

Removal of heavy metals by nanoadsorbents: A review

Achla Kaushal,^{1,*} S.K. Singh²

¹Chemical Engineering Department, Guru Nanak Dev Institute of Technology, Delhi, India

² Department of Environmental Engineering, Delhi Technological University, Delhi, India

REVIEW ARTICLE

ABSTRACT

Discharge of heavy metals from industrial, municipal, agricultural and domestic wastewater has become a serious threat for the ecosystem. New class of adsorbents developed during past couple of decades has helped to overcome this growing threat. They have gained popularity due to their distinct characteristic and have shown excellent potential in treatment of wastewater and industrial effluents to be reused for various purposes for the sustainable development of growing society. This paper presents a scientific review of the nanoadsorbents used in recent times in the removal of heavy metals from wastewater, highlighting their efficiency, advantages and the mechanism involved in the removal.

KEYWORDS

adsorption; heavy metals; mechanism; nanoadsorbent, removal efficiency

1. INTRODUCTION

Lead, mercury, nickel, chromium, thallium, zinc, copper, cobalt, selenium, arsenic and cadmium are the heavy metals known for their toxicity and persistency. Unlike organic pollutants, they do not easily degrade, but are mostly non-biodegradable. They find their way into water bodies through refineries, sludge disposal, mining operations, manufacturing industries such as paints, electronic and electrical devices, batteries, fertilizers, pesticides etc. Their presence in water may pose serious threats to all forms of life, because they may be mutagenic and carcinogenic. Their presence above prescribed limits in body can cause severe damages to vital organs of the body, such as kidney, liver and brain, reproductive and nervous system (Goel, 2006). The conventional methods of wastewater treatment employed since decades, such as ion exchange, lime coagulation, evaporation, reverse osmosis, electrochemical treatment methods, solvent extraction chemical precipitation and filtration, redox reactions resulted in low metal removal efficiencies for

high operational costs and hence these are reported as expensive and inadequate.

Adsorption is a known phenomenon in water treatment since ancient times. It is a common phenomenon in gaseous phase, but is used effectively in treatment of wastewater. Granular activated carbon (GAC) has been used for treatment of wastewaters for decades because of its properties, such as adsorption capacity, ion selectivity, thermal stability, ease of activation and regeneration and resistance to transportation losses. Red mud, green sand, slags are the industrial waste found effective adsorbents for organic and inorganic materials including heavy metals from wastewater (Vigneswaran and Moon, 1999). Living or dead cells produced by sea bacteria used for biosorption of trace heavy metals helped in detoxification of wastewater (Lopez-Cortes and Ochoa, 1999). Low cost adsorbents prepared from agricultural waste were proved very effective in removal of heavy metals from wastewater even at very low concentrations. Also, these adsorbents have found to be promising in long terms as there are many materials available locally and abundantly

Corresponding author: A.Kaushal

Tel: +919811200429

E. mail: achla001@hotmail.com

Received: 30-10-2016

Revised: 21-11-2016

Accepted: 05-12-2016

Available online: 01-01-2017

which can be utilized as low cost adsorbents (Babel and Kurniawan, 2003). Polymeric membranes used in wastewater treatment are cross linked polyamide, poly sulfone and cellulose acetate materials and exhibit special characteristics such as chemical stability, high flux rate, better metal ion binding with chelating mechanism and resistance to ultraviolet radiations, ozone and chlorine (Lakshmanan, 2013). During last few decades, new classes of materials have been developed, such as derivatives of carbon, carbonaceous nanoporous materials, inorganic nano materials, magnetic and nano-magnetic materials, microporous glasses, molecular sieves, polymers, ceramics, silica nanoparticles etc. (Kumar, 2009). They have gained interest of new generation of researchers due to vast scope of research in treatment of wastewater using materials with distinct characteristics of reuse for the sustainable development of growing society. They also have been reported to exhibit high adsorption capacity for heavy metals from wastewater as compared to the materials used traditionally and commercially as adsorbents.

2. NANO MATERIALS AS ADSORBENTS

Nano science and technology gained popularity in 1980 with the introduction of cluster science and STM (scanning tunnel microscope) (Mehta et al., 2015). Materials in nano size range (1-100 nm) exhibit distinct properties and effective process parameters because of the large number of particles, high surface area to volume ratio, specificity for pollutants, magnetic separation, surface chemistry and surface interactions (Lakshmanan, 2013). Various nano materials synthesised in recent times are carbon nanotubes, nanocages, nanocrystals, nanowires, nanoflakes, silica nanoparticles, cellulose nanocrystals and nanofibrils, fullerenes, hydroxyfullerenes and heterofullerenes. They can be synthesised from metals, their oxides and hydroxides (cobalt hydroxide), polymers and biopolymers, ceramics and derivatives of carbon etc. (Dabrowski, 2001; Jaroniec and Sayari, 2002; Knecht and Wright, 2004; Kumar, 2009; Oaki and Imai, 2007; Chwastowska et al., 2008; El Saliby et al., 2008; Donald, 2010; Fi and Li, 2010; Liu et al., 2012; Srivastava, 2013; Heimann et al., 2015) by sol-gel method, co-precipitation, micro-emulsion, direct oxidation, thermal decomposition, chemical, physical and electro vapour decomposition, microwave colloidal, polyol or hydrothermal method etc. (Chen and Mao, 2007). They find their extensive use in electronics as metals, semiconductors and insulators and in the field

of medicine. Application of nanoparticles is gaining attention in wastewater treatment for exhibiting high adsorption capacity for heavy metal ions from wastewater due to their high chemical potential and activity. Chemical potential and thermodynamic activity are important parameters to define the equilibrium concentrations and constants between the phases and also the rate of reaction between the phases (Kaufman, 2002).

2.1. Metal oxide nanoparticles

Nanoparticles can be synthesised from oxides of various metals such as iron, copper, titanium, manganese, magnesium, zinc, silica and aluminium. Metal elements have a distinct property to form oxides with a large variety of structural and electronic properties. In nanotechnology, the aim is to get nanostructures exhibiting distinct physical and chemical properties, different from bulk or single structured particles. This is due to the fact that the band gap between the oxide particles decrease with decrease in average size of the particles, resulting in change in conductivity and chemical reactivity (Fernández-García and José, 2007).

Metal oxide nanoparticles show higher extent of adsorption as compared to normal sized oxide due to metal-ligand precipitation or formation of ternary ligands (Stietiya and Wang, 2014). Adsorption mechanism of heavy metals on oxides of Zn, Cu and Fe as nanoadsorbents showed the dependence of metal removal efficiency on the pH of the solution. Removal of heavy metal ions from the solution increased with pH because of electrostatic interactions, precipitation and formation of metal complexes due to ionic or covalent bonding, depending either upon the chemistry between metal and the solution or on the nature of the functional group. Increase in the solution pH favours the deprotonation of nano sorbent surface, increasing the negatively charged sites and hence the forces of attraction between positively charged metal ions and the negative sites on adsorbents. On lowering the pH, competitive adsorption occurred between the competing metal ions and H⁺ ions in the solution (Mahdavi et al., 2012).

Fe₃O₄ nanoadsorbents synthesized by Nassar (2012) were used batch wise to study the removal of Pb(II) ions from aqueous solution. The maximum adsorption capacity of Pb(II) was 36 mg/g. Equilibrium was attained within 30 min and the equilibrium data fitted well into the Langmuir and Freundlich isotherm models. The adsorption process was endothermic

as temperature increased the amount of Pb(II) adsorbed. The thermodynamic studies showed that process was spontaneous. Kocabas-Atkali and Yurum (2013) synthesized anatase nanoadsorbent by sol-gel method followed by calcination at 400 °C to study the removal of lead, copper, and arsenic present in water supplies. The adsorbent showed maximum adsorption capacities for lead, copper and arsenic as 31.25, 23.74 and 16.98 mg/g, respectively. Adsorption capacity increased with pH for lead and copper, where as it remained constant for arsenic. The equilibrium data fitted well with the Langmuir, Freundlich, Redlich-Peterson and Sips isotherm modelling equations and followed pseudo second-order kinetic equation. Tang et al. (2013) synthesised an ultrafine nanoadsorbent, magnesium ferrite ($Mg_{0.27}Fe_{2.5}O_4$) nanocrystallites for removing arsenic from water by doping about 10% Mg^{2+} into $\alpha-Fe_2O_3$ by solvent thermal process with the help of in-situ self-formed NaCl to restrict the crystal growth. The average size of the nano material obtained was approximately 3.7 nm, the specific surface area was 438.2 m²/g and the value of specific magnetization was 32.9 emu/g, making it possible to separate easily for regeneration and reuse. Adsorption capacities were 127.4 mg/g and 83.2 mg/g for As(III) and As(V), respectively at pH 7. Manganese feroxyhyte ($\delta-Fe_{0.76}Mn_{0.24}OOH$) was prepared by Tresintsi et al. (2013) by continuous co-precipitation of $FeSO_4$ and $KMnO_4$ in the presence of strong oxidising agent to produce manganese feroxyhyte ($\delta-Fe_{0.76}Mn_{0.24}OOH$), in which Mn(IV) is homogeneously distributed into the crystal structure. This single-phase Fe/Mn oxyhydroxide nanoadsorbent was studied batch wise for the removal of arsenic, As(III) and As(V), present in drinking water. Experiments showed that at pH 7, adsorption capacity was 11.7 µg/mg and 6.7 µg/mg for As(V) and As(III) respectively. Fe-La composite oxide was synthesised by Zhang et al. (2014a) as nanoadsorbent for the removal of As(III) from aqueous solutions. Structure of Fe-La composite oxide was same as the crystal structure of $La(OH)_3$ as shown by SEM and TEM techniques. The maximum adsorption capacity for As(III) was 58.2 mg/g at optimum pH value of 7 and equilibrium time of 240 min; the equilibrium data fitted well into the Langmuir isotherm model. Alumina nanoadsorbent synthesized by solution combination synthesis method was used for the removal of Zn(II) ions and colour black G dye from wastewater. Equilibrium time obtained for both zinc ions and the dye was approximately 4.5 h. Maximum adsorption capacity obtained by alumina nanoadsorbent for Zn(II) ions was 1047.83 mg/g at pH 7 and for dye was 263.16

mg/g at pH 2. Kinetic data fitted better to pseudo first order model and equilibrium data fitted using the Langmuir isotherm model for both the contaminants (Bhargavi, et al., 2015).

2.2. Magnetic nanoparticles (MNPs)

Nano sized iron oxide particles exhibit super paramagnetism, an additional special property from common nanoparticles. Super paramagnetic nanoparticle have large surface area, are biocompatible, less toxic, chemically inert, offer small diffusion resistance and their surface can be modified with organic molecules, inorganic ions or some functional groups, which render them surfaces having good potential for removing heavy metals. Surface modifications of NPs make them, a) stable by preventing them from oxidation and b) selective and specific for uptake of heavy metal ions by providing specific reaction sites and functional groups. The functional groups -COOH, -NH₂, -OH and -SH groups etc. provide active sites for exchange of metal ions. Physical interactions (such as electrostatic and Vander Waal's interactions) and chemical interactions (such as chemical binding, complex formation and modified ligand combination) are responsible for the adsorption of metal ions on the adsorbent surface (Wang et al., 2012; Patwardhan, 2012).

Mercapto-functionalized nano- Fe_3O_4 magnetic polymers (SH- Fe_3O_4 -NMPs) were prepared for the removal of Hg(II) from wastewater showed optimum values of temperature and pH 308 K and 3.0, respectively. Adsorption efficiency increased with pH. Equilibrium was achieved within 1 h. Experimental data were fitted well with the Freundlich isotherm equation. Thermodynamic properties suggested that the adsorption processes was endothermic (Pan et al. 2012). Carboxymethyl- β -Cyclodextrin (CMCD)-monodisperse magnetite nanocrystals with average particle size of 10 nm were prepared by thermal decomposition of FeOOH for remediation of As(III), As(V), naphthol, and naphthalene. These nanocrystals showed potential application in wastewater remediation with single step magnetic separation (Chalasan and Vasudevan, 2012). Fe_3O_4 superparamagnetic nanocomposites coated with ascorbic acid were synthesized to remove arsenic from the wastewater by hydrothermal method. These nanoadsorbents had diameter less than 10 nm, surface area of approximately 179 m²/g, saturation magnetization value of 40 emu/g and super paramagnetic property at room temperature. The maximum adsorption capacity was 16.56 mg/g

and 46.06 mg/g for As(III) and As(V) respectively and the equilibrium data followed the Langmuir isotherm (Feng et al., 2012).

Metal removal efficiencies were compared (Parham et al., 2012) for Hg(II) for the unmodified Fe_3O_4 magnetic nanoparticles and Fe_3O_4 modified with 2-mercaptobenzthiazole. For initial Hg(II) concentration of 50 ng/mL, unmodified nanoparticles showed a removal of 43.47%, whereas the modified nanoparticle removed up to 98.6% of Hg(II) within 4 min. MNPs have a tendency to accumulate and to change their properties. MnFe_2O_4 MNPs synthesized by coating with amorphous oxide shells of Mn-Co exhibited a strong negative charge on their surfaces over wide range of pH. This prevented their accumulation in aqueous solution and resulted in excellent adsorption capacities of 481.2 mg/g for Pb(II), 386.2 mg/g for Cu(II) and 345.5 mg/g for Cd(II) (Ma et al., 2013). Moussa et al. (2013) synthesized ferrite coated apatite magnetic nanoadsorbent by co-precipitation method for the removal of Eu(III) ions from aqueous solutions. The MNPs possessed a crystalline structure with mean particle size 63 nm, specific surface area 85.11 m^2/g and a high thermal resistance up to 600 °C. With 5 mg adsorbent dose, the equilibrium was attained within 12 h. The maximum adsorbed capacity was 157.14 mg/g at pH 2.5. Fe_2O_3 nano composites of cellulose were synthesized by Yu et al. (2013) by pot chemical co-precipitation method for the removal of arsenic from aqueous solution. The MNPs had a surface area of 113 m^2/g and possessed a sensitive magnetic behaviour making it easily separable by application of magnetic field. Adsorption capacities to remove As(III) and As(V) were 23.16, 32.11 mg/g respectively. Data fitted well with the Langmuir and Freundlich isotherm model equations.

Li et al. (2013) studied removal of Cr(VI) from water through batch experiments with MNPs. The adsorbent was prepared by doping porous carbon with nitrogen (RHC-mag-CN), which was found to have specific area of 1136 m^2/g and superparamagnetic characteristics. Maximum Cr(VI) removal was 16 mg/g at pH 3. The Langmuir isotherm model described the process. Zargoosh et al. (2013) synthesized modified MNPs by the covalent immobilization of thiosalicylhydrazide on Fe_3O_4 NP surfaces for removing heavy metal ions from industrial effluents. Excellent maximum adsorption capacities obtained were 188.7, 107.5, 76.9, 51.3, and 27.7 mg/g for Pb(II), Cd(II), Cu(II), Zn(II), and Co(II), respectively. Other added advantages of modified nanoadsorbents were reusability, ease of separation after treatment,

environment friendly composition, and no interference of metal ions of alkaline earth metals category, making them perfect adsorbents for removal of heavy metals from wastewater. Zhang et al. (2014b) prepared Fe-Ti bimetallic oxide coated magnetic Fe_3O_4 nano composite magnetic adsorbent by co-precipitation for the removal of fluoride from drinking water having 10–20 nm diameter magnetic Fe_3O_4 core and a few nm thick amorphous adsorbent shell. It showed high adsorption capacity (57.22 mg/g) and super paramagnetism with a high value of saturation magnetization (18.4 emu/g) which allowed its easy magnetic separation after water treatment. Equilibrium was attained within 2 min and data fitted into Langmuir isotherm.

2.3. Carbon nano tubes (CNTs)

CNTs are the engineered materials exhibiting unique properties, such as electrical conductivity, optical activity, mechanical strength and surface morphologies. Their high porosity, light mass density, large specific area, hollow structure and strong interactions with pollutant molecules render them good adsorbents (Dresselhaus et al., 2001). Adsorption sites in CNT bundles are internal sites, interstitial channels, grooves and outside surface. Equilibrium is reached faster on external sites as compared to internal sites. The adsorption mechanism is mainly attributed to the chemical interactions between the surface functional groups of CNTs and the metal ions. Depending on the process of synthesis and purification, CNTs generally contain –OH, –C=O and –COOH groups. More Functional groups can be added to CNTs by oxidation with Pd, Ni or Pt as catalysts or can be removed from CNTs by heat treatment at high temperature, such as 2200 °C. CNTs show high preference for hydrophobic groups, such as benzene, hexane and cyclohexane than the hydrophilic groups such as alcohol. This preference can be reversed on functionalisation due to change in wettability of CNT surfaces, because H-atoms from functional groups of CNTs get replaced by metal ions resulting in drop in pH of the solution as more H^+ ions are released in the solution (Lu et al., 2006; Gotovac et al., 2007; Gadhav and Waghmare, 2014).

Maghemite nanotubes synthesized by microwave irradiation method were used for the removal of Cu(II), Zn(II), and Pb(II). Nano particles had a surface area of 321.6 m^2/g and magnetic saturation was 68.7 emu/g. They showed maximum adsorption capacities of 111.11 mg/g, 71.42 mg/g, and 84.95 mg/g for Cu(II), Pb(II), and Zn(II) respectively. The kinetic data indicated pseudo second-order equation

(Roy and Bhattacharya, 2012). Multiwall carbon nanotube-magnetite nanocomposites based magnetic nanoadsorbent prepared to study the removal of Pb(II) and Hg(II) showed maximum adsorption capacity of 65.40 mg/g and 65.52 mg/g respectively. Surface area obtained was 97.16 m²/g (Zhang et al., 2012). Ge et al. (2014) prepared sulfonated multi-walled CNTs (s-MWCNTs) by treating purified multi-walled CNTs (p-MWCNTs) at high temperature with concentrated sulfuric acid to remove Cu(II) ions from aqueous solutions. s-MWCNTs showed an enhanced adsorption capacity of 58.9% for Cu(II) on sulfonation. Adsorption process was explained well by the Freundlich and D-R isotherm models. Magnetic multiwalled CNT nanocomposite (MMWCNTs-C) were studied for the removal of Ni(II) ions from aqueous solution. The equilibrium data showed that the adsorption process was explained well by the pseudo-second-order kinetic model and the Langmuir isotherm model than the Freundlich isotherm model. Maximum monolayer adsorption capacity was calculated as 2.11 mg/g. The adsorption process of Ni(II) on MMWCNTs-C was spontaneous and favorable thermodynamically. Thermodynamic parameters indicated that the type of adsorption process was physisorption (Konicki et al., 2015).

Removal of Cu(II) ions from aqueous solutions was performed using CNT sheets, synthesized by chemical vapor deposition of ferrocene and cyclohexanol at 750 °C in the presence of nitrogen and functionalized with chitosan and concentrated HNO₃. Functionalization improved adsorption capacity of CNT sheets from 23.32 to 57.34 mg/g for initial Cu(II) ions concentration of 800 mg/L. Adsorption behavior was described by the Freundlich and Langmuir models and equilibrium data fitted well in pseudo-first-order and the pseudo-second-order equations (Tofiqy and Mohammadi, 2015). Huang et al. (2015) prepared Magnetic multi-wall carbon nanotubes (MMWCNTs) by wet chemical treatment process to study the removal of Cr(VI) ions in aqueous solutions. Results indicated that the adsorption capacity of MMWCNTs increased with the metal ion concentration and contact time and decreased with adsorbent dose. The adsorption data followed pseudo second-order kinetic model and the Langmuir isotherm model. The Gibbs free energy calculations indicated that the process was spontaneous and endothermic. Based on above findings, it was concluded that the MMWCNT show significant potential for adsorption of heavy metal ions from wastewater.

2.4. Chitosan

Chitosan, obtained from the waste of the shellfish processing industry as a byproduct, is a biopolymer consisting of natural polysaccharides and is a highly desirable adsorbent because of special characteristics, such as being abundant, inexpensive, chemically stable, biodegradable, nontoxic, biocompatible, renewable and hydrophilic. It exhibits good reactivity towards a wide range of pollutants. Its adsorption capacity for the toxic metal ions is excellent due to the presence of amine group (-NH₂), in its polymer matrix and partial positive charge, which attracts metal ions by the coordination linkage or by ion exchange in the solution. Chitosan coated magnetite nanoparticles, called the magnetised chitosan nanoparticles (MNCs), showed even higher rates of adsorption. Since chitosan is inactive on the surface of the magnetic nanoparticles and chitosan-heavy metal ions interactions are reversible. Therefore MNCs are easier to recover after water treatment under the effect of external magnetic field and are useful, potential and recyclable tool for removal of heavy metal ions from wastewater (Liu et al., 2009; Jassal et al., 2015).

Binary oxides of chitosan synthesized by template method was studied for removal of As(III) from water. It showed the maximum adsorption capacity of 16.94 mg/g. Ca(II) and Mg(II) present in water affected the adsorption process significantly. The solution pH showed no effects in the range 3-9. The results indicated that As(III) concentration reduced from 983.7 to 7.44 g/L during the experiment (Dhoble et al., 2011). Rahbar et al. (2014) synthesized non-toxic and low cost chitosan-coated magnetite nanoparticles (CCMN) as adsorbent to remove Hg(II) ions from aqueous solutions using a time saving and effective Box-Behnken method. The adsorption study using this method indicated 99.91% removal of Hg(II) at optimum pH of 5, initial metal ion concentration of 6.2 mg/L, and adsorbent dose of 0.67 g with in a very short equilibrium time. Experimental data was described best by pseudo-first-order kinetic model and Langmuir and Freundlich models isotherm models. High Hg(II) adsorption in short time was attributed to high density active sites on the adsorbent surface. Jassal et al. (2015) used MNCs for the removal of Zn(II), Cd(II), Pb(II) and Cu(II) ions. It was observed that MNCs adsorbed the metal ions to a good extent and their concentration decreased significantly from the solution in due course of time upon adsorption onto MNCs. The chitosan nanoparticles prepared by deacetylation of chitin were used to remove Fe(II), Mn(II), Zn(II) and Cu(II) metal

ions from water. The optimum study conditions were at 2 g/L of chitosan nanoparticles, mixing time of 30 min and pH value of 7 for 20 mg/L of each metal ion. Chitosan exhibited metal removal efficiencies of 99.94% for Fe(II), 80.85% for Mn(II), 90.49% for Zn(II) and 95.93% for Cu(II) ions (Abd-Elhakeem et al., 2015). The chitosan/TiO₂ composite nanofibers as adsorbents synthesized by (1) coating method (TiO₂ nanoparticles coated chitosan nanofibers) and (2) Entrapped method (electrospinning of chitosan/TiO₂ solutions) were studied batch wise for the removal of Pb(II) and Cu(II) ions. Experimental data for both the ions using both chitosan/TiO₂ nanofibers was described best by pseudo-first-order kinetic model and the Redlich–Peterson isotherm models. The maximum adsorption capacities were 710.3 mg/g and 579.1 mg/g for Cu(II) and Pb(II) ions for entrapped method at 30 mins of equilibrium time and 526.5 mg/g and 475.5 mg/g for Cu(II) and Pb(II) for the coating method at 45 mins of equilibrium time respectively. Study showed that the nanofibers prepared by entrapped method could be reused after five cycles on desorption without any significant loss in performance. On the other hand, the nanofibers prepared by coating method adsorbed less than 60% of the metal ions in the first cycle (Razzaz et al., 2016).

2.5. Silica nanoparticles

Silica is used widely in coatings of nanoparticles used in water purification techniques. Si coating activates the surfaces of the NPs having various functional groups due to the abundant presence of silanol groups on the silica layer. It also protects NPs from leaching low pH situations. It also facilitates the NPs with non-specific moieties, highly and group specific ligands. Polymer layered silicate nanocomposites possess improved properties at low filler contents. At neutral pH, acidity of SiNPs increases with increase in particle size, resulting in 5-20% ionisation of silanol groups, causing anionic Si surface attract cations by ion pairing (Wang et al., 2012; Patwardhan, 2012).

Sheet et al. (2014) used batch adsorption method to remove Zn(II), Ni(II), Cr(VI), Pb(II) and Cd(II) ions from aqueous solutions with the help of nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composites. Study showed that nanostructured graphite oxide adsorbed heavy metals in the order nickel > zinc > lead > cadmium > chromium. Graphite oxide showed good results for the removal of Ni(II) ions as per Langmuir adsorption

isotherm model and for other heavy metal ions, Freundlich isotherm model suggested adsorption of monolayer type. Silica/graphite oxide composite (2:3) was recommended as an efficient adsorbent for wastewater treatment over other two adsorbents. Removal of lead, cadmium, nickel, chromium and zinc from water was studied with activated carbon microparticles (AC_μPs) (average particle size 25 μ m), silica NPs (appeared as white aggregate at 10 μ m magnification) and silica/activated carbon (2:3) nanocomposite (average particle size 12nm). Of these, silica/AC (2:3) nano composite showed best efficiency in the removal of Ni ions as compared to AC_μPs and silica NPs. At 30 mg/L Ni ion concentration, % removal by AC_μP, SiNP and Si/AC (2:3) NC were 99.4, 70.3 and 92.1 respectively and at 200 mg/L, the removal efficiencies were 84.1, 60.1 and 87.6 mg/L by AC_μP, SiNP and Si/AC (2:3) NC respectively. Experimental data fitted poorly to the Langmuir isotherm as suggested by the correlation coefficients, whereas fitted well with the Freundlich isotherm model (Karnib et al., 2014). Amino modified silica nanoparticles used to study the adsorption of Zn(II), Cd(II), Hg(II), Cu(II) and Pb(II) from aqueous solutions were obtained from the treatment of industrial silica fumes at 80 °C by HNO₃. Silane coupling agents were used to functionalise their surface and modification was done using 1,8-Diaminophthalene and chloro-acetyl chloride. The results showed that the functionalized NPs showed good results for Cu(II), Hg(II) and Pb(II) ions (Kong et al., 2014). Araghi et al. (2015) synthesised mesoporous silica nanoparticles by embedding silica magnetic nanoparticles by cetyltrimethylammonium bromide and then followed by modification by silane coupling agent 3-aminopropyltriethoxysilane to remove Cr(VI) ions from aqueous solutions. The experimental data showed that the adsorption varied with pH. The Langmuir isotherm model showed increase in maximum adsorption capacity with temperature. Adsorption mechanism was understood by the quantum mechanical method, which indicated that the role of H-bonds and electrostatic interaction between the ions and the surface functional groups. The NPs showed fast adsorption, regeneration, easy separation from the solution on application of external magnetic field and reutilization. Mesoporous silica nanoparticles MCM-41, grafted from poly-amide derivative used as the supporting matrix was synthesized for the separation of Hg(II) from aqueous solutions. It was characterised by large ordered pores and high surface area. This novel material extracted and separated trace

Hg ions from aqueous solutions within 3 min in the pH range of 3-11 without influencing other components of the solution (He et al., 2015).

3. CONCLUSIONS

Treatment of wastewater loaded with toxic and hazardous waste to make it reusable is the biggest challenge for the sustainable growth of society in the present scenario. Adsorption with nano materials has emerged as one of the potential technologies to address this issue. Distinct properties of nano adsorbents, such as unique physical and chemical properties due to limited size and high density of surface make them capable to revolutionize the wastewater treatment technologies and advantageous over the conventional methods of water treatment. A constant research is needed for the development of efficient methods for the synthesis of cost effective adsorbents in treatment of wastewater. A knowledge about their toxicity and desorption characteristics for their reuse and recovery of heavy metals after the treatment will make them more productive and allow their full scale application in real wastewater and industrial effluent treatment. Further, there is a vast scope to explore the feasibility of other materials such as activated carbon fibres, molecular sieves, microporous glass, membranes, ceramic beads, polymeric materials, carbon nanoscrolls etc. as adsorbents in wastewater treatment, regeneration, reuse and recovery of heavy metals.

REFERENCES

Abd-Elhakeem, M.A., Ramadan, M.M. and Basaad, F.S. (2015) Removing of heavy metals from water by chitosan nanoparticles. *Journal of Advances in Chemistry*, 11, 1-7.

Araghi, S.H., Entezari, M.H. and Chamsaz, M. (2015) Modification of mesoporous silica magnetite nanoparticles by 3-aminopropyltriethoxysilane for the removal of Cr(VI) from aqueous solution. *Microporous and Mesoporous Materials*, 218, 101-111.

Babel, S. and Kurniawan, T. A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials*, 97, 219-243.

Bhargavi, R.J., Maheshwari, U. and Gupta, S. (2015) Synthesis and use of alumina nanoparticles as an adsorbent for the removal of Zn(II) and CBG dye from wastewater. *International Journal of Industrial Chemistry*, 6, 31-41.

Chalasan, R. and Vasudevan, S. (2012) Cyclodextrin functionalized magnetic iron oxide nanocrystal: a host-carrier for magnetic separation of non-polar molecules and arsenic from aqueous media. *Journal of Materials Chemistry*, 22, 14925-14931.

Chen, X. and Mao, S.S. (2007) Titanium dioxide nano materials: synthesis, properties, modification and applications. *Chemical Reviews*, 107, 2891-2959.

Chwastowska, J., Skwra, W., Sadowska-Bratec, M., Dudek, J., Dabrowska, M. and Pszonicki, L. (2008) Fullerene as sorbent for separation and determination of toxic elements by GF AAS. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/40/103/40103923.pdf

Dabrowski, A. (2001) Adsorption-from theory to practice. *Advances in Colloid and Interface Science*, 93, 135-224.

Dhoble, R.M., Lunge, S., Bhole, A.G. and Rayalu, S. (2011) Magnetic binary oxide particles (MBOP): a promising adsorbent in removal of As(III) in water. *Water Research*, 45, 4769-81.

Donald, I.W. (2010) Radioactive wastes. In: *Waste immobilization in glass and ceramic based hosts radioactive, toxic and hazardous wastes*. Wiley Online library. doi: 10.1002/9781444319354.ch5.

Dresselhaus, G., Dresselhaus, M.S. and Avouris, P. (2001) Carbon nanotubes synthesis, structure, properties and applications. Springer, Berlin.

El Saliby, I.J., Shon, H.K., Kandasamy, J. and Vigneswaran, S. (2008) Nanotechnology for wastewater treatment: in brief, In *wastewater treatment technologies*. In: *Encyclopedia of life support systems (EOLSS)*. Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford, UK.

Feng, L., Cao, M., Ma, X., Zhu, Y. and Hu, C. (2012) Superparamagnetic high-surface-area Fe₃O₄ nanoparticles as adsorbents for arsenic removal. *Journal of Hazardous Materials*, 217-218, 439-446.

Fernández-García, M. and José, A.R. (2007) Metal Oxide Nanoparticles, In: *Nanomaterials: Inorganic and Bioinorganic Perspectives*, CRC press.

Fi, J. and Li, J. (2010) Metal Oxide Nanomaterials for Water Treatment. In: *Nanotechnologies for the Life Sciences, 1999-2015*. John Wiley and Sons, NYC, USA.

Gadhav, A. and Waghmare, J. (2014) Removal of heavy metal ions from wastewater by carbon nano tubes. *International Journal of Chemical Sciences and Applications*, 5, 56-67.

Ge, Y., Li, Z., Xiao, D., Xiong, P. and Ye, N. (2014) Sulfonated multi-walled carbon nanotubes for the removal of copper(II) from aqueous solutions. *Journal of Industrial and Engineering Chemistry*, 20, 1765-1771.

Goel, P.K. (2006). *Water pollution, Causes, Effects and Control (Revised 2nd edition)*. New Age International Publishers, New Delhi, India.

Gotovac, S., Song, L., Kanoh, H. and Kaneko, K. (2007) Assembly structure control of single wall nanotubes with liquid phase naphthalene adsorption. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 300, 117-121.

He, C., Ren, L., Zhu, W., Xu, Y. and Qian, X. (2015) Removal of mercury from aqueous solution using mesoporous silica nanoparticles modified with polyamide receptor. *Journal of Colloid and Interface Science*, 458, 229-234.

Heimann, J., Morrow, L., Anderson, R. and Barron, A. (2015) Understanding the relative binding ability of hydroxyfullerene to divalent and trivalent metals. *Dalton Transactions*, 44, 4380-4388.

Huang, Z., Wang, X. and Yang, D. (2015) Adsorption of Cr(VI) in wastewater using magnetic multi-wall carbon nanotubes. *Water Science and Engineering*, 8, 226-232.

Jaroniec, M. and Sayari, A. (2002) *Nanoporous materials III*. Amsterdam, Netherlands: Elsevier Science B.V.

Jassal, P.S., Chand, N., Gupta, S. and Singh, R. (2015) Harnessing magnetic chitosan nanocomposites for the adsorption of heavy-metal ions from aqueous medium. *Journal of Water Resource and Hydraulic Engineering*, 4, 191-197.

- Karnib, M., Kabbani, A., Holail, H. and Olama, Z. (2014) Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia*, 50, 113-120.
- Kaufman, M. (2002) *Principles of thermodynamics*, CRC Press, pp. 213.
- Knetch, M.R. and Wright, D.W. (2004) Amine terminated dendrimers as biomimetic templates for silica nanosphere formation. *Langmuir*, 20, 4728-32.
- Kocabas-Atakli, Z.O. and Yurum, Y. (2013) Synthesis and characterisation of anatase nanoadsorbent and application in removal of lead, copper and arsenic from water. *Chemical Engineering Journal*, 225, 625-635.
- Kong, X., Yang, B., Xiong, H., Zhou, Y., Xue, S., Xu, B. and Wang, S. (2014) Selective removal of heavy metal ions from aqueous solutions with surface functionalized silica nanoparticles by different functional groups. *Journal of Central South University*, 21, 3575-3579.
- Konicki, W., Pelech, I. and Mijowska, E. (2015) Removal of Ni²⁺ from aqueous solutions by adsorption onto magnetic multiwalled carbon nanotube nanocomposite. *Polish Journal of Chemical Technology*, 16, 87-94.
- Kumar, C.S.S.R. (2009) *Metal oxide nanomaterials*, In: *nanomaterials for life sciences Vol.2: Nanostructure oxides*. Weinheim, Germany: Wiley-VCH Verlag GmbH and Co., KGaA.
- Lakshmanan, R. (2013) *Application of magnetic nanoparticles and reactive filter materials for wastewater treatment* (Doctoral dissertation). Royal Institute of Technology, School of Biotechnology, Stockholm.
- Li, Y., Zhu, S., Liu, Q., Chen, Z., Gu, J. and Zhu, C. (2013) N-doped porous carbon with magnetic particles formed in situ for enhanced Cr(VI) removal. *Water Research*, 2013, 4188-4197.
- Liu, X., Hu, Q., Fang, Z., Zhang, X. and Zhang, B. (2009) Magnetic chitosan nanocomposites: A useful recyclable tool for heavy metal ion removal. *Langmuir*, 25, 3-8.
- Liu, X., Zhang, S. and Pan B. (2012) Potential of carbon nanotubes in water treatment. In: *Recent progress in carbon nanotubes*, Book 2, InTech.
- Lopez-Cortes, A. and Ochoa, J.L. (1999) *Adsorption and its applications in industry and environment protection*, Dabrowski, A. (Ed.), 120B, 903, Amsterdam, the Netherlands: Elsevier.
- Lu, C.S., Chung, Y.L. and Chang, K.F. (2006) Adsorption thermodynamics and kinetic studies of trihalomethanes on multiwalled CNTs. *Journal of Hazardous Materials*, 138, 304-310.
- Ma, Z., Zhao, D., Chang, Y., Xing, S., Wu, Y. and Gao, Y. (2013) Synthesis of MnFe₂O₄@Mn-Co oxide core-shell nanoparticles and their excellent performance for heavy metal removal. *Dalton Transactions*, 42, 14261-14267.
- Mahdavi, S., Jalali, M. and Afkhami, A. (2012) Removal of heavy metals from aqueous solution using Fe₂O₃, ZnO, CuO nanoparticles. *Journal of Nanoparticle Research*, 14, 171-188.
- Mehta, D., Mazumdar, S. and Singh, S.K. (2015) Magnetic adsorbents for the treatment of water/wastewater- A review. *Journal of Water Process Engineering*, 7, 244-265.
- Moussa, S.I., Sheha, R.R., Saad, E.A. and Tadros, N.A. (2013) Synthesis and characterization of magnetic nano-materials for removal of Eu³⁺ ions from aqueous solutions. *Journal of Radioanalytical Chemistry*, 295, 929-935.
- Nassar, N. N. (2012) Rapid removal and recovery of Pb(II) from wastewater by magnetic nanoadsorbents. *Journal of Hazardous Materials*, 184, 538-546.
- Oaki, Y. and Imai, H. (2007) Biomimetic morphological design for manganese oxide and cobalt hydroxide nanoflakes with a mosaic interior. *Journal of Materials Chemistry*, 17, 316-321.
- Pan, S., Shen, H., Xu, q., Luo, J. and Hu, M. (2012) Surface mercapto engineered magnetic Fe₃O₄ nanoadsorbent for the removal of mercury from aqueous solutions. *Journal of Colloid and Interface Science*, 365, 204-212.
- Parham, H., Zargar, B. and Shiralipour, R. (2012) Fast and efficient removal of mercury from water samples using magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole. *Journal of Hazardous Materials*, 205-206, 94-100.
- Patwardhan, S.V. (2012) Chemistry of aqueous silica nanoparticle surfaces and the mechanism of selective peptide adsorption. *Journal of American Chemical Society*, 134, 6244-6256.
- Rahbar, N., Jahangiri, A., Boumi, S. and Khodayar, M.J. (2014) Mercury removal from aqueous solutions with chitosan-coated magnetite nanoparticles optimized using the box-behnken design. *Jundishapur Journal of Natural Pharmaceutical Products*, 9, e15913.
- Razzaz, A., Ghorban, S., Hosayni, L., Irani, M. and Aliabadi, M. (2016) Chitosan nanofibers functionalized by TiO₂ nanoparticles for the removal of heavy metal ions. *Journal of the Taiwan Institute of Chemical Engineers*, 58, 333-343.
- Roy, A. and Bhattacharya, J. (2012) Removal of Cu(II), Zn(II) and Pb(II) from water using microwave-assisted synthesized maghemite nanotubes. *Chemical Engineering Journal*, 211-212, 493-500.
- Sheet, I., Kabbani, A. and Holail, H. (2014) Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/ graphite oxide composite. *Energy Procedia*, 50, 130-138.
- Srivastava, S. (2013) Sorption of divalent metal ions from aqueous solutions by oxidized carbon nanotubes and nanocages: A review. *Advanced Materials Letters*, 4, 2-8.
- Stietiya, M.H. and Wang, J.J. (2014) Zinc and cadmium adsorption to aluminium oxide nanoparticles affected by naturally occurring ligands. *Environmental Quality*, 43, 498-506.
- Tang, W., Su, Y., Li, Q., Gao, S. and Shang, J.K. (2013) Superparamagnetic magnesium ferrite nanoadsorbent for effective arsenic (III, V) removal and easy magnetic separation. *Water Research*, 47, 3624-3634.
- Tofighy, M.A. and Mohammadi, T. (2015) Copper ions removal from aqueous solutions using acid-chitosan functionalized carbon nanotubes sheets. *Desalination and Water Treatment*, doi:10.1080/19443994.2015.1072738.
- Tresintsi, S., Simeonidis, K., Estrade, S., Martinez-Boubeta, C., Vourlias, G., Pinakidou, F., Katsikini, M., Paloura, E.C., Stavropoulos, G. and Mitrakas, M. (2013) Tetravalent manganese ferrihydrite: A novel nanoadsorbent equally selective for As(III) and As(V) removal from drinking water. *Environmental Science and Technology*, 47, 9699-9705.
- Vigneswaran, H. and Moon, H. (1999) *Adsorption and its Applications in Industry and Environment Protection*. In: A. Dabrowski (Ed.), 120B, Elsevier, Amsterdam.
- Wang, X., Guo, Y., Yang, L., Han, M., Zhao, J. and Cheng, X. (2012) Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. *Journal of Environmental and Analytical Toxicology*, 2, 2-7.
- Yu, X., Tong, S., Ge, M., Zuo, J., Cao, C. and Song, W. (2013) One-step synthesis of magnetic composites of cellulose@iron oxide nanoparticles for arsenic removal. *Journal of Materials Chemistry A*, 1, 959-965.

- Zargoosh, K., Abedini, H., Abdolmaleki, A. and Molavian, M.R. (2013) Effective removal of heavy metal ions from industrial wastes using thiosalicylhydrazide-modified magnetic nanoparticles. *Industrial Engineering and Chemistry Research*, 52, 14944–14954.
- Zhang, W., Chen, J. and Zhang, G.S. (2014a) Preparation and evaluation of Fe-La composite oxide nano-adsorbent for As(III) removal from aqueous solutions. *Huanjing Kexue/Environmental Science*, 35, 4198-4204.
- Zhang, C., Chen, L., Wang, T.J., Su, C.L. and Jin, Y. (2014b) Synthesis and properties of a magnetic core-shell composite nano-adsorbent for fluoride removal from drinking water. *Applied Surface Science*, 317, 552-559.
- Zhang, C., Sui, J., Li, J., Tang, Y. and Cai, W. (2012) Efficient removal of heavy metal ions by thiol-functionalized super magnetic carbon nanotubes. *Chemical Engineering Journal*, 210, 45–52.