Application of Nanomaterials for the Removal of Pollutants from Effluent Streams

Gayathri Gangadhar, Utkarsh Maheshwari and Suresh Gupta

Abstract: Rapid industrialization with the increase in the population leads to the water crisis. The number of industries using heavy metals such as copper, chromium, nickel, zinc, etc. in their process is also leaving behind the effluent containing a large amount of heavy metals which discharged directly to the water bodies. There are constraints set by the regulatory bodies of government on the industries to maintain an upper level discharge limit for each of the metal ion. There are various methods available for the removal of metal ions which are selected according to the requirement.

Adsorption is one of the optimal solutions for the removal of metal ions from industrial effluent streams. It is helpful in reducing the operational cost and size of equipment along with the increase recovery of metal ions. Adsorption is a surface phenomenon so the foremost property required for a perfect adsorbent is the higher surface area. Nanoparticles are now being preferred to be used as an adsorbent due to their large surface area which is a very important characteristic for a desired adsorbent. Development of nanoparticles has been the subject of enormous interest since the past decade. They have incredible adsorption properties due to the presence of high-energy adsorption sites and they also have excellent binding energies or interaction potentials for physisorption than traditional adsorbents. This study summarized the use of nanomaterial for the removal of metal ions from wastewater streams. It also highlights the various types of nanomaterials, their fabrication method and characteristics. The mechanism of metal adsorption onto various nanomaterials is also described in this study.

Keywords: Adsorption, Binding energy, Heavymetals, Nanoparticles, Physisorption, Surface area, Wastewater.

INTRODUCTION

As a result of increased industrial activities both flora and fauna are getting affected by the excessive pollution which is disturbing their ecological balance. Industries that use hazardous chemicals have the potential to pollute water resources through the discharge of the effluent to rivers and other water bodies. Industrial effluents include different wastes such as organic and inorganic. Heavy metal ions, aromatic compounds and dyes are often present in the environment due to industrial pollution [1].

As a result of the strict environmental regulation, it is required to remove dyes, heavy metals and organic matter from wastewater before it is discharged to water bodies as these are toxic and even carcinogenic in nature [2]. The inorganic waste is mainly composed of heavy metals such as copper in the form of Cu (II), chromium as Cr (VI), zinc as Zn (II), arsenic as As (II), cobalt as Co (II), nickel as Ni (II), lead as Pb (II), cadmium as Cd (II), etc. Presence of heavy metals in wastewater even at trace levels is considered to be highly risky for mankind [3]. Thus the demand for developing technologies leading to an effective removal of these ions from the effluent streams has become a great challenge.

Nowadays owing to the stringent environmental laws and regulations various methods of removing the heavy metal ions from effluent streams have been proposed. The various conventional methods developed so far are filtration, chemical treatment, UV radiation, adsorption, distillation, precipitation, ion exchange, electrochemical technologies etc. The various filtration methods use biosand filters, ceramic filters, charcoal bed and activated carbon bed. These filters are ineffective in removing organic contaminants, unable to handle high turbidity and bacteria growth on filter media. Filters require regular backwashing which causes high maintenance cost. In chemical precipitation, removal of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The main drawback of this method is the production of large amount of sludge containing toxic compounds [4]. In ion exchange cations are exchanged for H⁺ or Na⁺. Ion exchange resins are synthetic polymers having active ion group such as SO₃H. Zeolites are the natural materials that can be used as ion exchange media. Even though some modified zeolites such as zeocarb and chalcarb have greater affinity for Ni and Pb, the usage of this method for inorganic effluent treatment is restricted because of high cost, requirement of pretreatment.

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and partial removal of certain ions [5, 6]. UV radiation and chemical treatment do not treat turbidity, chemical contamination, heavy metals and some protozoa. Distillation is not suitable for removing chemical contaminants such as pesticides, fertilizers and volatile carbon compounds as their boiling point is lower than water. Distillation process is slow and energy consuming (a heating source is required), making it expensive. It also consumes large amounts of water if the coolant used in the distillation process is water. Materials such as iron and copper in plumbing systems can be corroded by distilled water. The electrochemical technologies such as the electrochemical oxidation and electrochemical coagulation have been used for industrial waste water treatment. But electrochemical process is mainly used as pre-treatment step to enhance the biodegradability of waste water [7].

Among these techniques, adsorption is attractive in terms of design, operation and scale up, high capacity, insensitivity to toxic substances, ease of regeneration and low cost. It does not use toxic solvents and minimizes degradation [8, 9]. The quality of the effluent generated is also better than the rest of the processes because the adsorbent has a high affinity towards the metal ions. The affinity may be due to electrostatic forces of the solute to the adsorbent surface, van der Waals attraction or chemisorptions. It also has an advantage of reversibility, where the adsorptive bed can be regenerated when it gets exhausted with metal ions. This process is mostly preferred as it requires low maintenance cost, has high metal removal efficiency, easy to operate and uses solid adsorbent which resists degradation [2, 3, 10].

The main selection parameters of adsorbents are the high adsorption capacity, fast kinetics, and low cost. The various adsorbents such as activated alumina, activated carbon, calcite, rare earth oxides, etc., which are used for the removal of metal ions and other pollutants from wastewater streams. The main disadvantage related to commercial activated carbon is that it is non selective and ineffective against disperse and vat dyes and it is expensive [2, 11]. Regarding the ease of availability and cost, low cost adsorbents have gained attention in the present scenario. The various low cost adsorbents are neem sawdust, timber bark, tree fern, metal hydroxide sludge, red mud, fly ash, etc. The low voidage value of commercial and low cost adsorbents causes the decrease in the available sites for adsorption and results to low adsorption capacity [12]. Considering the efficiency and capacity as important parameters in the selection of adsorbents, the researchers have proposed new particles on nano-meter scale called as the nanoparticle.

WHAT IS NANOPARTICLE?

Nanoscience and nanotechnology are the emerging fields of science which offer a significant scientific and technological advancement in different fields such as medical, electrical, environmental engineering, etc. The word ‘nano’ comes from the Greek word ‘nanos’ meaning ‘dwarf’. Nano term refers to something of a scale of 10⁻⁹ m. Nanoscience deals with the study of atoms, molecules, and objects having size on the nanometer scale. Nanotechnology is the manipulation of matter for the use in particular applications through certain chemical and / or physical processes to create materials having nanosized dimensions in the range of 1-100 nm with the specific properties. Nanoscience is gaining much importance nowadays as the properties such as quantum, mechanical and thermodynamics, which are not visible on the macroscale, are accessible on nanometre scale [13]. New materials with amazing characteristics can be produced by putting molecules with desired properties together. Nanoparticles have greater surface area to volume ratios than larger particles. This causes them to be more reactive than other materials. Nanoparticles have vast applications in the field of biomedical, electrical, environmental engineering fields, etc.

NANOADSORBENTS

Nanoadsorbents find wide range of applications in engineering field as they are efficient biocompatible adsorbents having large specific surface area, more active sites and low intra-particle resistances. Nanoadsorbents have nanoscale pores, high selectivity, high surface area, high permeability, good mechanical stability and good thermal stability [14, 15]. Nanomaterials could be of four types [15].

- Carbon based materials composed mostly of carbon and they are available in the form of hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. Carbon nanotubes can remove pollutants from industrial waste water for the fact that they can establish π-π electrostatic interactions [16].
- Metal based nanomaterials include quantum dots, nanogold, nanosilver, and metal oxides, such as titanium dioxide.
- Dendrimers are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be adapted to perform specific chemical functions. This property makes it useful for catalysis.
- Composites, nanoparticles are combined with other nanoparticles. Nanoparticles, such as nanosized clays, are added to enhance mechanical, thermal, barrier, and flame-retardant properties.

The various nanoadsorbents proposed are nanotubes, nanomesh, nano-filtration membranes, nanofibrous alumina filters, magnetic nanoparticles, nanoporous ceramics and clays, cyclodextrin nanoporous polymer, polypyrrole-carbon nanotube composite, etc. [14]. Carbon nanotubes have large specific surface area, small hollow and layered structures making them promising adsorbents for various organic pollutants and metal ions removal. They can be easily modified by chemical treatment to increase their adsorption capacity [10]. Nanotubes provide faster flow rates despite smaller pores because of smooth interior of the nanotubes. It saves energy as it exhibits fast flow rates that reduce the amount of pressure required to push the water through the tubes. It can be cleaned by ultrasonification and autoclaving at 121°C for 30 minutes and reuse with the same filtering efficiency [17].

Gas adsorption in carbon nanotubes and nanotube bundles is an important issue for both fundamental research and its technological application. The adsorption energy and...
charge transfer of H₂ in the interstitial and the groove sites of tube bundle are considerably larger than those on the surface site and also the pore site is more favourable than the surface [17]. Thus, the molecule adsorption of the nanotube bundle is stronger than that on an individual tube. Titanium nanotube is reported to be an effective adsorbent for removing Cu(II) within a range of sodium content >7.23 wt%. The removal capacity is found to be 120 mg/g at pH value of 5 [18].

Nanomesh is prepared by comprising nanotubes on a flexible porous medium sufficient to attach at least one functional chemical group to the nanotube. Different functional groups are attached to the nanotubes so as to remove different types of contaminants. Multi walled carbon nanotubes coated with alumina is reported to be an efficient adsorbent for the removal of Pb (II) from industrial effluent. Percentage Pb (II) removal is increased with the increase in effluent pH between 3 and 7, speed of agitation, contact time and adsorbent dosage [10, 19]. Multi waved carbon nanotubes are mixed with polyacrylic acid/PVA mixture to generate uniform nanofibres through electrospinning. Cu(II) ions are effectively removed with multi waved carbon nanotubes and reinforced nanofibrous mats immobilized with zero valent iron nanoparticles [20]. Functionalized nanotubes provide multiple bonding sites to the organic/inorganic polymer matrix. Carbon nanotubes are functionalised by adding functional groups such as hydroxyl, carboxyl and carbonyl. Amino groups attached to the carbon nanotubes offer high reactivity and can react with many chemicals. It has been reported that amino functionalised multiwalled carbon nanotubes offer the best adsorption capacity for Cd(II) [21]. The steps involved in the development of amino functionalised carbon naotubes are carboxylation, acylation and amidation which are represented by Eqs. 1 – 3 [22].

\[
\text{MWNT} + n\text{H}_2\text{SO}_4 + m\text{HNO}_3 \rightarrow \text{MWNT} - \text{COOH} \quad (1)
\]

\[
\text{MWNT} + \text{SOCl}_2 \rightarrow \text{MWNT} - \text{COCl} \quad (2)
\]

\[
\text{MWNT} + \text{Diamine compound (R)} \rightarrow \text{MWNT} - \text{CO-R} \quad (3)
\]

Another interesting adsorbent is the nanoparticle having magnetic properties. Advantages of magnetic nanoparticle is that, they can be easily removed from water under magnetic field and have small diffusion resistance. A set of alginate polymers mainly with magnetite, maghenite and jacobsite are investigated to have the ability to remove heavy metal ions such as Co (II), Cr (VI), Ni (II), Pb (II), Cu (II) and organic dyes [13, 23]. Iron oxide nanoparticles synthesized hydrothermally is reported to be a suitable adsorbing media for purification of water from As (V) ions even below the maximum concentration limit of 10 µg [24].

**FABRICATION OF NANOMATERIALS**

There are mainly two approaches for the fabrication of nanostructures. These are top down approach and bottom up approaches. Top down synthesis includes mechanical processes such as mechanical alloying, high energy ball milling, equal channel angular pressing, high pressure torsion and accumulative roll bonding. Bottom up method includes colloidal dispersion, inert gas condensation, electro deposition, spray pyrolysis, high temperature evaporation, flame synthesis and plasma synthesis techniques. A hybrid of these two approaches is lithography which involves the growth of thin films as well as etching. Both methods of fabrication are important but bottom up method is mostly preferred. The top down synthesize method has some disadvantages such as crystallographic damage to the processed patterns, internal stress and additional defects may be introduced during the etching steps. In the bottom up method materials are built up from the bottom like atom by atom, molecule by molecule, cluster by cluster sequence. Bottom up approach offers a better chance to get nanostructures with comparatively less defects, more homogenous chemical composition and better range of ordering as it is driven mainly by Gibb’s free energy. So the nanostuctures produced by bottom up method are in a state of close to thermodynamic equilibrium [25-27].

The properties of the nanomaterials vary with the type of fabrication route. The most significant characteristics of nanomaterials are the grain size in case of a single phase material; phase size in case of multiphase materials; composition of the material, distribution of phases in case of multiphase components. Various methods are recommended and given below for the synthesis of nanostructured materials on the basis of starting phase and the nature of the end product obtained [27]:

a) If the starting phase is vapour, the techniques available are:
- Inert gas condensation (IGC), produces 3D product
- Physical vapour condensation, produces 1D product
- Evaporation and sputtering
- Plasma processing, produces 3D product
- Chemical vapour condensation, 2D and 3D product
- Chemical reactions, 3D product

b) If the starting phase is a liquid, the techniques available are:
- Rapid solidification, 3D product
- Electro-deposition, 1D and 3D product
- Chemical reactions, 3D product

c) For solid phase, the techniques available are
- Mechanical alloying, 3D product
- Spark erosion, 3D product
- Sliding wear, 3D product

Out of the above mentioned techniques IGC technique produces particles of well defined grain size, narrow size distribution and high purity. IGC is a bottom up approach consisting of two steps – evaporation of the material and rapid controlled condensation so as to produce the required particle size.

**FABRICATION OF MEMBRANES USING NANOMATERIALS**

Polymeric membrane and ceramic membrane filtration find a lot of importance in water treatment. The performance of membrane filtration is limited by fouling. Membrane
fouling is caused by rejected colloids, chemicals and microbes which demands high energy, costly clean-up and replacement of membranes [28]. It has been reported that membrane fouling can be reduced to satisfactory levels by adding nanomaterials to the membranes. Nanomaterial also enhances properties like mechanical strength, selectivity and reactivity. Ceramic membranes can be made using metal oxides such as iron oxide, Al₂O₃, ZrO₂, TiO₂ [29]. The development of low fouling membranes using nanoparticles offers both high degree of control over membrane characteristics and the ability to produce ceramic membranes in the nano-filtration membrane range. Ceramic membranes derived from alumina have high permeability, porosity and narrow pore size distribution. The pore size distribution of ceramic membrane can be controlled by controlling the size of alumoxane nanoparticles and sintering conditions. Alumoxane nanoparticles are the aluminium oxide nanoparticles whose surface is functionalised by organic molecules. Increase in sintering temperature (>1000°C) tends to increase the pore size of the membrane as the alumoxane nanoparticles transform to α-alumina particles. Earlier studies stated that fabricated ceramic membranes with alumoxane nanoparticles have pore size in the range of 10 to 20 nm under the sintering temperatures in the range of 600 to 1000°C [30].

The most popular deposition techniques for sol gel coating are dip-coating and spin-coating technique. The traditional method of coating is dip coating. As this method is time consuming and uses lot of solution, alternative methods are developed. The wet-spraying technique can be a good alternative to this technique when thickness uniformity is not important. In this method the polyelectrolyte solution is sprayed on a vertical surface from an atomiser producing thin, smooth and stratified films. The unique properties of this method are lower consumption of solution and time [31]. Spin coating method can be used to produce multilayered coating. Wet spraying has the advantages in comparison with a spin-coating process such as high speed of deposition, high automation potential and the flexibility in the shape of the substrate (tubular and planar) [29]. Spraying on a spinning substrate is an appropriate method for the formation of multilayered coating on nanoparticle with uniform thickness. This may be due to the fact that the conventional spraying method solution drains along the substrate by gravity but in spinning draining is promoted by centrifugal force [31, 32].

For the preparation of modified Al₂O₃ membrane, nano sized γ-Al₂O₃ grains are coated on the membrane. The dried membrane is immersed in a solution containing aluminium isopropoxide and dimethyl benzene. Aluminium isopropoxide gets adsorbed on the Al₂O₃ membrane surface. The thickness of the adsorbed layer depends on the temperature, the concentration of aluminium isopropoxide and the soaking time [33].

Tubular ceramic absorbers are developed by depositing nanoscale iron particles on porous alumina tubes for the removal of As(V) (an extremely toxic contaminant even in low concentrations). Batch experiment for the removal of As(V) is conducted at room temperature by adding a constant mass of iron oxide (0.5 g/L) to a solution of changing initial As(V) concentration. MES buffer (C₆H₁₃NO₃S) is used to set the pH 5. Samples are centrifuged and filtered using a 0.22 mm filter after 48 hrs. All samples are acidified using 0.3% HNO₃ and the arsenic content in the supernatant solution is analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) [34].

SYNTHESIS OF NANOTUBES AND NANO-COMPOSITES

The synthesis of nanotubes can be done by different techniques such as arc evaporation, sputtering, chemical vapour evaporation, chemical vapour deposition and plasma enhanced chemical vapour deposition (PECVD). The most commonly used method for the fabrication of carbon nanotubes is electric arc discharge method. The arc occurs in the gas filled space between two conductive electrodes. At an average temperature of 4000 K, the nanotubes are formed in the plasma. Co, Ni, or mixtures of certain other metals are the catalysts which are added to the evaporated single shell carbon nanotubes. During the arc discharge method, web like structures are formed around the electrodes having 10-100 single shell nanotubes. The catalyst addition leads to impurities as it is added along with graphite to the system. Fabrication process is followed by purification step as around 33% of the carbon clusters formed does not contain nanotubes with desired tube like structure [35]. A new method has been reported in the literature for the fabrication of carbon nanotube field emitter by attaching single wall carbon nanotube with high graphitization on Sn or Ni layered glass substrate. 100 nm thicknesses of nanotubes are deposited on Sn layer and annealed at 300°C [36].

For the fabrication of titania nanotubes (TNT), three methods have been reported, which are template assisted method, electrochemical method and hydrothermal method. TNT was first synthesized using template assisted method [37]. Electrochemical anodic oxidation and hydrothermal treatment succeeded the template assisted method. The template assisted method increases complexity of the process as TNTs are vulnerable to get damaged during the fabrication process. Electrochemical anodic oxidation method does not have the potential to produce heaps of TNTs and cost of the process is also high. The limitations of other methods are overcome by the hydrothermal treatment, as it is an easily modifiable method and produces powdered TNTs in random alignments. The important factors in the fabrication of TNTs are applied temperature, treatment time, type of alkali solution used and Ti precursor [38]. Modifications can be made on the TNTs produced by this method to obtain different nanostructures such as single nano wire, branched nano wire, nano rods and nano belts so as to improve the properties of TNTs. Different concentrations of NaOH can be used to fabricate modified nanostructures from TNT [39]. The quantity and length of TNTs increase with an increase in the temperature (100-200°C). A larger inner diameter of TNTs emerged at a synthesis temperature of 150°C [40]. Enhanced physical and mechanical properties can be obtained by using nano sized materials as reinforcement in titanium matrix composite [41]. TNTs can be used in the removal of Co²⁺, Cu²⁺, Ni²⁺, NH₄⁺ [H] and NO₂ [42]. The adsorption capacity of metal ions by TNT is found out by immersion method. In this method 0.1g TNT is
added to 100 mL of desired concentration of Cu (II). Equilibrium concentration is obtained by keeping the sample in a reciprocating shaker with isothermal conditions. Centrifugation at 8000 rpm separates the liquid and solid phases. The resultant supernatant can be used for analyzing Cu (II) ions by atomic absorption spectrometry [43]. The adsorption capacity of Cu (II) is found to be low at acidic conditions and increases sharply by increasing the pH value up to 5. This may be due to the fact that TNT is negatively charged above the pH value 3 [44]. pH value above 5 is not recommended as copper will precipitate at high pH [45,46].

Magnetite (Fe₃O₄) nanoparticles can be synthesized by the thermal decomposition method without using toxic organic concentration of surfactants and solvents. The various methods available for the synthesizing of magnetite are co-precipitation, thermal decomposition, micro emulsion route, hydrothermal synthesis route and continuous flow techniques. Thermal decomposition is selected over other methods as it offers excellent particle size control of Fe₃O₄ particles. Generally thermal decomposition of iron pentacarbonyl (FeCO₅) is used to synthesize nano disperse γ-Fe₂O₃ with average diameter of 4 to 16 nm. Poly ethylene oxide (PEO) is used instead of iron pentacarbonyl because it is costly and toxic. PEO is considered as a green solvent due to its low toxicity and high boiling point. PEO functions both as solvent and surfactant to synthesize Fe₃O₄. The synthesis is carried out by using iron acrolignitrate Fe(acac)₃. It is observed that as the volume of PEO increases, concentration of Fe(acac)₃ precursor decreases which results in the production of Fe₃O₄ nanoparticles having small sizes [47]. The adsorption properties of Fe₃O₄ are similar to that of nano-composites powdered activated carbon. It is fabricated by modified impregnation method using HNO₃ as the carbon modifying agent. They are excellent in the removal of methyl orange by adsorption [48]. The batch experiment is carried out by shaking 5 ml of organic dyes solution with magnetic composites at 250 rpm at room temperature with an initial pH value of 0.1. Measurement of concentration of dye after the removal of nanoparticles is done using UV-vis spectrophotometer at a wavelength of 450 nm for methyl orange [49], 663 nm for methylene blue and 433 nm for cresol red [50]. The magnetic nanoparticles can be regenerated for reuse by treating the nanoparticles with methanolic solution of acetic acid as eluent or using water with a pH > 8. Methanolic solution is excellent option for the desorption of methylene blue [51].

A summarized version of particle size of Fe₃O₄ nanoparticles synthesized at various concentration of Fe (acac)₃ precursor is shown in the Table 1 [50].

Carbon nanocages (CNC), synthesized using a supercritical fluid deposition method, are reported as an excellent adsorbent than commercially available activated carbons for the removal of Pb (II) ions from aqueous solutions. The catalysts used are Co/Mo/MgO, which are heated at a rate of 5°C/min in a reaction cell in the presence of argon. The flow rate of argon is maintained at 200 ml/min for reducing the catalysts. p-xylene (3mL) is placed in the front part of the delivery cell separated by a piston, followed by the charging of CO₂ to maintain a constant pressure. The catalyst is agitated in 3 M HNO₃ solution for 4 h and is removed after the completion of reaction. Scanning electron microscopy (SEM) images show the high porosity of CNCs [52]. Average pore diameter is obtained in the range of 19-24 nm. The iron/graphite core-shell nanocages are prepared by the pyrolysis of acetylene with iron carbonyl. Heat treatment is given to the nanoparticles in the presence of iodine to remove the metallic core so as to obtain CNCs with good graphitization and high purity [53]. The batch experiment is carried out by preparing 1000 mg/dm³ of stock solution of Pb²⁺ in deionised water by dissolving Pb(NO₃)₂. This stock solution is used to make 25 mg/dm³ of Pb²⁺ solution. pH of the solution is adjusted with 0.01 M NaOH. 10mg of adsorbent is added to 20 ml of the 25mg/dm³ solution and stirred for 4 h to achieve adsorption equilibrium [52,54]. As there is an increase in the adsorption of Pb²⁺ ions with increase in pH, ion exchange mechanism exists on the surface of adsorbent between the H⁺ ions and metal ions. Pb hydroxide complexes are produced at pH > 6 [55].

Magnetic hydroxyapatite nanoparticles (MNHAP) have been synthesized by coprecipitation method [56]. Appropriate amount of FeCl₃·4H₂O (1.85 mmol) and FeCl₂·6H₂O (3.7 mmol) are dissolved in 30mL of deoxygenated water under a nitrogen atmosphere at room temperature. 10 mL of 25% NH₄OH solution is added to the resulting solution under vigorous mechanical agitation (300 rpm) which forms a black precipitate. After 15 min, an amount of 50 mL of Ca (NO₃)₂·4H₂O (33.7 mmol) and 50 mL of (NH₄)₂HPO₄ (20 mmol) at pH value 11 are added dropwise to precipitate with simultaneous agitation for 30 min. The resulting suspension is heated at 90°C for 2 hrs followed by cooling to obtain the precipitate which is separated by magnet followed by washing with deionised water and drying at 90°C. The washed precipitate is ground to form the MNHAP adsorbents. This method is reported to produce MNHAP with spherical shape with a diameter of about 28 nm. MNHAP adsorbents have been reported to be effective for the removal of Cd (II) and Zn (II) ions from aqueous solutions. The properties of this magnetic adsorbent such as size and morphology (porosity), adsorption efficiency towards Cd (II) and Zn (II), surface area (142.5m²/g), strong magnetic response (59.4 emu/g), structure and zeta potential of suspensions are characterized by SEM, energy dispersive analysis system of X-ray (EDAX), BET surface area measurements, magnetization curves, X-ray powder diffraction (XRD) analysis, magnetization curves and zeta potential respectively. In the batch experiment 0.002 g adsorbent and 20 ml metal solution with a pH value of 5±0.1

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<th>Concentration of Fe(acac)₃, ppm</th>
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are taken in conical flasks and kept on a constant temperature bath oscillator at room temperature. MNHAP are separated by using permanent magnet [56].

Fe₃O₄ coated polypropylene (Ppy) magnetic nanocomposite fabricated by in situ polymerization of pyrrole monomer. This is reported to be an efficient adsorbent for the removal of highly toxic Cr (VI). Structure and morphology of the prepared nanocomposite are characterized by total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction pattern, Field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM). Magnetic nature of the nanocomposite is confirmed by Electron spin resonance (ESR) studies. 100% adsorption is achieved at a pH value 2 with 200 mg/L Cr (VI) aqueous solution. ATR-FTIR and X-ray photoelectron spectroscopy (XPS) confirms adsorption of Cr (VI) on the surface of the adsorbent and also proposed the possible mechanism of adsorptions as ion exchange and reduction on the surface of the nanocomposite [57]. The batch experiments are performed by mixing 50 mL of Cr (VI) and the adsorbent followed by agitation in thermostatic shaker at 200 rpm for 24 h. Removal Cr (VI) ions by nanocomposites decreases from 100% (at pH = 2.0) to 57% (at pH = 11.0) [58]. Adsorption experiments for Pb (II), Cd (II) and Ni (II) ions are carried out using the batch technique at 25–55°C. It is reported that an average of 120 mg of wet magnetic nanoabsorbents are added to 10 mL of Pb (II), Cd (II) and Ni (II) solution of various concentrations (from 50 mg L⁻¹ to 400 mg L⁻¹) and shaken in a thermostatic water-bath shaker operated at 230 rpm. The magnetic nanoabsorbents are removed after equilibrium is reached using a permanent Nd-Fe-B magnet. The concentrations of Pb (II), Cd (II) and Ni (II) ions are measured using Inductive Couple Plasma Mass Spectrometry. For the kinetic experiments, samples are collected at various interval and the concentrations of heavy metals are determined [59].

Nano iron oxide impregnated granular activated carbon (nFe-GAC) is an effective adsorbent for the removal of phosphate from aqueous solutions. The batch process steps include addition of nFe-GAC to a centrifuge containing polypropylene and phosphate solution at various concentrations mainly 250, 500 and 1000 mg/L. Samples are kept in a water bath shaker for 13 days at 25°C, supernatant is collected at regular intervals and the phosphate concentration is measured using spectrophotometer. The kinetics of phosphate adsorption by nFe-GAC involves a fast initial sorption followed by a much slower adsorption process [60, 61].

Nano-crystalline calcium hydroxyapatite (HAp) has the potential to remove Ni (II) from aqueous solutions. Solution precipitation method is used to synthesize Nano-crystalline hydroxyapatite adsorbents. (NH₄)₂HPO₄ and Ca(NO₃)₂·4H₂O are the starting materials and pH is adjusted by using ammonia solution. Ca(NO₃)₂·4H₂O suspension is made by continuous agitation at a temperature maintained at 25°C and a solution of (NH₄)₂HPO₄ is slowly added dropwise to it. Centrifugation at a rotation speed of 3000 rpm is used to remove the HAp precipitate and the resulting powder is dried at 100°C. The particles produced are characterized by Transmission electron microscopy (TEM). The crystalline shapes and sizes are characterized by diffraction (amplitude) contrast and, for crystalline materials, by high resolution (phase contrast) imaging, BET method for specific surface area and crystal phase by X-ray [56,62]. TEM micrograph of the HAp powder shows that the HAp crystalline structure after drying is more or less needle shaped, with size in the range 20–30 nm [62]. Batch experiments are performed in a stirred tank reactor (300 rpm) by filling it with nickel sulfate solution and 0.4g of nano-HAp at 20±1°C. The solution has initial pH of 6.6. Residual metal ion concentration is measured by taking samples at constant time intervals. The same procedure is followed for the removal of Sn⁴⁺ [63]. The equilibrium sorption of these ions increases with increase in temperature due to increase in the mobility of the ions. A swelling effect is produced within the internal structure of the nano-HAp when the temperature is increased for enabling metal ions to penetrate more [64].

Nano zero valent iron (nZVI) particles are used for the removal of Cd (II), Cr (IV), Ni (II) and Pb (II). The usual method reported for the synthesis of nZVI is the ‘bottom-up’ approach and also called as liquid phase reduction by the drop wise addition of NaBH₄ to FeCl₃ or Fecl₂·4H₂O provided continuous stirring. The reaction occurring during the process is given by Eq. 4.

\[
4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^0 + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2 \uparrow
\]  

nZVI particles are then washed with iso-propanol or absolute ethanol to prevent oxidation. nZVI synthesis is done in an anaerobic chamber by purging with O₂-free Ar (95% Ar : 5% H₂). The lifetime and using efficiency of nZVI are affected by metal concentration, pH, and temperature. The properties of the nZVI are characterized using XPS, XRD, HR-TEM and SEM/EDX [65-70]. SEM images of fresh nZVI particles show that the particles are composed of separate spherical particles in the size range of 20-200 nm in the form of aggregates and chains [65]. The temperature effect on adsorption of Cd⁰⁺ is carried out at different temperatures. 0.5g/L nZVI is added to 60 mL of 112.5mg/L Cd²⁺ solution. The samples are kept on a temperature controlled shaker. Results show that a rise in the temperature results in increasing cadmium adsorption rate which indicates that the process is endothermic [65].

CuFe₂O₄/sawdust nano magnetic composite with a mass ratio of 1:10, synthesized by chemical co-precipitation method is reported to be used for the removal of cyanine acid blue (CAB) from aqueous solution [70, 71]. The properties of the nanocomposite are characterized by Fourier transform infrared spectroscopy (FTIR) and SEM. SEM image shows that the composite has a spherical shape with 50 nm particle size. The FTIR spectroscopic analysis of sawdust nanomagnetic composite indicates that broad bands are at 3406–3556 cm⁻¹. The co-precipitation method involves the dissolution of sawdust in a 50ml solution containing Cu (II) chloride (0.1ml) and ferric chloride (0.2ml) at 60°C. Suspension pH is raised to 10 by the addition of NaOH solution with vigorous agitation. The magnetic precipitate formed is washed and dried at 105°C [72,73]. Adsorption affinity for Cu(II) [74], Pb(II) [75], and Cd(II) is increased by grafting amino groups on the silica surface of the nanomaterial [70,76]. The experimental procedure remains
Nano structure alumina is reported as a good adsorbent for the removal of heavy metals such as Pb(II), Ni(II), Zn(II) and Cu(II) [77]. The adsorption process follows pseudo-second-order reaction kinetics. Equilibrium data are well fitted by the Langmuir and Freundlich adsorption isotherms. The adsorption capacity of nano structure alumina for Pb(II), Ni(II) and Zn(II) are 125, 83.33 and 58.82 mg g\(^{-1}\) respectively. Batch experimental studies are carried out in Erlenmeyer flasks which contain nanostructured γ-Al\(_2\)O\(_3\) and metal ion solution at pH value of 4. The samples are mixed well. After 3 hrs, solid-liquid phases are separated by centrifugation. The properties of nano structure alumina are characterised by SEM, BET and FTIR [78, 79]. The SEM and TEM images indicate that the alumina nanoparticle has a mean diameter of 53 nm and the modified alumina nanoparticle has a mean diameter of 75 nm [79].

The modified anodic aluminium oxide membrane is able to remove heavy metal ions from aqueous solution as polyrhodanine has the ability to form coordinate compounds with specific metal ions. Polyrhodanine is deposited onto the inner surface of anodic aluminium oxide (AAO) membrane by vapour deposition polymerization method. Polyrhodanine is fabricated by adding iron chloride to rhodanine aqueous solution which is forming coordinate compounds. Magnetic nanoparticles are formed after injecting sodium borohydride. Fe ions induce oxidation of rhodanine monomers initiating the polymerization rhodanine. Polyrhodanine magnetic nanoparticles are obtained at the end of polymerization [80].

The fabrication process of polyrhodanine magnetic nanoparticles is shown in Fig. (1) [80].

TEM images indicate that the PR-MNPs have an average diameter of 10 nm. BET surface area is obtained as 94.65 m\(^2\)/g. The modified anodic aluminium oxide membrane is able to remove heavy metal ions from aqueous solution as polyrhodanine has the ability to form coordinate compounds with specific metal ions. Polyrhodanine is deposited onto the inner surface of anodic aluminium oxide (AAO) membrane by vapour deposition polymerization method. The heavy metal removal capability of the AAO-polyrhodanine membrane in form of cartridge is investigated. Aqueous solution of heavy metal ions (10 ml) is passed through the membrane at 2 ml/h (Fig. 2) and final metal ion concentration is measured. Kinetic study is carried out by collecting aliquots of filtered solution as a function of time [81].

**MECHANISM OF HEAVY METAL REMOVAL USING NANOADSORBENTS**

Fe\(_3\)O\(_4\) magnetic nanoparticles (MNPs) modified with 3-aminopropyltriethoxysilane (APS), copolymers of acrylic acid (AA) and crotonic acid (CA) are good adsorbents for removing heavy metal ions such as Cd (II), Zn (II), Pb (II) and Cu (II) from aqueous solutions. The surface of the adsorbents is in carboxyl form and has less adsorption of heavy metal ions when pH is less than pH of zero point (between 3 and 4). The carboxyls turn into carboxylate anions and the adsorption increases gradually until pH > pH\(_{pzc}\) which is due to increase in alkalinity. Finally, carboxyls completely turn into carboxylate anions. The probable adsorption mechanism is shown in Fig. (3). Chelation
between the ions and the carboxylate anion provide the main interaction between metal ions and adsorbents [82].

Micro-nano structure poly (ether sulfones)/poly (ethyleneimine) (PES/PEI) nanofibrous membrane is utilized as an adsorbent for the removal anionic dyes and heavy metal ions from aqueous solutions. Amino and imino groups on the PEI macromolecular chains provide the main adsorption sites. They possess bifunctional properties to adsorb cationic and anionic target compounds at different pH values in aqueous solutions [83]. A relatively high concentration of protons are available to protonate amine and imino groups of PEI chain to form NH$_3^+$ and NH$_2^+$ at low pH values. This can lead to strong electrostatic repulsion of the cationic metal ions to be adsorbed. At lower proton concentrations (pH of 5-7) the availability of protons to protonate NH$_2$ and NH to form NH$_3^+$ and NH$_2^+$ groups would be less. A metal complex can be formed when neutral nitrogen of amine and imino group with lone pair of electrons binds a metal ion [84, 85]. The adsorption capacity of the anionic dyes decreases with increase in solution pH value from 1 to 7 and it increases with increase in pH from 1 to 7 for heavy metal ions. The adsorption of anionic dyes on PES/PEI nanofibrous membrane is reported to be endothermic and the adsorption of heavy metal ions on PES/PEI nanofibrous membrane is exothermic [86].

Amino-functionalized materials are reported to be efficient for the removal of heavy metals. Electrostatic interaction [87], ion exchange [88], hydrogen bonding [89], are the ways by which the removal of anionic metal species can be achieved. For the removal cationic metal species, coordination interaction between metal ions and amino groups may be the possible mechanism [90-92]. For the removal of Cu (II), the chemical reactions observed are given by Eq. 5 – 7.

Protonation/deprotonation reaction of the amine groups of the NH$_2$-NMPs in the solution:

\[ -\text{NH}_2 + \text{H}^+ \leftrightarrow \text{NH}_3^+ \]  \hspace{1cm} (5)

Formation of surface complexes of Cu$^{2+}$ with the amine groups through coordination interactions:

\[ -\text{NH}_2 + \text{Cu}^{2+} \leftrightarrow \text{NH}_2\text{Cu}^{2+} \]  \hspace{1cm} (6)

\[ -\text{NH}_2 + \text{OH}^+ \leftrightarrow -\text{NH}_2\text{OH}^- \]  \hspace{1cm} (7)

\[ -\text{NH}_2\text{OH}^- + \text{Cu}^{2+} \ (\text{or CuOH}^+ \leftrightarrow -\text{NH}_2\text{OH} - ...\text{Cu}^{2+} \ (\text{or -NH}_2\text{OH} - ...\text{CuOH}^+) \]  \hspace{1cm} (8)

Low pH values favour the protonation of the amine groups, causing less number of NH$_2$ sites available on the adsorbents surface for Cu (II) adsorption through coordination interactions. This leads to an increase in the electrostatic repulsion between the Cu (II) ions and the adsorbent surface which causes a decrease in the Cu (II) adsorption with decrease in pH values. As the pH increases, the deprotonation reaction is favoured. This is due to the
increase in the number of NH$_3$$_2$ sites on the surface of the adsorbents for Cu (II) adsorption which results in increased adsorption capacity. At high pH values, adsorption capacity decreases as adsorption of OH$^-$ is favoured, but adsorption capacity increases through electrostatic attraction as indicated in the last reaction [93].

CONCLUSIONS

Advancements in nanoscience and engineering are giving new opportunities to develop more cost-effective and environmentally acceptable water treatment technology. The property of having higher specific surface area leading to a higher capacity makes the nanoparticles one of the best adsorbents for the effective removal of heavy metals from waste water. They also exhibit various advantages such as fast kinetics, and preferable sorption toward heavy metals in effluent streams. As discussed, earlier nanosorbents such as CNTs, TNTs, nanometal oxides, magnetic nanoparticles etc are reported to be successful in removing various heavy metal ions such as Pb(II), Ni(II), Zn(II), Cu(II), Co(II), Cd(II) from industrial wastewater. Some aspects such as the toxicity and cost effectiveness are to be studied in detail to make the process economically feasible on an industrial scale.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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