Chapter 8
Nanoparticles and Nanocomposites for Heavy Metals Removal

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Abstract Contamination of heavy metals in water is of great concern. Nanomaterials owing to their smaller size and higher surface area exhibit unique physicochemical characteristics that enable potential application in the removal of heavy metals. Nanoparticles and nanocomposites find a major application in heavy metals due to their tunable properties, facile synthesis and stability. This chapter gives an overview of the application of nanoparticles and nanocomposites in the removal of heavy metals from wastewater. Nanomaterials-assisted techniques in the removal of heavy metals include adsorption, membrane separation and photocatalysis. Nanostructured materials in the form of nanoadsorbents, nanomembranes and nanophotocatalyst provide higher reactivity and show specific affinity to targeted heavy metals. Several nanoparticles exhibit strong antimicrobial properties.

Keywords Nanomaterial · Heavy metal · Adsorption · Membrane · Nanosorbents

1 Introduction

Hygienic water is essential for the survival of lives on earth. Lack of drinking water remains a major issue today. Although three-fourths of the earth's surface is covered by water, resources of freshwater are tremendously deteriorating. Increasing

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industrial activities, rapid population growth, change in lifestyle and climate change have decreased the accessibility of freshwater resources. Volcanic eruptions, modern farming and mining activities produce hazardous pollutants including organics, pharmaceutical products, pathogens and heavy metals in the aquatic environment. Among all pollutants, the presence of heavy metals remains a prime concern due to their non-degradability, toxic and carcinogenic nature. Heavy metals are defined as metals having a density greater than 4000 kg/m^3. Chromium (Cr), cadmium (Cd), zinc (Zn), lead (Pb), mercury (Hg), copper (Cu), nickel (Ni) and arsenic (As) are a few examples of soluble forms of heavy metals and are considered to be an emerging pollutant [1]. These heavy metals are essential in most of the industrial and biological activities. Metallurgical, metal plating, electroplating, leather tanning, batteries, fertilizers and machinery manufacturing industries are responsible for heavy metal contamination as they release enormous amount of wastewater containing heavy metals [2]. Many regulatory bodies impose maximum permissible limits for the discharge of heavy metals in wastewater. However, most of the industrial effluent does not meet the standard permissible limits proposed by environmental and human organizations. The heavy metals laden polluted water is discharged into water sources and remains in soil, surface and groundwater. Intake of these heavy metals causes a severe threat to human health. Nevertheless, the presence of heavy metals beyond the acceptance level results in environmental health hazard both to marine and land living creatures [3]. Heavy metals accumulate inside the human body through the food chain and produce major health disorder. These heavy metals are non-persistent and cannot be decomposed or metabolized naturally [4]. The sources, maximum permissible limit given World Health Organization (WHO), and health issues associated with heavy metals are provided in Table 1.

Elimination of heavy metals remains a challenging issue and it is mandatory to reduce or prevent their toxic effects on living bodies [1]. Currently, nanotechnology finds its wide application in all branches of science and technology. The tendency to fabricate and formulate the particles with specific structures and functional groups by means of nanosized elements encouraged nanotechnology as a great resource. Recognizing the scope and utilities of nanotechnology and understanding the importance of water quality, scientists have attempted the usage of nanotechnology in wastewater remediation. In wastewater treatment, nanotechnology is being incorporated along with conventional methods to improve the efficiency of the process. Various researchers have identified several nanomaterials and found their efficacy in the removal of heavy metals. In this chapter, the application of different nanoparticles and nanocomposites and technologies implied for the removal of heavy metals has been discussed.

Table 1 Heavy metals, maximum permissible limit in drinking water, health issues and sources

Heavy metals	Maximum permissible limit	Health issues	Sources	References
Cr (VI)	0.01 mg/L	Haemorrhage, hemolysis, acute renal failure	Electroplating industries	[5]
Cd (II)	0.003 mg/L	Affects kidney, lungs, skeleton system and liver	Battery, alloys, electroplating industries	[6]
Zn (II)	5 mg/L	Causes anaemia, vomiting, nausea, stomach upset and skin irritation	Insecticides, fungicides, pipes, galvanic and paint industries	[7]
Pb (II)	0.01 mg/L	Produces nephritic syndrome, hepatitis, anaemia and lead poisoning affects the nerves, bones and brain	Oil extraction, lead extraction, batteries, ceramic, glass	[8]
Hg (II)	0.001 mg/L	Vomiting, fever, diarrhea, caustic gastroenteritis	Mining operations, electroplating industries	[9]
Cu (II)	0.01 mg/L	Headache hemorrhage, hemolysis,	Household plumbing and battery applications	[10]
Ni (II)	0.07 mg/L	Dermatitis and hair loss	Alloys and nickel plating industries	[7]
As (V)	0.01 mg/L	Nausea, vomiting, painful neuropathy	Paints, agricultural applications, mining and smelting industries	[11]

2 Conventional Methods for Heavy Metal Removal

In the present scenario, there is a vast demand for pure water. It is mandatory to eliminate all heavy metals present in industrial wastewater before their discharge into the aquatic ecosystem. The most common methods employed in the removal of heavy metals are chemical precipitation, ion exchange, solvent extraction, chemical leaching, photoelectrocatalysis, reverse osmosis, membrane technology and adsorption [12]. Several techniques available for the removal of heavy metals for the past decades are provided in Table 2.

Most of the techniques remain ineffective in the treatment of the large volume of solution of less concentration of heavy metals. However, some of the techniques are effective, but face the problem of the generation of secondary waste. Effectiveness, operation cost, long-term sustainability and energy consumption are the major issues associated with all technologies. Very few of them are difficult to implement at an industrial scale. The negative impact of heavy metals on the environment paves

Table 2 Conventional techniques for the removal of heavy metals associated with advantages and disadvantages

Technique	Advantages	Disadvantages	References
Chemical precipitation	Effective and easy to operate for a broad range	Formation of secondary pollutants	[13]
Coagulation-flocculation	Effective in the removal of microorganisms	High cost	[14]
Ion exchange	Effective and applicable to inorganic/organic pollutants	High cost and be applicable for small scale	[15]
Precipitation	Easy applicable	Secondary pollution	[14]
Membrane technology	Applicable to inorganic pollutants	Energy intensive	[16]
Electrochemical treatment	Very effective in the removal of heavy metals	Requires large investment and energy intensive	[17]
Adsorption	Simple and economical	Hazardous by-products	[18]

the way to finding an economical, effective and eco-friendly technology. Recently, nanotechnology has gained much attraction in liquid waste treatment and they are recognized as high-performance technology.

3 Role and Properties of Nanoparticles and Nanocomposites

Nanomaterials are a new class of emerging engineering material. Nanoparticles (NPs) are nanomaterials having a size in the range of 1–100 nm on at least one dimension. Nanoparticles are highly specific in nature and they differ from bulk materials owing to large surface area, higher stability and greater resistance. These features allow them to find vast application in wastewater remediation, particularly in the removal of heavy metals [19]. Nanomaterials exhibit unique and amazing properties. For instance, gold nanoparticles get converted into liquid form at room temperature, silver nanoparticles display excellent antimicrobial activities, platinum nanoparticles acts as a superior catalyst and aluminum nanoparticles turn off into combustible ingredient. Thus, these newly created properties offered by nanoscale materials find their application in heavy metals removal.

Nanocomposite is a composite material in which at least one of the components should dimension in the range of nanometers (10–100 nm). Nanocomposites are formulated by incorporating fine species onto a large solid matrix to conquer the restrictions of nanoparticles [20]. To remove heavy metals from contaminated water, several low cost, high efficiency and reusable nanoparticles and nanocomposites are being developed. Nanoparticles and nanocomposites find a major application in the field of adsorption, photocatalysis, membrane technologies and antibacterial agent.

3.1 Properties of Nanomaterials and Nanocomposites

Several properties listed below enable nanoparticles and nanoparticles to find a major potential in the removal of heavy metals [21]. Properties include:

- Increased surface-to-volume ratio
- Higher reactivity
- Higher adsorption capacity
- Higher dissolution activity
- Reduction in size: As the size of nanoparticles gets reduced, the proportion of atoms present on the surface of the particles increases, thus creating a more reactive surface
- Change in the reactive surface: Increased surface produced due to reduced particle size causes a change in surface free energy which in turn alters the chemical reactivity
- Change in atomic structure: As the size of the particle gets reduced, the defects may be produced on the surface
- Change in electronic structure: The smaller size of the particles produced lies in the lower energy state

3.2 Classification of Nanomaterials

Nanomaterials exist in different forms of structure namely nanotubes, nanorods and nanowires. Nanomaterials are classified into four types based on the nature of composite of the materials. They are as follows:

(i) Carbon-based nanomaterials
(ii) Metal-based nanomaterials
(iii) Dendrimers
(iv) Composites

3.2.1 Carbon-Based Nanomaterials

Carbon-based nanomaterials generally contain carbon as a main ingredient. These materials usually have the shapes of ellipsoids, hollow spheres and tubes. Elliptical and spherical shaped materials are called fullerenes whereas cylindrical form is referred to as nanotubes [22]. Most of carbon-based nanomaterials find application in electronic devices.

3.2.2 Metal-Based Nanomaterials

Noble metallic nanomaterials, metallic oxide nanomaterials including iron oxide, zinc oxide, titanium oxide and quantum dots come under the category of metal-based nanomaterials. Quantum dot, a closely assembled semiconductor crystal, encloses billions of atoms and size is in the range of nanoscale. Metal-based nanomaterials are extensively used in cream application.

3.2.3 Dendrimers

Nanosized polymers fall under the category of dendrimers-based nanomaterials. Generally, the surface of these materials has several chain ends. Molecules containing several functional groups could be tailored to these end chains in order to a new nanomaterial. These materials are mostly used in catalysis and drug delivery.

3.2.4 Nanocomposites

Nanocomposite is a combination of nanomaterial with another nanomaterial or with bulky material. Nanoparticles especially nanosized clay, metals are added to a standard matrix in order to enhance the mechanical, thermal, optical and physical properties.

3.3 Synthesis of Nanoparticles

The synthesis technique adopted for the preparation of nanoparticles decides the final characteristics of nanoparticles. Top-down and bottom-up are the two methods commonly used for the synthesis of nanoparticles. The synthesis procedure controls the size, shape and structure of nanoparticles. Wet chemical synthesis, solvent combustion technique, hydrothermal technique, sol–gel technique and mechanical milling technique are the most commonly used methods for synthesizing nanoparticles [23]. Among all, wet chemical synthesis, sol–gel technique and hydrothermal technique are highly preferred because the process is easier, highly reproducible and requires less investment. Wet chemical synthesis otherwise known as the liquid phase synthesis technique is simple to operate. Different solutions of quantified morality are mixed under a controllable heat to begin the nanoparticle formation through precipitation [24]. Then the excess amount of solution is drained and precipates are dried and grinded. This technique is operated usually at low temperatures and therefore saves energy. This technique has control in the stoichiometry of nanoparticles. This technique offers the advantage of control over the final characteristics of synthesized nanomaterial. Sol–gel is another popular and cheaper technique to synthesize nanoparticles. The nanoparticles produced by this technique are smaller in size and size distribution is narrow due to the linear growth of particles across the gel. This technique involves hydrolysis of precursors (metal alkoxides or metal chlorides) with water and alcohol. They are mixed to form a gel. They are then calcined to remove gel and nanoparticles are left behind [25]. Hydrothermal technique involves the synthesis of nanoparticles at higher temperatures and pressures and in a closed atmosphere. This technique involves the mixing of precursor with strong alkali and allowed to react in a Teflon-lined autoclave. The synthesized nanoparticles are then washed with excess water to remove excessive alkali. Then the particles are dried and ground. This technique offers the advantages of easy preparation, larger yield and high controllability in size. Metallic and non-metallic hybrid nanoparticles could be synthesized by this method [26].

3.4 Techniques Associated with Nanostructured Materials in Heavy Metals Removal

Nanomaterials in the form of nanocomposites, nanoadsorbents, molecularly imprinted polymers, nanomembranes, nanocatalyst and bioactive nanoparticles find their application in wastewater remediation for the removal of toxic metal ions, pathogens, organic and inorganic pollutants from water [27]. Features especially paramagnetism, quantum captivity effect, and semiconducting attainment offer additional advantages to finding potential in heavy metals removal [28]. Various researches are focused on the fabrication of different new nanomaterials from different sources. However, main attention should be given to the usage cost of nanomaterial.

Various conventional methods including coagulation, chemical precipitation, photocatalysis, electrochemical treatment, adsorption and membrane processes are processed to remove heavy metals. Among all, three processes namely adsorption, membrane-based process [29] and photocatalytic reduction are mainly focused on heavy metals removal in large-scale applications. The application of nanoparticles and nanocomposites in heavy metal removal is given in Fig. 1.

3.4.1 Adsorption

Heavy metals are removed by means of adsorption where metal ions are held up on the surface of a nanomaterial. Compared with several conventional methods, adsorption remains an effective and efficient technique in the removal of heavy metals from wastewater. Easy accessibility, flexibility, high proficiency, simpler design, less space requirement and less capital investment offer additional advantages and researchers are focusing huge attention on the expulsion of heavy metals using adsorbents [30]. Adsorption of heavy metals on the surface of solids adsorbents is gaining importance. Usually, in the adsorption process, the desired quantity of nanomaterial is added to heavy metal laden water. Heavy metals diffuse onto the exterior surface of the nanoadsorbent, then diffuse into the interior pores and gets accumulated on the pores by means of physical or chemical forces. In case of polymer-based adsorbents, adsorption is usually via complex formation and electrostatic interaction.

Fig. 1 Application of nanoparticles and nanocomposites in heavy metals removal

3.4.2 Photo Catalysis

Photocatalysis emerges as one of the best processes in wastewater remediation techniques as it has a tendency to destroy or reduce the contaminant instead of separating it. Photocatalysis is a combination of light and catalytic reactions. Usually, semiconducting materials act as photocatalyst. Here light is used to excite the electrons to produce electron–hole pairs. Semiconductors while being irradiated with light sources release oxidative free radicals which have a tendency to destroy organic pollutant and reduce heavy metal ions. While being irradiated with light, photons are produced and electrons get excited to a higher level creating electron hair poles on the surface of the semiconductors. Electron hair poles further produce free radicals mainly superoxide radical and hydroxyl radical which detoxifies heavy metals [31].

3.4.3 Membrane-Based Processes

Membrane separation is another budding technology in the removal of heavy metals. Integration of nanoparticles into membranes has enhanced the water permeability of membranes. In ordinary membrane separation, separation is achieved based on membrane pore size. Smaller particles pass through the pores of membranes whereas larger particles get retained on the surface of the pores. Major issue concerned with nanofiltration is that nanomembrane as its pore size is very small, and movement of water through is difficult which reduces membrane flux. The incorporation of nanomaterials in the membranes increases the permeation. Metal oxide nanoparticles, nanotubes, CNTs, polymer nanocomposites, etc. are coated on the surface of the membrane to improve the selectivity of membranes [32]. The addition of nanoparticles induces modification in the characteristics of the membrane, which produces better removal efficiency. These nanoparticles create a pathway for water transport. Currently, adsorptive membranes have been fabricated for the removal of heavy metals. Adsorptive membranes have the potential to trap heavy metals in the membrane matrix as well as permit the passage of water thereby producing clean permeates. Generally, ultrafiltration membranes are employed as adsorptive membrane. However, to overcome the difficulty faced with low rejection of heavy metals, nowadays nanoparticles are incorporated into ultrafiltration membranes to achieve excellent heavy metal removal.

4 Nanoadsorbents in Adsorption

Generally, adsorbents should contain enormous active binding sites. Most of the conventional adsorbents suffer from several disadvantages including low adsorption capacity, lack of functional tenability, recyclability and reusability. Recently usage of nanoscale materials and nanocomposites as nanoadsorbents overcomes all those difficulties. Properties of nanoadsorbents, including the presence of a large number of binding sites, active functional groups, larger specific area and lower flocculent generation have attracted researchers to use nano-structured materials as appropriate adsorbents in the removal of heavy metals from contaminated [33]. Nanoparticles have a tendency to penetrate deep into a contaminant, which in turn increases the reactivity that could not be possible by conventional adsorbents [34]. Nanoadsorbents could be incorporated with prevailing treatment processes in columns or slurry reactors [35]. Carbon-based metals, bimetals, metal oxides, ferrite, magnetite, polymer based, chitosan and zeolites have been extensively employed in the removal of heavy metals. These nanostructured substances remove heavy metals by adsorbing them on their surface. Various nanoadsorbents used for the removal of heavy metals are listed in Table 3.

4.1 Carbon-Based Nanoadsorbents

Carbon-based nanomaterials provide unique physical and chemical features and emerge as the most appropriate nanoadsorbents. Numerous research including carbon-based nanocomposite, graphene and carbon nanotubes (CNTs) have been employed in the removal of various HMs. Carbon nanotubes (CNTs) is one of the eminent examples for carbon-based nanomaterial used for the elimination of HM from wastewater. CNTs are cylinder-shaped macromolecule rolled up in the form of tubes [36]. CNTs on the basis of the arrangement of graphene sheets are divided into two types, single-walled carbon nanotubes and multi-walled carbon nanotubes. Single-walled carbon nanotubes (SWCNTs) contain single graphene sheet rolled up whereas multi-walled carbon nanotubes (MWCNTs) contain multiple sheets of graphene roll-up. Tunable physical, chemical, electrical and structural properties enable it to find a wide application as adsorbent, membranes, catalyst and filters in

Table 3 Nanoadsorbents in the removal of heavy metal ions

S.No	Nanoadsorbents	Heavy metal removed	Removal efficiency or adsorption capacity	References
1	SWCNT	Hg^{2+}	4.16%	[53]
2	SWCNT	Ni^{2+}	9.22 mg/g	[54]
3	MWCNT	Mn^{7+}	71.5%	[55]
4	MWCNT	Ni^{2+}	7.53 mg/g	[54]
5	CNT-COO^-	Hg^{2+}	3.300 mmol/g	[56]
6	CNT-CONH2	Cd^{2+}	1.563 mmol/g	[56]
7	Porous graphene	As^{3+}	90%	[57]
8	rGO-Sulfophenylazo	Cd^{2+}	26.7%	[58]
9	–COOH functionalized GO	Hg^{2+}	12.2%	[59]
10	Amino functionalized mesoporous silica	Cr^{6+}	8.205%	[60]
11	Graphene Oxide (GO)	Pb^{2+}	35.6%	[61]
12	GO/Fe_3O_4	Cu^{2+}	18.3 mg/g	[62]
13	Graphene nanosheets (GNs)	Pb^{2+}	22.4%	[63]
14	MnO_2/GNs	Hg^{2+}	10.8%	[64]
15	GO/Mn-doped Fe(III)oxide	Cd^{2+} and Cu^{2+}	87.2 and 129.7 mg/g	[65]
16	Goethite (a-FeOOH)	Cu^{2+}	149.25 mg/g	[66]
17	γ-Fe_2O_3	Cu^{2+}	26.8%	[67]
18	Amino functionalized silica gel in Tea Polyphenol extracts	Pb^{2+}	98.1%	[68]
19	Thiol and amino functionalized SBA-15 Silica	Hg^{2+}	29.2%	[69]
20	Ionic liquid-functionalized silica	Pb^{2+}	20.23%	[70]
21	Hematite-Magnetite hybrid	Pb^{2+}	97.67%	[71]
22	Hematite-Magnetite hybrid	Cr^{3+}	99.50%	[71]
23	Maghemite NP	As^{5+}	50%	[72]
24	Magnetite NP	Pb^{2+}	100%	[46]
25	Magnetite NP	Zn^{2+}	100%	[46]
26	Grafted silica (SiN_2)	Pb^{2+}	0.184 mmol/g	[73]
27	Carboxyl functionalized magnetite NP	Cu^{2+}	98.3%	[74]
28	Chitosan-Fe0 nanoparticles	Cr^{6+}	60.2 mg/g	[75]
29	Highly mesoporous silica (containing nanospheres) anchored with 2,5-dimercapto-1,3,4-thiadiazole	Pb^{2+}	67.2 mg/g	[76]

(continued)

Table 3 (continued)

S.No	Nanoadsorbents	Heavy metal removed	Removal efficiency or adsorption capacity	References
30	ZnO nanoparticles	Cd^{2+}	387 mg/g	[77]
31	Resin supported nanoscale zerovalent iron	Cr^{6+}	84.4%	[78]
32	Humic acid coated Fe3O4 magnetic nanoparticle	Pb^{2+}	92 mg/g	[79]
33	Fe@MgO nanocomposite	Pb^{2+}	147.64	[80]
34	Thiol-lignocellulose sodium bentonite (TLSB) nanocomposites	Zn^{2+}	35.72%	[81]
35	Silica-coated iron oxide magnetic nanocomposites (Fe3O4@SiO2)	Hg^{2+}	94.12	[82]
36	Polypyrrole-iron oxide–seaweed nanocomposite	Cr^{6+}	99.12%	[83]
37	Polypyrrole-iron oxide—seaweed nanocomposite	Pb^{2+}	99.54%	[84]

wastewater remediation. As CNTs are hydrophobic in nature, they usually aggregate in aqueous media forming grooves and spaces that aid in the adsorption of pollutants [37]. Active sites with high surface area and pore size enhance the adsorption capacity of CNTs in the removal of HMs. CNTs remove HMs through physical, chemical and electrostatic attraction [38].

Graphene, one of the carbon-based nanomaterials plays a vital part in wastewater remediation. The higher surface area with the presence of various characteristic functional groups enables graphene to find special attention in the removal of heavy metals [39]. Graphene oxide particularly plays a major role in the removal of many contaminants due to the presence of oxygen-derived derived functionalities [40]. The heavy metals are removed through complexation formation by means of adsorption of heavy metal ions on the active oxygen sites of graphene.

4.2 Metal- and Metal-Oxide-Based Nanoadsorbents

Metals and metal oxide nanoparticles served as active materials in the expulsion of heavy metals from wastewater. Metallic nanoparticles are unstable as they tend to agglomerate and find little application as adsorbents in the removal of heavy metals. Moreover, the separation of metallic nanoparticles is a tedious one. Among the metallic nanoadsorbents, zero-valent iron is the most commonly used metallic nanoadsorbent as they are highly stable, less toxic and possesses a higher surface area and large adsorption capacity. Most heavy metals including chromium, arsenic, zinc, copper, etc. are removed by zero-valent iron. Bimetallic nanoparticles also remain an effective nanoadsorbent in the removal of heavy metals. Fe/Ni nanoparticles were used for the removal of copper and nitrate ions with a removal efficiency of 99.7 and 40.4% respectively [41]. Numerous researches have been carried out to make it obvious that metallic oxides could be used as nanoadsorbents. On the basis of magnetic property, metal oxide nanoadsorbents are classified as magnetic and non-magnetic metal oxide nanoparticles. Oxides of zinc, copper, manganese, cerium and aluminum fall under the category of non-magnetic metal oxide nanoadsorbents. CuO nanoparticles were effectively used for the removal of Cr (VI) and Pb (II) ions from contaminated water with adsorption capacities of 15.62 and 37.02 mg/g, respectively [42].

Apart from traditional metal oxide nanoparticles, alkaline metal oxide nanoparticles have also been applied in the removal of heavy metals. Comparatively, they are less toxic and environment friendly. Many researchers have explored the admirable features of MgO nanoparticles in the removal of heavy metals. MgO nanoparticles effectively removed Pb (II) and Cd (II) ions with adsorption capacity of 1980 and 1500 mg/g respectively. MgO nanoparticles are found to high surface area. Al_2O_3 nanoparticles are present in soils and remain a better nanoadsorbent owing to their higher stability. It has various structural phases including α, β, γ, θ and χ phases. Fascinating properties of strong interatomic bonding, electrical insulation, high thermal conductivity, greater compressive strength and corrosion resistance enable it to remain as a potential nanoadsorbent. Silica, an additional metal oxide nanoadsorbent has immense application in the removal of heavy metals as they possess tunable surface properties, characteristic pore-size and larger surface area [43]. Also nanosilica is non toxic.

Magnetic metal oxide nanoparticles play a vital part in current research, particularly in the removal of heavy metals as it has acquired the combined advantage of nanostructure and magnetic properties. Magnetic metal oxide nanoparticles could be easily separated under the application of an external magnet and they can be effectively reused [44]. Utilization of magnetic metal oxide nanoparticles in wastewater remediation enables the process efficient, probitable and relieable [45]. Compared with non-magnetic nanoparticles they have a higher surface area, are less toxic, ease of dispersion, biocompatibility and ease of separation. Researchers investigated several magnetic metal oxide nanoparticles in the removal of heavy metals. Iron oxide nanoparticles occupy an integral part in the removal of heavy metals. Also, they possess high adsorption capacity. Iron oxide exists in three forms namely magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and haematite (α-Fe_2O_3). Magnetite and maghemite possess spinal structures. Haematite (α-Fe_2O_3) is non-magnetic in nature and has a corundum structure. Maghemite Fe_3O_4 nanoparticles are the most widely nanoadsorbent and have been used in the removal of Mn (II), Zn (II), Cu (II) and Pb (II), respectively. The adsorption capacity of synthesized Fe_3O_4 was higher compared with commercial Fe_3O_4 in the removal of As (II) and Cu (II) [46].

4.3 Polymer-Based Nanoadsorbents or Polymer Nanocomposites

Polymer-based nanoadsorbents or polymer nanocomposites remain ideal adsorbents in the removal of heavy metal as they have the higher specific surface area and adsorption capacity. To overcome the problem of agglomerization, nanoparticles are converted into polymer nanocomposites by impregnating nanoparticles on polymer skeleton [47]. Higher skeletal strength, easy degradability and tunable surface functional groups make polymer-based nanoadsorbents a perfect choice in heavy metal removal. The presence of specific functionalities including $–NH_2$, $–COOH$, $–SO_3H$ increased the selectivity toward specific metal and promoted adsorption capacity. These nanoadsorbents are classified on the basis of polymers used.

Chitosan is an eco-friendly, biocompatible, hydrophilic and non-toxic polymer. It is a commonly used polymer in wastewater treatment as it has the potential to form complexes with several heavy metals. The availability of amino groups enhances the interaction towards heavy metal ions through chelation. Adsorption capacity and selectivity of chitosan can be improved by chemical transformations. Dubey et al. investigated the adsorption performance of chitosan alginate nanoparticles in the removal of Hg (II) ions [48]. Saad et al. synthesized ZnO/chitosan nanoparticles and explored their efficiency in the removal of Cu (II), Cd (II) and Pb (II) [49].

Chitin, a natural polymer is also used in the removal of heavy metals. Liu et al. compared the adsorptive capacity of chitin nanofibrils with chitin microparticles in the removal of Cr (III), Zn (II), Ni (II), Cd (II), Cu (II) and Pb (II). The adsorption capacity of chitin nanofibrils is high compared with chitin micro particles due to the presence of a large surface area and pores [50].

Many polymers including cellulose, lignin, starch, conducting, non-conducting polymers and a variety of natural biopolymers are also used in the removal of heavy metals [51].

4.4 Zeolite-Based Nanoparticles

Zeolite in the form of nano-sized particles is extensively used in the removal of heavy metals as they are highly porous and have high surface activity. In one report, Deravanesiyan et al. explored the adsorption performance of alumina NPs immobilized zeolite in the removal of Pb (II) and Cr (III) and compared the adsorption efficiency with alumina nanoparticles and zeolite granules. The results showed that the efficiency of alumina NPs immobilized zeolite is higher than alumina nanoparticles and zeolite granules [52].

5 Functionalization of Nanoparticles

Usually, nanoscale adsorbents tend to agglomerate which makes them difficult to separation.

To overcome this difficulty, nanoparticles are functionalized. It offers higher adsorption capacity and facilitates separation easier. Functionalization could be achieved through coating with carbon, polymers, inorganic molecules, and biomolecules. Atoms present on the surface of the nanoparticles are mostly unsaturated and have a tendency to bind with other atoms easily [85]. Consequently, most of the nanomaterials are functionalized by surface modification. Also, surface modification improves the mechanical, magnetic, rheological, electrical and optical properties [86]. Suitable surface functionalization provided specific functional groups to expel targeted metal ions from polluted water. Normally, magnetic nanoparticles are functionalized with hydrophilic gents containing polyethylene glycol (PEG), polyvinyl alcohol (PVA) and polyvinyl pyrrollidine (PVP) to increase the surface volume ratio [87].

The surface of metal oxide has been modified by adding surfactant which in turn enhances the adsorption capacity. In one study, Pham et al. modified the surface of alumina with sodium dodecyl sulphate (SDS) in order to increase the removal efficiency of ammonium ions. The adsorption capacity of carbon nanotubes is enhanced by surface-modified functionalization of acid treatment and grafting techniques [88].

Nguyen et al. modified the surface of alumina particles by coating them with two surfactants namely sodium dodecyl sulphate (SDS) and sodium tetradecyl sulphate (STS) and compared their removal efficiency towards cadmium ions. The results showed that the removal efficiency increased from 67 to 95% on adding surfactants [89]. The surface of silica has been modified by incorporating amino and thiol functionalities to achieve better adsorption capacity. Li et al. 2019 modified the surface of silica with nitrilotriacetic acid and its adsorption capacity towards in removal of lead, cadmium and copper ions [90]. Kotsyuda et al. modified the surface of silica nanospheres with 3-aminopropyl and phenyl groups and studied its adsorption characteristics in the removal of Cu (II). The results revealed that adsorption capacity increases with an increase in amino groups [91].

6 Nanocomposites Membranes in Membrane-Based Processes

In nanocomposite membranes, addition of nanoparticles improves the properties of porosity, permeation, hydrophilicity, swelling, antifouling and mechanical strength [92]. Generally, ZnO, TiO_2, SiO_2, iron oxides, GO and CNTs are incorporated in the development of nanocomposite membranes. Multifunctional nanomaterial incorporated into the membrane matrix has been developed to improve the water permeability [93]. The nanocomposite membranes offer additional advantages of

Table 4 Nanocomposite membrane in the removal of heavy metal ions

S.No	Nanocomposite membranes	Heavy metal	Removal efficiency (%)	References
1	Activated bentonite clay nanoparticle imparted on polyetherimide membrane	Cu^{2+}	82.5	[96]
2	Fe_3O_4-talc nanocomposites incorporated in polysulfone membrane	Ni^{2+}	96.2	[97]
3	Chitosan membrane embedded with 1.25 wt% zeolite nanoparticle	As^{3+}	94.9	[98]
4	Poly(acrylonitrile)-co-poly(methylacrylate) copolymer-polyaniline nanocomposite	Cr^{6+}	99.3	[99]
5	Ceramic hollow fiber membrane (CHFM) derived from rice husk ash	Ni^{2+}	99.99	[100]
		Zn^{2+}	99.79	
		Pb^{2+}	99.99	

no sludge formation, single-step process, pretreatment is not required and could be reused. Sunil et al. fabricated an $AlTi_2O_6$ incorporated polysulfone (PSF) composite membrane and explored its improved hydrophilicity towards the removal of heavy metals [94] Ghaemi et al. developed a PPy@Al_2O_3 polymeric nanocomposites membrane by adding PPy@Al_2O_3 into a polyether sulfone (PES) membrane matrix and explored its performance in removal of copper ions. The results showed that PPy@Al_2O_3 enhanced the water permeability, increased copper rejection and decreased membrane surface roughness [92]. In other reports, the performance of PES-based nanocomposite membrane incorporated with polyaniline-modified GO nanoparticles in the removal of lead ions was discussed. It was reported the addition of polyaniline-modified GO nanoparticles showed better removal efficiency and also decreased the viscosity of the membrane [95]. Few nanocomposites membranes used in the removal of heavy metals are provided in Table 4.

7 Bioactive Nanoagents

The most serious threat is infectious diseases caused by infectious microorganisms. Nano antimicrobials are used as antibiotics for effective treatment. Bacterial growth control remains a challenging task. Liu et al. explored the antibacterial activities of graphite, graphite oxide, graphene oxide and reduced graphene oxide using membrane and oxidative stress. E. coli as a model bacterium [101]. E. coli cells were incubated in an isotonic saline solution containing dispersions of graphite, graphite oxide, graphene oxide and reduced graphene oxide in the concentration range of 40 lg/mg. Bacterial cell death rate was evaluated by colony counting method. The difference in antibacterial activity was observed among the four substances. Graphene and graphene oxide exhibited higher bacterial inactivation percentages than graphite and graphite oxide. The antibacterial activities of graphene-based materials are due to their size, oxidation capacity and dispensability. Shao et al. evaluated the antibacterial property of silver nanoparticle decorated grapheme oxide (GO-Ag) nanocomposite by using Gram-negative E. coli ATCC 25,922 and Gram-positive S. aureus ATCC 6538. The antibacterial property of GO-Ag nanocomposite was determined by determining antibacterial ratios based on the number of bacteria colonies [102].

8 Nanophotocatalysts in Photocatalysis

Researchers have focused on the usage of lighter responsive semiconductive nanomaterials especially titanium dioxide (TiO_2) and zinc oxide (ZnO) in the removal of pollutants. However, less attention is paid to the removal of heavy metals using nanomaterials as photocatalysts as heavy metals are difficult to degrade. Meanwhile, nanoparticle photocatalysts could reduce the harmful effects of heavy metals by converting them into lesser harmful metals. For example, Cr (VI) is highly toxic compared with Cr (III). In most of the wastewater techniques, Cr (VI) is reduced to Cr (III). Based on this photocatalyst approach, Cr (VI) is also reduced to Cr (III). Usually, $TiO_{2,}$ MnO, Fe_2O_3, CeO_2, MgO, ZnO are commonly used photocatalysts in the removal of heavy metals.

Mayo et al. explored the adsorption behavior of magnetite nanoparticles in the removal of As (III) and As (V) and reported the relationship between size and removal efficiency. Kar et al. 2019 developed an iron oxide (II) bismuth carbonate hybrid photocatalyst and explored reduction behavior in the reduction of Cr (VI) reduced to Cr (III) [103]. Kumar et al. 2018 synthesized a hybrid WO3/reduced graphene oxide (rGO) nanocomposite photocatalyst to reduce of Cr (VI) to Cr (III). To overcome the large bandgap felt with traditional semiconducting photocatalyst, nanocomposite photocatalysts are produced by doping metallic non-metallic substances [104]. Froing the atom available on the surface of the nanocomposite photocatalyst reduces the bandgap, which in turn reduces the energy required to irradiate a photon. Various nanophotocatalysts used for the removal of heavy metals are listed in Table 5.

9 Conclusion

The present chapter has shown the potential application of nanoparticles and nanocomposite for the removal of heavy metals from wastewater. They are promising nanotools for the detoxification of heavy metals owing to their physicochemical properties of higher surface area, tunable by functionalization and reusability. Numerous research in the literature showed the applicability of nanoparticles and nanocomposites in the removal of various kinds of heavy metals and inferred that the removal of heavy metals depends on the affinity of heavy metals towards nanomaterials. Different studies described magnetic-based nanoparticles and nanocomposites as

Table 5 Nanophotocatalyst in the removal of heavy metal ions

S.No	Nanophotocatalyst	Heavy metal	Removal efficiency (%)	References
1	WO_3	Cr^{6+}	90	[104]
2	TiO_2	Cd^{2+}	98	[105]
		Pb^{2+}	99	
3	$CdS/CuInS_2$ nanoplates	Cr^{6+}	100	[106]
4	Graphene-based TiO_2	Zn^{2+}	100	[107]
5	CeO_2/SnO_2/rGO nanocomposites	Pb^{2+}	80	[108]
		Cd^{2+}	80	
6	Zirconium-selenophosphate nanocomposite	Pb^{2+}	100	[109]
		Zn^{2+}	95	

having a remarkable role in the removal of heavy metals and separation was easier. Several pioneering platforms have established the potential of nanoparticles and nanocomposites as eco-friendly materials in the removal of heavy metals. Current development in the synthesis and fabrication of nanoparticles and nanocomposites displays promising perspectives; nevertheless, practical applicability in real application remains challenging. An almost challenging issue in nanotechnology is the possible conversion of lab-scale research findings to commercial-scale application.

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