carbon and oxide based nanomaterials, such as; activated carbon, carbon nanotubes, graphene and ferric oxides, manganese oxides, titanium oxides, magnesium oxides and zinc oxides, respectively (Mandel *et al.*, 2012; Rao *et al.*, 2006; Aillon *et al.*, 2009; Ray, 2010; Zhou *et al.*, 2011; Li and Zhang, 2009; Vollath, 2013; Zhang *et al.*, 2013) play a significant role in adsorbate-adsorbent systems.

These nanoparticles have infinite applications in many scientific and industrialized fields, including; wastewater purification, catalysis and magnetic devices. Carbon and oxide based nanoparticles were reported as nano-adsorbents for the removal of various metal ions from wastewater, such as; Ni^{2+} , Cr^{3+} , Cr^{6+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , As^{3+} , As^{5+} , Th^{4+} , Eu^{3+} , Sr^{2+} , Zn^{2+} and U^{6+} (Dean *et al.*, 1972; Stafiej and Pyszynska, 2007; Sadegh *et al.*, 2014; Rickerby and Morrison, 2007; Brumfiel, 2003; Theron *et al.*, 2008; Cloete, 2010; Mandel *et al.*, 2012; Chen and Mao, 2007; Rao *et al.*, 2006; Aillon *et al.*, 2009; Ray, 2010; Zhou *et al.*, 2011; Liu *et al.*, 2009; Vollath, 2013; Zhang *et al.*, 2013).

Carbon based nanomaterials (Bhatkhande *et al.*, 2002) have been used widely for heavy metals removal in recent decades, due to their non toxicity and high sorption capacities. Activated carbon was used initially as sorbents, however; due to the difficulties associated with heavy metals removal at ppb levels carbon nanotubes, fullerene and graphene were synthesized and used as nanosorbents to overcome this issue.

Activated carbon: Activated carbons typically have high porosity, high surface area and prepared from readily available carbonaceous precursors, such as; coal, wood, coconut shells and agricultural wastes (Mauter and Elimelech, 2008; Di Natale *et al.*, 2008; Selvi *et al.*, 2001; Graydon *et al.*, 2009; Patnukao *et al.*, 2008). Activated carbons are extensively used for the removal of inorganic and organic pollutants from effluent streams of polluted aquatic sources. It was found that activated carbon possesses a significant weak acidic ion exchange character enabling them to remove trace metal contaminants and to adsorb hazardous pollutants from wastewater. The sorption of pentavalent arsenic on a Granular Activated Carbon (GAC) was experimentally studied (Mauter and Elimelech, 2008). Activated carbon prepared from coconut tree sawdust was used as an adsorbent for the removal of Cr (VI) from aqueous solution (Di Natale *et al.*, 2008). Sorption and stability of mercury on activated carbon for emission control were also reported (Selvi *et al.*, 2001). Powder Activated Carbon (PAC) prepared from *Eucalyptus camaldulensis* Dehn bark was studied for its sorption capacities (q_m) at 60°C, where q_m for Cu (II) and Pb (II) were calculated to be 0.85 and 0.89 mmol g^{-1} , respectively (Graydon *et al.*, 2009). A novel sodium polyacrylate grafted activated carbon was produced using gamma radiation to increase the number of functional groups on the surface(106). This grafting technique can be potentially applied to other adsorbents to increase the efficiency of metal ion sorption by activated carbon

Table 2: Data of maximum adsorption capacity of heavy metal ions with activated carbon

Adsorbents	q _m	SA	RP	Conditions	References
Granular AC	As (V): 2.5	950	NA	pH: 2-11.5, contact time: 72 h C ₀ : 0.5-10, T: 283-328 K	Di Natale <i>et al.</i> (2008)
AC	Cr (VI): 3.46	486	99	pH: 10, contact time: 180 min C ₀ : 5-20, T: 298 K	Selvi <i>et al.</i> (2001)
BPL AC	Hg (II): 110.8	1026	NA	pH: 2.88, C ₀ : 5.7 mL L ⁻¹ , T: 298 K	Graydon <i>et al.</i> (2009)
HGR AC	Hg (II): 101.6	482	NA	pH: 2.88, C ₀ : 5.7 mL L ⁻¹ , T: 298 K	Patnukao <i>et al.</i> (2008)
BPL-S AC	Hg (II): 95.4	1142	NA	pH: 2.88, C ₀ : 5.7 mL L ⁻¹ , T: 298 K	Ewecharoen <i>et al.</i> (2009)
FC-S AC	Hg (II): 89.5	160	NA	pH: 2.88, C ₀ : 5.7 mL L ⁻¹ , T: 298 K	Iijima (1991)
Powdered AC	Cu (II): 0.85, Pb (II): 0.89	1,239	NA	pH: 3-6, contact time: 45 min C ₀ : 0.1-10, T: 298-333 K	Pyrzynska and Bystrzejewski (2010)
AC	Ni (II): 44.1	899	NA	pH: 3.92, C ₀ : 145, T: 298 K	Li <i>et al.</i> (2002a)
PAAS-grafted AC	Ni (II): 55.7	892	NA	pH: 3.92, C ₀ : 145, T: 298 K	Li <i>et al.</i> (2003a)
AC	Cu (II): 0.4, Co (II): 0.46	3.5	20	pH: 5-9, contact time: 4 h, C ₀ : 2-20	Li <i>et al.</i> (2003b)

AC: Activated carbon, NA: Not available, q_m: Maximum adsorption capacity (mg g⁻¹), SA: Surface area (m² g⁻¹), RP: Removal percentage (%), C₀: Initial concentration (mg L⁻¹), T: Temperature, PAAS: Sodium polyacrylate

(Patnukao *et al.*, 2008). Their high sorption ability and lower price make activated carbons suitable materials for removal of heavy metal. The concise data in form of summary will be well elucidated from Table 2.

Carbon nanotubes (CNTs): Carbon nanotubes (CNTs) were first developed by Iijima (1991). Due to their unique structural, electronic, optoelectronic, semiconductor, as well as mechanical, chemical and physical properties (Zare *et al.*, 2013; Sadegh *et al.*, 2014), they have been extensively used to remove heavy metals in wastewater treatment (Gupta and Suhas, 2009; Dean *et al.*, 1972; Demirbas, 2008; Stafiej and Pyrzynska, 2007; Mahmoodian *et al.*, 2015; Saleh and Gupta, 2012a, b; Gupta *et al.*, 2011a, 2013a, b; Gupta and Saleh, 2013; Gupta and Nayak, 2012; Pahlavan *et al.*, 2014).

The CNTs were used as, nanosorbents separately and showed high sorption efficiency for divalent metal ions. The advantages and limitations of metals sorption onto activated carbon, carbon nanotubes and carbon-encapsulate magnetic nanoparticles, through sorption studies based on Co²⁺ and Cu²⁺ were reported by Pyrzynska and Bystrzejewski (2010), their results showed that carbon nanomaterials have significantly higher sorption efficiency compared to activated carbons. Meanwhile, Stafiej and Pyrzynska (2007) found out that solution conditions, including pH and metal ions concentrations, could affect the adsorption characteristics of carbon nanotubes, whereas the Freundlich adsorption model agreed well with their experimental data. Oxidized CNTs also shows exceptionally high sorption capacity and efficiency for Pb (II), Cd (II) and Cr (VI) from polluted water (Li *et al.*, 2002a, 2003a). CNTs were also reported as excellent adsorbents for multi-component sorption of metal ions (Li *et al.*, 2003b). The sorption mechanisms were reported to be governed by the surface features, ion exchange process and

electrochemical potential (Gao *et al.*, 2009). The later plays a noteworthy role in multi-component sorption where redox reactions, not only on the adsorbent surface but also among the different adsorbates, are likely to occur. The MWCNTs were found to adsorb ²⁴³Am with extraordinarily high efficiency by forming very stable complexes (Wang *et al.*, 2005). The sorption characteristic of Pb (II) from aqueous solution was studied using oxidized MWCNTs (Xu *et al.*, 2008). The reported results showed a slope of V/m and intercept of C₀V/m for the same initial concentration of Pb (II) and the same content of oxidized MWCNTs for each experimental data (Xu *et al.*, 2008). Oxidized MWCNTs were also applied to adsorb Ni (II) from aqueous solution (Chen and Wang, 2006). The predominant mechanism of Ni (II) sorption onto MWCNTs was reported to be ion exchange at low pH values by strong surface complexation at high pH values (Chen and Wang, 2006). It was also reported that oxidized MWCNTs can be potentially promising materials for the pre-concentration and solidification of metal ions (Chen *et al.*, 2007).

The sorption and desorption kinetics of ¹⁵²⁺¹⁵⁴Eu (III) on MWCNTs have also been studied and reported (Tan *et al.*, 2008). It was found that MWCNTs were suitable material for pre-concentration of lanthanides from large volumes of aqueous solutions in radioactive nuclear waste management with the strong surface complexation and/or chemisorption mechanism (Tan *et al.*, 2008). With the aid of FITEQL 3.2, (Chen *et al.*, 2008) characterized the surface properties of MWCNTs at different ionic strengths and pH values and modeled Sr (II) and Eu (III) sorption onto oxidized MWCNTs by applying surface complexation model and found that the Diffuse Layer Model (DLM) fitted the experimental data very well. The removal of divalent metal ions (Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺ and Zn²⁺) from aqueous solution using various kinds of CNTs have been studied (Rao *et al.*, 2007). It was suggested that

Table 3: Data of maximum adsorption capacity of heavy metal ions with carbon nanotubes

Adsorbents	q_m	SA	RP	Conditions	References
MWCNTs	Co (II): 2.77	70-100	30	pH: 5-9, contact time: 4 h, C_0 : 2-20	Pyrzynska and Bystrzejewski (2010)
CEMNPs	Cu (II): 3.21	6-11	60	pH: 5-6, contact time: 4 h, C_0 : 2-20	Pyrzynska and Bystrzejewski (2010)
MWCNTs	Cu (II): 3.49 Pb (II): 2.96 Co (II): 2.60	40-600	NA	pH: 3-9, C_0 : 2-10, T: 298 K	Stafiej and Pyrzynska (2007)
CNTs	Pb (II): 7.5	NA	NA	pH: 3-7, contact time: 6 h C_0 : 2-14, T: 298 K	Li <i>et al.</i> (2002b)
CNTs	Cd (II): 5.1	122	NA	pH: 5.5, C_0 : 1.18-9.50, T: 298 K	Li <i>et al.</i> (2003a)
MWCNTs	Cu (II): 28.49 Pb (II): 97.08 Cd (II): 10.86	NA		pH: 5, C_0 : 5-30, T: 298 K	Li <i>et al.</i> (2003b)
CNTs-ox	Ni (II): 0.03 Cu (II): 0.04 Cd (II): 0.02 Zn (II): 0.01	77	NA	pH: 2-12, C_0 : 1-5, T: 298 K	Gao <i>et al.</i> (2009)
MWCNTs-ox	Pb (II): 9.92	197	90	pH: 6-10, contact time: 1 h C_0 : 0.1, T: 293 K	Wang <i>et al.</i> (2005)

CNTs: Carbon nanotubes, NA: Not available, q_m : Maximum adsorption capacity (mg g^{-1}), SA: Surface area ($\text{m}^2 \text{g}^{-1}$), RP: Removal percentage (%), C_0 : Initial concentration (mg L^{-1}), T: Temperature, MWCNTs: Multiwalled carbon nanotubes, CEMNPs: Carbon-encapsulated magnetic nanoparticles, CNTs-ox : Oxidized carbon nanotubes, MWCNTs-ox: Oxidized multiwalled carbon nanotubes

CNTs were promising adsorbents for environmental protection application because of the superior sorption capacity and effective desorption of divalent metal ions (Rao *et al.*, 2007). The CNTs can be potentially produced on large scale using different methods such as chemical vapor deposition, to reduce the cost of CNTs and increase the use of CNTs in environmental protection applications in future. The concise data in form of summary will be well elucidated from Table 3.

Graphene (G) and Graphene Oxide (GO): Graphene (G), which can be used as nanosorbent, is typically made of one and/or several atomics layered graphite's and possesses special two-dimensional structure and good mechanical, thermal properties.

The few-layered Graphene Oxide (GO) nanosheets have been synthesized through the modified Hummers method have been synthesized (Zhan *et al.*, 2004). These graphene nanosheets can be used as sorbents for the removal of Cd^{2+} and Co^{2+} ions from aqueous solution (Zhan *et al.*, 2004). It was reported that the metal ions sorption on nanosheets was dependent on pH, ionic strength (Zhan *et al.*, 2004). The abundant oxygen-containing functional groups on the surfaces of Graphene Oxide (GO) nanosheets were reported to play an important role on sorption (Zhan *et al.*, 2004).

Magnetite-graphene adsorbents with a particle size of ~10 nm were reported for the high binding capacity for As^{3+} and As^{5+} (Chandra *et al.*, 2010). The MGA (10 mg) was dispersed in 10 mL of deionized water by ultrasonication in an ice bath. The EDC of 50 mL and a Na_2CO_3 - NaHCO_3 (1:9) buffer solution were added to adjust the pH of the system to approximately 9. After carboxyl groups on MGO were activated in 1 h, a solution containing 100 mg of MEA was added dropwise to the

system. With the protection of argon, the reaction lasted for 24 h. The precipitate was collected by magnetic separation and was then dispersed in water by ultrasonication. The resulting black powder was collected by freeze-drying. The high binding capacity was resulted due to the increased adsorption sites in the graphene composite (Chandra *et al.*, 2010). The strong functional groups on Graphene Oxide (GO) surface, makes GO a potential adsorbent for metal ion complexation through both electrostatic and coordinate approaches. Generally, GO presents high adsorption capacity on cationic metals. Graphene Nanosheets (GN) can be used for adsorption of both cationic and anionic metals. After modification of GO with organics or metal oxides, GO composites can also be used for anionic metal removal due to surface modified functionalization.

Cu^{2+} -GO interaction in aqueous solution showed that Cu^{2+} causes GO sheets to be folded and form large aggregates (Yang *et al.*, 2010). The coordination between Cu^{2+} and oxygen atoms on GO was the primary driving force. The GO has a Cu^{2+} adsorption capacity of 46.6 mg g^{-1} , higher than that of carbon nanotubes (28.5 mg g^{-1}) and active carbon ($4-5 \text{ mg g}^{-1}$) (Selvi *et al.*, 2001).

The removal of Cd^{2+} , Co^{2+} , Pb^{2+} (Zhao *et al.*, 2011a) and U(VI) (Zhao *et al.*, 2012) ions from aqueous solutions have been studied by synthesizing few-layered GO nanosheets (GOS). They found that the abundant oxygen-containing functional groups on GO surfaces played an important role in metal sorption, which was in agreement to the reported results by Wang *et al.* (2010). The Cd^{2+} and Co^{2+} sorption on GOS was also strongly dependent on pH and weakly dependent on ionic strength. The presence of humic acid reduced Cd^{2+} and

Table 4: Data of maximum adsorption capacity of heavy metal ions with graphene and graphene oxide

Adsorbents	q_m	SA	RP	Conditions	References
FGO	Co (II): 106.3	NA	NA	pH: 6-9, T: 303-333 K	Zhao <i>et al.</i> (2011a)
	Cd (II): 68.2				
M-RGO composites	As (III): 7.81	137-148	99.9	pH: 7, contact time: 120 min C ₀ : 3-7, T: 283-323 K	Chandra <i>et al.</i> (2010)
	As (V): 4.23				
GO	Cu (II): 46.6	NA	NA	pH: 5, C ₀ : 19.2-21.8	Yang <i>et al.</i> (2010)
FGO	Pb (II): 842	3.8	NA	pH: 6, C ₀ : 120, T: 293 K	Zhao <i>et al.</i> (2011b)
2-or 3-layered G	Pb (II): 400	4.1	NA	pH: 6, C ₀ : 120, T: 293 K	Zhao <i>et al.</i> (2011a)
FGO	U (VI): 97.5	NA	NA	pH: 5, T: 293 K	Zhao <i>et al.</i> (2012)
GO	Hg (II): 30	NA	NA	pH: 2, C ₀ : 200	Gao <i>et al.</i> (2011)
EDTA-GO	Pb (II): 479	623	NA	pH: 6.8, contact time: 10-30	Madarang <i>et al.</i> (2012)
				C ₀ : 1-100, T: 323 K	
GO	Pb (II): 367	430	NA	pH: 2-8.2, contact time: 24 h C ₀ : 1-100, T: 323 K	Madarang <i>et al.</i> (2012)
EDTA-RGO	Pb (II): 228	730	NA	pH: 2-8.2, contact time: 24 h	Madarang <i>et al.</i> (2012)
				C ₀ : 1-100, T: 323 K	

G: Graphene, NA: Not available, q_m : Maximum adsorption capacity (mg g^{-1}), SA: Surface area ($\text{m}^2 \text{g}^{-1}$), RP: Removal percentage (%), C₀: Initial concentration (mg L^{-1}), T: Temperature, GO: Graphene oxide, FGO: Few-layered GO, M-RGO: Mngnetite-reduced graphene oxide, EDTA: Ethylenediaminetetra acetic acid

Co²⁺ sorption on GOS at pH<8. The maximum sorption capacities of Cd²⁺ and Co²⁺ on GOS at pH 6.0 and 30°C were about 106.3 and 68.2 mg g^{-1} , respectively. The complexation reactions between humic substances and polyvalent metal ions are important determinants of metal speciation in soils and aquatic ecosystems. An understanding of these reactions is important in many contexts, for example: Trace element geochemistry and mobility or micronutrient nutrition of, or toxicity to, plants and aquatic fauna. Complexation with humic acid has been shown to decrease the uptake of cadmium by terrestrial plants in solution culture (Rate, 2010). For Pb²⁺, the maximum adsorption capacities were about 842, 1150 and 1850 mg g^{-1} at 20, 40 and 60°C, respectively, but sorption capacity of U(VI) at pH 5.0, 20°C was 97.5 mg g^{-1} (Zhao *et al.*, 2012). Modification of GO with organics can change the surface functional groups for better adsorption of various metal species. A modified GO with thiol groups by diazonium chemistry was reported to adsorb 6-fold higher concentration of Hg²⁺ ions than GO and activated carbon (Gao *et al.*, 2011). The steps involved in the thionation are as follows: 100 mg GO was dispersed in 100 mL DMF and sonicated for 1 h. After removing undispersed GO by centrifugation at 1000 rpm for 10 min, a homogeneous solution of GO in DMF was obtained. Then, 300 mg P₄S₁₀ was added to the solution and the reaction flask was evacuated to 5103 mbar at 100°C for 2 min to remove traces of water in the flask. The thionation was performed for 12 h under vacuum and continuous stirring at 120°C. Finally, the reaction product was collected by filtering the solution through a 0.45 μm polyamide membrane filter and was extensively washed first with 100 mL of water, followed by 100 mL ethanol and acetone, respectively. If the reaction was performed at the boiling point of DMF (152-154°C) under reflux for 36 h, TrGO was obtained with a higher degree of

reduction, but less thiol groups. The reduction degree of TrGO can be determined by measuring the UV-vis absorption as well as the sheet resistance.

When N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (EDTA-silane) was used to obtain a chelate complex of GO for Pb²⁺ removal, the adsorption was fast and completed within 20 min, with an adsorption capacity of 479 mg g^{-1} at pH 6.8 (Madarang *et al.*, 2012). Compared to activated carbon and carbon nanotubes, GO and GN proved to be a better adsorbents for many of noxious water pollutants. The concise data in form of summary will be well elucidated from Table 4.

CONCLUSION

Advances in nanoscale science and engineering are providing new opportunities to develop more low cost effective adsorbent and environmentally acceptable water treatment techniques. Nanomaterials have a number of specific physicochemical properties that make them particularly attractive for wastewater purification. Recent researches had indicated that use of nanomaterials as, adsorbents is a very useful and powerful tool for the removal of metal such as; Ni²⁺, Cr³⁺, Cr⁶⁺, Cu²⁺, Cd²⁺, Co²⁺, Hg²⁺, Pb²⁺, As³⁺, As⁵⁺, Th⁴⁺, Eu³⁺, Sr²⁺, Zn²⁺ and U⁶⁺ due to their unique structure and specific surface characteristics. These materials are capable to remove noxious metal ions even at low concentration i.e., up to ppb level also, with a very high selectivity and adsorption capacity. These unique and specific properties of nanosorbents make them ideal materials for wastewater treatment technology. Although, carbon based nanomaterials, such as; carbon active, carbon nanotubes, graphene, graphene oxide and on the other hand oxide based nanomaterials, such as; ferric oxides, manganese

oxides, titanium oxides, magnesium oxides and zinc oxides, are used very efficiently and successfully in removal of noxious metal ions from wastewater, several problems still remain; large scale wastewater treatment is the essential one.

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