

Review on nanoadsorbents: a solution for heavy metal removal from wastewater

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Abstract: Elimination of heavy metals from contaminated streams is of prime concern due to their ability to cause toxic chaos with the metabolism of flora and fauna alike. Use of advanced nano-engineered technologies such as the innovative combination of surface chemistry, chemical engineering fundamentals and nanotechnology opens up particularly attractive horizons towards treatment of heavy metal contaminated water resources. The obtained product of surface engineered nanoadsorbent produced has successfully proven to show rapid adsorption rate and superior sorption efficiency towards the removal of a wide range of defiant heavy metal contaminants in wastewater. The use of these materials in water treatment results in markedly improved performance features like large surface area, good volumetric potential, extra shelf-lifetime, less mechanical stress, stability under operational conditions with excellent sorption behaviour, no secondary pollution, strong chelating capabilities and they are easy to recover and reuse. This review intends to serve as a one-stop-reference by bringing together all the recent research works on nanoparticles synthesis and its advantages as adsorbents in the treatment of heavy metal polluted wastewater that have so far been undertaken, thereby providing researchers with a deep insight and bridging the gap between past, present and future of the elegant nanosorbents.

1 Introduction

Humongous amount of wastewater is being released into various water bodies such as river streams and oceans. The municipal wastewater comprises of several organic and inorganic elements. While the former includes carbohydrates, lignin, fats, proteins and so on, the latter includes arsenic, cadmium, chromium, copper, lead, mercury, zinc and so on [1]. The impact of its release into the environment is severe and the marine life is directly affected due to this unleash which in turn influences the food chain. Consequently, it is essential to treat the water before its introduction into the surroundings [2]. There has been a significant increase in effort concerning the development of an effective water treatment strategy in recent years [1–3]. The removal of toxic heavy metals such as Cr(VI), Cd(II), Cu(II), As(I), Pb(II) and Zn(II) from water discharged from tanneries, electroplating units, metal and wood processing industries is a prime requisite as discharge of untreated effluents results in severe environmental and public health issues [3].

Presently, an array of water treatment strategies such as, precipitation [4], ion exchange [5], reverse osmosis [6], membrane filtration [7], and oxidation [8] have been established as standard regulated protocols by the WHO for release of effluents into the environment. However, these conventional techniques have some flaws such as toxic sludge formation, high sensitivity to pH of solution, corrosion problems and also some of the processes are not economically feasible which render the process of heavy metal removal unproductive [3, 9–14]. The adsorption technology on the other hand, due to its low cost, high efficiency and simplicity of operation, is regarded as the most promising method to remove even trace amounts of heavy metal ions from effluents [3, 9–15]. Even though traditional sorbents are capable of removing heavy metals from wastewater, their subtle sorption capacities and efficiencies limit their applications in concentrated solutions, which

has called for the development of various cost effective adsorbents for the removal of heavy metals from wastewater contaminated with metals [9, 13]. In order to address the issues posed by the use of these conventional sorbents, nanomaterials have been produced as a novelty to enable efficient removal of heavy metal ions from wastewater [10, 14, 16].

Nifty nanocomposites of metal oxides, carbon, and polymers have been developed as potential adsorbents for environmental remediation, pollution control and a wide range of other bioprocess based industrial applications [10, 14, 16, 17]. Their unique properties such as high surface to volume ratio, surface modifiability, biocompatibility, reversibility and the comparatively low cost has enabled them to gain escalating prominence as efficient adsorbents [10, 14, 16–21]. Most of the metal nanoadsorbents studied are iron oxide nanoparticles commonly called magnetic nanoparticles (MNPs) [18, 19]. The presence of iron gives them magnetic properties that allow them to be easily separated from the wastewater using simple magnetic field. Also, they are relatively less toxic and cheaper. However, there are certain limitations where the separation may require large external magnetic fields if these MNPs are too small in size. This adds up to the cost of the entire treatment process [18, 19]. There are other metal oxide nanoparticles including that of titanium, cerium and zinc. They are cheaper and have higher surface area when reduced to the nanoscale. However, at such a small size the metals tend to be unstable and begin to agglomerate which could hinder their ability to adsorb other heavy metals in the wastewater. The use of activated carbon as an effective adsorbent has been seen in several applications. Now carbon nanotubes (CNTs) are being explored for their capability as an adsorbent for removing heavy metals from wastewater [20–22]. They possess high-energy binding sites due to the carbon in them, which is a useful property for the purpose of adsorption [20]. Nevertheless, there have been concerns raised on the toxicity of CNTs and their effect on human health and

environment and there is the downside of limited selectivity to various adsorbates [21, 22]. To overcome these problems, new nanoadsorbents are being investigated so as to incorporate the adsorption capacity of the carbon with less toxicity. Polymeric nanoadsorbents have also been used for applications in the treatment of wastewater and they show good adsorption properties such as good pore sizes and flexible functional groups that widens their selectivity. Yet there are disadvantages due to some inadequacies in their molecular structure. It is difficult to synthesise them with good selectivity to the target adsorbate and laborious to recycle them if they are of low purity [14].

Bare nanoparticles, prone to oxidation by atmospheric oxygen are easily aggregated in aqueous systems which have necessitated the surface modification of these nanoparticles for their stabilisation and subsequent applications as adsorbents [23]. In such surface modified adsorbents, the molecular makeup is significantly different from that of the core of the nanoparticles. Modifications in the surface layer of nanoparticles confer properties which facilitate enhanced adsorption [10, 14, 16–19]. The control of size and polydispersity are also important parameters that need to be considered while developing novel separation processes since these dimensions play a significant role in determining the properties of nanoparticles [20–22]. This paper presents a review of the recent research developments in the application of various nanoparticles for the removal of heavy metals As(V), Cu(II), Hg(II), Co(II), Cr(VI), Pb(II) and Cd(II) from water/wastewater.

2 Nanoparticles for the removal of specific metals

2.1 Removal of arsenic

Generally, natural waters contain low levels of total arsenic in two different ionic states, the pentavalent arsenate [As(V)] and/or trivalent arsenite [As(III)] in the concentration range of 1–10 µg/L [24]. Arsenic contamination occurs due to industrial processes like mining and smelting and also can be observed in coal-fired power plants. Exposure to arsenic can lead to lung, skin, kidney and bladder cancers, and neurological disorders, loss of appetite, nausea, pigmentation changes and hyperkeratosis in humans [24, 25]. Up-to-date details of the metal nanoadsorbents for removal of arsenic in water/wastewater are provided in Table 1.

There has been a flourishing attention in using MNPs for the removal of heavy metal ions from wastewater. This further facilitates easy separation from the reaction mixture using a simple magnetic field. Haematite (α -Fe₂O₃), magnetite (Fe₃O₄) and goethite (α -FeOOH) nanoparticles synthesised by ferrihydrate precipitation methods, were found to be effective for the removal of As(V) ions in a pH dependent manner [26]. Chen *et al.* [25] prepared porous ultrafine α -Fe₂O₃ nanoparticles with high-affinity hydroxyl groups on the surface and used for the removal of As(V) in wastewater. However, there were problems of poor aggregation and separation of adsorbents. These issues were overcome by preparation of the mesoporous magnetic γ -Fe₂O₃ nanostructures through atmospheric calcination of composite Fe₃O₄/phenol-formaldehyde resin structures [27]. Ghosh *et al.* [28] synthesised hydrazine sulphate modified goethite nanoparticles to remove As(V) from wastewater. 99% of As(V) could be removed with an adsorbent dose of 6 g/L from an initial As(V) concentration of 50 mg/L with a contact time of 240 min. The desorption study showed that the loaded adsorbent could be regenerated well without loss of adsorption efficiency when treated with dilute sodium hydroxide solution of pH 13.0. Ascorbic acid-coated Fe₃O₄ nanoparticles were synthesised and evaluated as an adsorbent to remove arsenic from wastewater. At an initial arsenic concentration of 0.1 mg/L, the removal percentage for As(III) is 50%, while that for As(V) is 30% during the initial adsorption time of 30 min [29]. Another example for arsenic removal by adsorption is the use of binary metal oxide nanoparticles. Easy magnetic separation was achieved by the synthesis of ultrafine superparamagnetic magnesium ferrite nanocrystallites by doping Mg(II) into α -Fe₂O₃ using a solvothermal process. At 10% concentration of magnesium, enhanced As(III) and As(V) adsorption was observed in a low

equilibrium arsenic concentration, which has been attributed to the alteration of the α -Fe₂O₃ microstructure by Mg(II) [30].

Nabi *et al.* [31] synthesised pure and iron-doped TiO₂ particles by the sol-gel method and tested them for the removal of arsenic from water. The iron-doping helps in enhancing the adsorption capacity of the TiO₂ nanoparticles by preventing the increase in its grain size and hence, maintaining the required surface area for the adsorption process. Titania nanoparticles with high affinity towards arsenic ions were synthesised by liquid impregnation method with some modifications [32]. In batch studies, over 90% of As(III) removal was observed for both types of pure and metal-doped titania nanoparticles with 2 mg/L as the initial metal concentration in solution. Consequently, the effect of fixed bed columns of nanoparticles coated on glass bead was also studied for As(III) removal under different operating conditions. Simple and easy regeneration of nanoparticles by regenerating the column using 10% NaOH solution is possible. Martinson *et al.* [33] synthesised CuO nanoparticles and studied them for the removal of As(III) and As(V) from wastewater. In addition to a maximum adsorption capacity for As(III) and As(V), 90% of As(III) and 99% of As(V) were removed in 30 and 5 min, respectively, when their initial concentration was 0.9 mg/L with CuO nanoparticle loading of 2 g/L. X-ray photoelectron spectroscopy (XPS) studies showed that the As(III) was oxidised and then adsorbed in the form of As(V) on the surface of CuO.

Hydrous cerium oxide (HCO) nanoparticles were used as a nanosorbent for the removal of As(III) and As(V) from water [34]. Around 87% of As(III) and 83% of As(V) were removed within 30 min from water samples containing initial concentrations of 124 µg/L As(III) and 92 µg/L As(V) when the HCO nanoparticle loading concentration is 0.02 g/L. Liu *et al.* [35] synthesised porous magnesium oxide (MgO) nanoflakes and used them for the removal of As(III) from aqueous solutions. The high As(III) sorption capacity was dependent on the *in-situ* formation of Mg(OH)₂, by the interaction of MgO nanoflakes with water. Also, these nanoflakes were capable of reacting with As(III) to form a magnesium-arsenite compound, which in turn contributes to the high As(III) sorption capacity of MgO nanoflakes. With initial As(III) concentration of 94.9 mg/L and equal loading of 0.5 g/L of MgO nanopowders and commercial MgO powders, 92% of As(III) was removed within 360 min using the former, while only one-third of As(III) was removed using the latter. This indicates that the MgO nanoflakes can be used as potential adsorbents for the removal of arsenic from contaminated water. The potential effect on the removal of arsenic using CuO nanoparticle was determined and it removes maximum sorbent in the contact time of 300 min, at their broader pH range with the temperature of 25°C [36]. About 100% of the Cu(II) has been removed and the nanoadsorbent could be effectively regenerated and reused using NaOH solution.

Hang *et al.* [37] carried out a simple hydrothermal process followed by heat treatment for the synthesis of highly porous aggregates of hydrous zirconium oxide (ZrO₂·xH₂O) nanoparticles with a large surface area. Batch studies also showed that high removal of As(III) and As(V) adsorption was possibly enhanced due to the formation of inner-sphere surface complexes by arsenic on the surface of the ZrO₂·xH₂O nanoparticles. About 66% of arsenic was removed within 10 min of contact with 0.15 g/L of ZrO₂·xH₂O when the equilibrium concentration of As(III) was 6.5 µg/L. In a similar study by Cui *et al.* [38], under low equilibrium arsenic concentrations, the amount of arsenic adsorbed by ZrO₂·xH₂O nanoparticles were about 0.92 mg/g for As(III) and 5.2 mg/g for As(V), respectively. For an initial As(V) concentration of 0.089 mg/L, around 92% of As(V) was adsorbed in 30 min with the ZrO₂ loading concentration of 0.02 g/L.

Composite of multi-wall CNTs and manganese dioxide (MWCNT/MnO₂) was fabricated for the separation of As(III) and As(V) from wastewater [39]. The presence of MnO₂ in the nanocomposite allows for the conversion of As(III) to As(V) which can then be easily adsorbed by the MWCNT. During the process of arsenic removal, the MnO₂ oxidises As(III) and itself gets reduced from Mn(IV) to Mn(II). Hence, this nanoadsorbent combines the

oxidative properties of MnO₂ with the adsorption properties of MWCNT for the effective removal of arsenic from wastewater [39]. MWCNT–zirconia nanohybrid (MWCNT–ZrO₂) was synthesised and studied as a possible adsorbent for the segregation of arsenic from wastewater. A notable advantage of this adsorbent is that the adsorption process is pH independent and also the adsorption capacity is much higher for both As(III) and As(V) compared to that of iron oxide coated MWCNTs [40]. Chen *et al.* [41] reported that multi-walled boron nitride nanotubes (BNNTs) functionalised with MNPs were used for adsorption of arsenic at pH 6.9 and room temperature. The mechanism for As(V) adsorption was speculated to be an interplay of chemical complexation and physical electrostatic attraction with a preference for chemisorption. The removal ability showed only slight fluctuations in a pH range from 5.0 to 11.0, indicating that the functionalised BNNT could be used in a wide range of pH for As(V) adsorption and might be suitable for practical applications under standard conditions of wastewater at near neutral pH [41].

2.2 Removal of copper

Copper plays an important role in enzyme synthesis, tissues and bones development in humans. However, it also shows toxic effects and is a carcinogen when consumed in excess. It can also result in its deposition in liver, which in turn causes vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failures and ultimately gastrointestinal bleeding in humans [42]. The US EPA (1991) has established 50 µg/L as the allowed limit for copper in water. The different nanoadsorbents studied for Cu(II) removal are listed in Table 1.

Synthetic nanoFe₃O₄ particles were studied for the adsorption of copper from aqueous solutions. A total of 97.8% of Cu(II) was removed with a contact time of 60 min at an initial copper concentration of 1.07 g/L [43]. Primary amino groups were developed over the MNP surface by aminopropyl triethoxysilane to produce amino-functionalised MNPs. The produced functionalised nanoadsorbents were able to remove 98% copper from both polluted river and tap water [44]. Li *et al.* [45] discussed the preparation of amine functionalised magnetic silica nanoparticles using sol–gel method. At lower pH, protonation of the amine group

Table 1a Nanoadsorbents for the removal of arsenic, copper, mercury, cobalt, chromium, lead and cadmium metals from wastewater

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Arsenic (As(III) & As(V)) ions											
Mesoporous magnetic γ-Fe ₂ O ₃	–	–	35.7	As(III) As(V)	73.2	–	–	–	–	–	[25]
Goethite nanoparticles	Wet-chemical synthesis method	<10	167.8	As(V)	76	240	3.0	298 K	Pseudo-second order	Langmuir	[28]
Ascorbic acid-coated Fe ₃ O ₄ nanoparticles	Hydrothermal process	<10	179	As(V) As(III)	16.56 46.06	30	2.0–7.0	RT	–	Langmuir	[29]
Magnesium ferrite nanocrystallites	Solvo-thermal process	–	~438	As(V) As(III)	10 9.3	–	7.0	RT	–	–	[30]
Titanium dioxide nanoparticles	Sol-gel method	108	–	As(V)	20.4	–	–	–	–	Langmuir	[31]
Iron-doped titania nanoparticles coated on Glass Beads	Liquid impregnation method	30–40	–	As(III)	0.59	–	7	–	Pseudo second order	Langmuir, Freundlich	[32]
CuO nanoparticles	Microwave irradiation	12–18	85	As(V) As(III)	22.6 26.9	30	6.0–10.0	–	–	–	[33]
Cerium oxide nanoparticles	Precipitation process	4	198	As(V) As(III)	107 170	30	3.0–11.0	298 K	Pseudo-second order	Freundlich, Langmuir and Redlich Peterson	[34]
Magnesium oxide nanoflakes	Hydrothermal process	>100	115.9	As(III)	506.6	360	–	–	Pseudo-second order	Langmuir	[35]
CuO nanoparticle	Thermal refluxing technique	–	52.11	As	1.0862	300	8	298K	Pseudo second order kinetics	Langmuir, Freundlich	[36]
Zirconium oxide nanoparticles	Hydrothermal process	~5	327.1	As(V) As(III)	32.4 83	720	5.0	303 K	–	Langmuir	[38]
Multiwall carbon nanotube–zirconia nanohybrid	Microwave Accelerated Reaction	–	–	As(V) As(III)	5 2	360	6	–	Pseudo second order kinetics	Langmuir, Freundlich	[40]
Multiwalled boron nitride nanotubes	Sonochemical synthesis	~20–50	~95.9	As(V)	0.96	720	6.9	RT	–	Langmuir, Freundlich, and Dubinin-Radushkevich	[41]

Table 1b

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Copper (Cu(II)) ions											
Mesoporous silica / multi-walled carbon nanotubes	–	–	100.554	Cu(II)	74.627	–	6.2	308	Pseudo second order	Langmuir	[11]
Magnetite nanoparticles	Covalent binding	–	–	Cu(II)	25.77	5	6	298 K	Pseudo second order	–	[44]
Magnetic silica nanoparticles	Sol-gel method	–	–	Cu(II)	22.4	–	–	–	–	–	[45]
Chitosan coated magnetic nanoparticles	Co-precipitation method	30–40	–	Cu(II)	236.7	30	6	303K	Pseudo second order	Langmuir	[47]
Chitosan coated magnetic nanoparticles	–	30	–	Cu(II)	96.15	180	2–5	–	–	Langmuir	[48]
ZnO nanoplates	Solvo-thermal process followed by annealing	10–15	147	Cu(II)	1600	–	–	–	–	Freundlich	[49]
Magnesium oxide nanoparticles	Modified wet chemical technique	70	–	Cu(II)	593	120	3–4	343 K	Pseudo-first order	Freundlich	[50]
Zinc oxide nanoparticles	Modified wet chemical technique	24.7	–	Cu(II)	226	120	3–4	343	Pseudo-first order	Freundlich	
Chitosan/multiwall carbon nanotubes composite	Sonochemical method	200	135.1	Cu(II)	454.5	–	–	–	–	–	[51]

Table 1c

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Mercury (Hg(II)) ions											
Magnetic mesoporous silica modified with poly (1-vinylimidazole) oligomer	Aqueous coprecipitation	10–20	–	Hg(II)	346	–	7	298	–	–	[55]
Magnetic mesoporous silica	Coprecipitation followed by ultrasonication	~111	–	Hg(II)	207.7	<15	6	295.5	–	Langmuir, Freundlich	[56]
Chitosan-glutaraldehyde functionalized on magnetic nanoparticles	–	–	–	Hg(II)	152	–	5	298	–	–	[57]
Poly(aniline -co-5-sulfo-2-anisidine nanoparticles	Chemical oxidative copolymerization	120	–	Hg(II)	2070	–	–	303	Pseudo-second order	Langmuir	[61]
Magnetic nanoadsorbent	Conventional radical polymerisation	~80	–	Hg(II)	59.45	360	–	298K	Pseudo-second order	–	[115]
Multi-walled carbon nanotubes	–	–	–	Hg(II)	0.486	120	8	RT	Pseudo-second order	Langmuir	[59]
Multi-walled carbon nanotubes	–	–	–	Hg(II)	84.66	5	6	RT	Pseudo-second order	Langmuir	[60]
Poly(1-amino-5-chloroanthraquinon) nanofibrils	–	20–70	–	Hg(II)	771.5	20	6	298	Pseudo-second order	Langmuir	[62]

Table 1d

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Cobalt (Co(II)) ions											
Ag/Fe bimetallic nanoparticles	–	70–100	–	Co(II)	81.96	–	–	RT	Pseudo-second order	Langmuir	[67]
Nanosized zero-valent iron	Borohydride reduction method	20–80	14.2	Co(II)	–	10	6.4–8.7	–	–	–	[68]
Nano-Zirconium vanadate particles	Precipitation	50–60	–	Co(II)	8.27	–	–	298K	–	–	[71]
Silver nanoparticles	Biological reduction method	1–100	–	Co(II)	–	10–50	–	303–333	–	Freundlich	[70]
Carbon nanotubes	Oxidation	30–40	–	Co(II)	85.74	–	–	–	First order and second order reaction	Langmuir, Freundlich	[108]

Table 1e

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Chromium (Cr(VI) and Cr(III)) ions											
Smart Magnetic Graphene	Solid-State Microwave Induced Process	~4.5 nm	–	Cr(VI)	4.86	120	~6.5	333	–	Langmuir	[72]
Ceria hollow nanospheres	Microwave-assisted aqueous hydrothermal process	260	72	Cr(VI)	15.4	30	7	–	–	–	[73]
Chitosan/Clay nano composites	Solvent casting method	–	–	Cr(VI)	357.14	180	3	–	Pseudo-second order	Langmuir	[74]
Polypyrrole-polyaniline nanofibers	<i>In situ</i> simultaneous polymerization	–	–	Cr(VI)	227	180	–	–	Pseudo second order	Langmuir	[75]
Multiwalled Carbon Nanotubes	Chemical vapor deposition	10–30	93.59	Cr(VI)	2.679	9900	2.88	306.15	–	Langmuir	[76]
Polyglycidyl methacrylate graft with functionalized iron oxide	Radical polymerization	–	–	Cr(VI)	162.9	1–30	4	–	Pseudo second order	Langmuir, Freundlich	[79]
Mesoporous silica nanoadsorbent	Co-condensation	10.1	760.5	Cr(III)	13.81	30	5.2	RT	–	Langmuir, Freundlich	[80]
Nano-alumina	–	75	42.62	Cr(III)	100.0	90	5	RT	–	Langmuir, Freundlich	[111]

lowers the adsorption efficiency, while at higher pH, strong complexation occurs between Cu(II) and the free amine group, thus increasing adsorption. Therefore, this makes MNPs attractive for heavy metal removal in wastewater. Sodium dodecyl sulphate-coated Fe₃O₄ nanoparticles (SDS-Fe₃O₄ NPs) were investigated for the removal of copper from water. The removal of the heavy metal possibly followed the mechanism of electrostatic attraction and ion exchange due to the presence of charges in the particles. The adsorption rate was also found to be fast [46]. Neeraj *et al.* [47] employed cMNPs for capable of sequestering 99% of 100 mg/L of Cu(II) ions in aqueous solution with an adsorbent dosage of 2.0 g/L at a contact time of 30 min. The saturated cMNPs could

be easily regenerated using a consecutive acid base treatment using 0.1 N HCl and 0.1 N NaOH, wherein the regenerated adsorbent exhibited excellent reusability (>95%) for five consecutive cycles. Zhou *et al.* [48] studied cMNPs modified with α -ketoglutaric acid to enhance the adsorption efficiency and achieve a maximum adsorption capacity for Cu(II) ions adsorption. The Cu(II) removal percentage was found to be 89.75% for initial Cu(II) concentration of 200 ppm with 7 g/L dose of the adsorbent.

Porous ZnO nanoplates were synthesised using solvothermal method followed by an annealing process. Ethylene glycol was employed for improving its morphology [49]. The nanoplates were found to have high adsorption capacity for Cu(II) ions. For the

Table 1f

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Lead (Pb(II)) ions											
Iron oxide nanoparticles	Coprecipitation	22 ± 1.5	40	Pb(II)	36	120	2–3	298	–	Langmuir, Freundlich	[82]
Magnetic alginate nanobeads	Coprecipitation	–	–	Pb(II)	50	120	7	303	Pseudo second order	Langmuir	[83]
Nanoporous Alginate-SBA-15	Encapsulation of nanoporous SBA-15 in calcium alginate	–	–	Pb(I)	222.22	–	–	–	Pseudo second order	Langmuir	[86]
Manganese oxide nanoparticles	Redox	–	79.31	Pb(I)	352.55	–	–	298 K	–	Langmuir	[87]
Methyl cellulose and nano chitosan	–	–	–	Pb(II)	144	300	6	–	Second order	Freundlich	[89]
Kaolin clay and nano chitosan	–	–	–	Pb(II)	156	300	6	–	Second order	Freundlich	
Nano-alumina	–	75	42.62	Pb(II)	100.0	90	5	RT	–	Langmuir, Freundlich	[111]
Graphene oxide integrated with magnetic chitosan nanoparticles	–	–	–	Pb(II)	85	–	5	–	Second order	Langmuir	[91]
Mesoporous nano silica particles	Precipitation method	10	–	Pb(II)	155.71	60	4.4	298	Second order	Langmuir, Freundlich	[92]
Chitosan-Montmorillonite nanocomposites	–	2–6	–	Pb(II)	92	–	6	–	–	–	[85]
Poly acrylic-acid/acrylonitrile-attapulgite nanoparticles	Polymerization	–	108.33	Pb(II)	109.9	–	9.0	298	Second order	Freundlich	[93]

Table 1g

Adsorbent	Preparation	Size range (nm)	Surface area (m ² /g)	Adsorbate	Adsorption capacity (mg/g)	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
Cadmium (Cd(II)) ions											
Magnetic nanoparticles	–	25	56.95	Cd(II)	18.8	60	–	–	Pseudo second order	Langmuir, Freundlich	[98]
Nano-alumina	–	75	42.62	Cd(II)	83.33	90	5	RT	–	Langmuir, Freundlich	[111]
Carbonaceous nanoadsorbents	–	20–40	–	Cd(II)	50	120	7	RT	Pseudo second order	Langmuir, Freundlich	[103]
Nanosilica	Sol-gel method	4.17	920	Cd(II)	10	90	7	298	First order	Langmuir, Freundlich, Dubinin–Radushkevich	[104]
Multi-walled carbon nanotubes	–	–	–	Cd(II)	25.7	30	8	298	Pseudo second order	Langmuir	[105]
Cerium oxide Iron oxide Titanium oxide	–	–	–	Cd(II)	49.1 101.1 12.2	4320	–	–	Pseudo second order	Freundlich	[99]

purpose of removing copper from electroplating industrial wastewater, Rafiq *et al.* [50] prepared magnesium and zinc oxide nanoadsorbents. It was found that both the adsorbents were capable of removing 92–98% of copper with adsorbent dosages of 0.3 and 0.2 g for zinc and MgO nanoadsorbents, respectively. When the two nanoadsorbents were compared, MgO showed better removal efficiency.

Recently, utilisation of CNTs as nanosorbent has created great attention because the hollow, layered cylindrical structure of graphene material provides them with typically high specific surface areas, superior mechanical strength, thermal and chemical stabilities and respectively elevated sorption potential for various heavy metals removal [20–22]. CNTs were prepared via the chemical vapour deposition method in which acetylene gas was

used as the carbon source and argon was used as an oxidation protection gas. The nanotubes were then functionalised by oxidation with nitric acid. The nitric acid treated CNTs act as an effective adsorbent and the maximum removal of Cu(II) was found to be 98.39% in wastewater. Salam *et al.* [51] synthesised chitosan/MWCNTs composite for adsorption of Cu(II) ions from water. Even in the presence of other heavy metals like Cd(II), Zn(II) and Ni(II), copper ions are highly adsorbed. This is due to the copper ion's ability to be reduced easily onto the carbonaceous surface of the nanoadsorbent after getting attracted to the active site. The reduced copper then leaves the surface and makes way for the adsorption of other ions. MWCNTs were applied for the adsorption of copper and the effect of humic acid (HA) and fulvic acid (FA) in the process was studied by Sheng *et al.* [52]. It was found that both these acids enhanced the adsorption of copper at lower pH and they showed less adsorption at higher pH. At low pH, both HA and FA which are negatively charged gets adsorbed on to the positively charged MWCNTs followed by better copper adsorption due to the strong complexation ability of the surface adsorbed HA/FA [52]. Radiation-induced chitosan(acrylamidoglycolic acid-co-acrylic acid) magnetic nanopolymer was fabricated and tested for the removal of heavy metals, especially copper, from waste water. The hydrogel network containing the MNPs helps enhance the process of adsorption and gets easily separated due to their magnetic properties [53].

2.3 Removal of mercury

Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment. It causes various disorders in humans, including neurological, nephrological, immunological, cardiac, motor, reproductive and even genetic [54]. Table 1 shows the various nanoadsorbents explored for the recovery of mercury from wastewater.

Shan *et al.* [55] developed poly(1-vinylimidazole) oligomer coated magnetite silica nanospheres (FSPV) as a nanoadsorbent to remove Hg(II) from water. 10–20 nm sized FSPV spheres have saturation magnetisation is 44.7 emu/g and can be separated easily from water with a simple magnetic process in 5 min. After five consecutive cycles of adsorption followed by desorption with HCl, the adsorbent could retain 94% of its initial adsorption capacity. Thiol-functionalised mesoporous (~2.1 nm) silica-coated magnetic nanospheres employed for rapid and efficient Hg(II) removal [56]. The particles were characterised by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy and XPS and the results confirm that the SiO₂ and thiol groups cover the surface of the Fe₃O₄ particles. Hg(II) was desorbed easily using thiourea in a 3 M HCl solution and the nanospheres could be reused without loss of their activity in repetitive adsorption cycles. Kyzas *et al.* [57] tested two modified chitosan derivatives where glutaraldehyde alone was cross-linked with chitosan and the other adsorbent was chitosan cross-linked with glutaraldehyde and functionalised with MNPs for Hg(II) removal. The optimum pH for adsorption and desorption were found to be 5.0 and 2.0, respectively. The reusability was high that, even after the fourth cycle the adsorbent could retain 90% of its initial adsorption capacity. The covalent binding of carboxymethyl chitosan on MNP through the carbodiimide activation was reported by Nasirimoghaddam *et al.* [58]. The developed adsorbents exhibited rapid removal of Hg(II) ions from aqueous solutions with maximum of 92.4% removal at room temperature. 85% of the removed mercury was desorbed from nanoparticles using 0.1 M sulfuric acid and it was possible to reuse the adsorbents for next cycles.

Tawabini *et al.* [59] employed MWCNTs for the separation of Hg(II) ions from wastewater. These nanosorbents were capable of removing Hg(II) from contaminated water more efficiently when used at a pH between 4.0 and 8.0 and when the solution to be treated was agitated at a speed of 150 rpm. For improving the process of adsorption, functionalised MWCNTs were prepared by introducing amine and thiol groups to the side walls of the tubes through the reaction of ethylenediamine, cyanuric chloride and sodium 2-mercaptoethanol one after the other [60]. Polymeric

nanosorbents like poly(aniline (AN)-co-5-sulfo-2-anisidine (SA)) and poly(1-amino-5-chloroanthraquinone) (PACA) were used for the removal of Hg(II) in wastewater [61, 62]. Monomers of AN and SA were used to synthesise copolymeric nanoparticles and the reactive ratio of these co-monomers were found to be 2.05 (AN) and 0.02 (SA) [61].

2.4 Removal of cobalt

Cobalt has been used in electroplating, petrochemical, and paint and pigment industries and in alloys with iron and other metals. Therefore, cobalt contamination of water is seen more often in these industries. It is also released into the environment through coal combustion [63]. Cobalt is less toxic compared to most other metals present in wastewater. However, at higher concentrations it causes nausea, asthma, gastrointestinal problems and damage to the thyroid and liver [63, 64]. A number of nanoadsorbents have been used for the removal of cobalt from aqueous solution whose adsorption conditions are listed in Table 1.

MNPs were used for the removal of Co(II) ion from aqueous solutions [19, 43, 65–67]. 99.2% removal of Co(II) was obtained within 10 min at pH 5.4 with a dose rate of 2.57 g of the adsorbent/L of the aqueous solution [43]. Huang *et al.* [67] synthesised Ag/Fe bimetallic nanoparticles by a simple two-step method and polyvinyl pyrrolidone was used to protect the nanoparticles from oxidation. These nanoparticles were used as adsorbents to remove 99% Co(II) from aqueous solution in 5 min. Borohydride reduction method was used to synthesise nanosized zero-valent iron for the removal of aqueous Co(II) ions over a wide range of concentrations, from 1 to 1000 mg/L [68]. Rapid uptake of Co(II) ions was observed with these nanoparticles as the pH increases. The nanoparticles can be regenerated and were found to be effective for the Co(II) removal due to their large adsorption capacity. Zari *et al.* [69] studied the effect of sonication time for the removal of Co(II) from wastewater in the presence of zero valence iron (ZVI) nanoparticles. The maximum removal efficiency for Co(II) is about 59% at 30 min with sonication, which is higher than the removal efficiency of the nanoparticle without sonication. This is because, during sonication the zero valence nanoclusters break down into an optimal size with greater surface to volume ratio for the adsorption of Co(II) ions. However, at very high sonication times, the nanoparticles tend to aggregate and increase in size. The sonication time of 30 min is required due to the kinetic mechanism of electron transfer from ZVI nanoparticles to Co(II) ions. Siva *et al.* [70] synthesised silver nanoparticles (AgNPs) by a biological reduction method using *Cyperusrotundus* grass extract which were further used to prepare phenol-formaldehyde resin (PFR) encapsulated silver nanocomposites (PFR-AgNPs). Column experiments were carried out with a fixed-bed glass column packed with 3.5 g PFR-AgNPs for the removal of Co(II) ion solution. The adsorption process was exothermic in nature and the spent adsorbent could be regenerated by using 5% (w/w) NaCl solution. Nano-zirconium vanadate ions are prepared to remove cobalt using three strategies of homogeneous precipitation, hydrothermal synthesis and sol-gel precipitation where maximum adsorbent rate of 8.27 mg/g of cobalt was removed using alkaline treated sol-gel precipitation method compared to the other methods [71].

2.5 Removal of chromium

The most common sources of chromium pollution are electroplating, leather tanning, dye, photographic and cement industries. Several industrial effluents contain chromium, which gets accumulated in the food chain and causes severe ailments ranging from skin irritation to lung carcinoma. Therefore, it is important to remove this metal ion, Cr(VI) from the industrial effluents before being discharged into the environment [19]. Different types of nanoadsorbents have been studied for the removal of chromium ions in wastewater, which are shown in Table 1.

Gollavelli *et al.* [72] synthesised smart magnetic graphene exhibiting 99% chromium removal efficiency from wastewater. Adsorption was found to increase with increase in temperature and initial concentration of the adsorbent. The adsorption of Cr(VI)

ions from aqueous solution by ethylenediamine-modified cMNP resin in a batch adsorption system. The optimum adsorption was observed at pH 2.0 and the sorbents were successfully regenerated using 0.1 N NaOH solutions. Cao *et al.* [73] synthesised ceria hollow nanospheres composed of CeO₂ nanocrystals via a template-free and microwave-assisted aqueous hydrothermal process. It is a low cost and environment friendly method of synthesis. These ceria hollow nanospheres show a high adsorption capacity for heavy metal ions which is comparatively more than that for other ceria based nanomaterials. Chitosan/clay nanocomposites were prepared by solvent casting method with the properties of hydrophilicity of an organic polycation and the adsorption capacity of an inorganic polyanion [74]. There were also small amounts of montmorillonite-Na⁺ in the chitosan matrix. 93.5% of the Cr(VI) was removed with adsorbent dose 50 mg/L at a contact period of 180 min with initial Cr(VI) concentration of 100 ppm at wide range of pH.

Bhaumik *et al.* [75] synthesised polypyrrole (PPy)–polyaniline (PANI) nanofibers through the coupling of PPy⁺ and PANI⁺ free radicals by the polymerisation of their monomers in the presence of FeCl₃ oxidant. These nanoadsorbents were then studied for the removal of Cr(VI) from wastewater. The metal removal mechanism was found to be a combination of anion exchange and Cr(VI) reduction to Cr(III). Hu *et al.* [76] studied MWCNTs for the removal of chromium from water. The redox reactions at the surface of the adsorbent is a major contributor to the removal of Cr(VI). Gupta *et al.* [77] also studied MWCNTs for the adsorption of chromium from aqueous solution. Its properties of adsorption were found to be better than that of the regular activated carbon which shows problems in adsorption of hydrophilic substances. To improve adsorption composites of MWCNT/nanoiron oxide were prepared and their adsorption studies were conducted. The MWCNT/nanoiron oxide show higher adsorption capability of nearly 90% after a contact time of 60 min.

Parida *et al.* [78] immobilised TiO₂ nanoparticles on mesoporous MCM-41 and studied their ability to adsorb Cr(VI). The adsorption of Cr(VI) onto 20% of TiO₂-MCM-41 at pH 5.5 and 323 K was 91% at 100 mg/L Cr(VI) ion concentration in 80 min. The adsorption followed a second-order kinetics with higher values of intra-particle diffusion rate. Thermodynamic parameters suggested that the adsorption process is endothermic in nature and desorption studies indicated a chemisorption mode. A copolymer of the polyglycidyl methacrylate graft with functionalised iron oxide are used as the adsorbent in the removal of Cr(VI), at their effective pH 4.0 with the maximum adsorbent capacity of 132.5 and 162.9 mg/g, respectively [79]. A mesoporous silica nanoadsorbent surface modified with two distinct groups of nitrogen and sulphur and has been used in the treatment of metal Cr(III) ions from the waste pollutants [80]. The above synthesised nanoadsorbent via co-condensation strategy removes Cr(III) in the contact time of 30 min, pH 5.2 at the adsorption rate of 98% with the maximum adsorption capacity of 30 mg/g [80].

2.6 Removal of lead

Pb(II), when present in high quantities in water, is one of the most toxic heavy metals causing adverse health problems such as anaemia, encephalopathy, hepatitis, nephritic syndrome and the likes, when its concentration in drinking water is above the limit of 5 ng/mL. Due to this, it is necessary to eliminate the Pb(II) ions from wastewater before being used further [81]. Table 1 shows the nanosorbents studied for removal of lead ions in wastewater.

MNPs are cost-effective adsorbents that provide high adsorption capacity of Pb(II) ions from water, rapid adsorption rate and simple separation assisted by magnetic field and easy regeneration [81–84]. Superparamagnetic polyethylene glycol coated MNPs were synthesised by chemical co-precipitation method for the removal of Pb(II) from wastewater. The adsorption process of magnetic nanosorbents was rapid and the equilibrium was achieved at pH 6.0 within 10 min [82]. The adsorption rate increased as temperature increased, suggesting an endothermic adsorption and the optimal pH value for Pb(II) adsorption was

around 5.5. Magnetically separable alginate nanobeads were synthesised and it was found that these beads were capable of removing 92.5% Pb(II) from wastewater at pH 7.0 [83]. The optimum pH was found to be 7.0 at which the maximum adsorption was 92.5% for initial Pb(II) concentration of 400 mg/L. Desorption studies show that the adsorbent can be regenerated with no reduction in adsorption rate up to the fifth cycle. Magnetic chitosan nanocomposites based on amine functionalised MNPs were removed with maximum efficiency of 94.6% Pb(II) ions. However, the nanocomposites showed lower adsorption compared to the MNPs. The adsorption increases with increase in pH till 6.0 [84].

Bio-nanoparticle-composites prepared from carboxymethyl chitosan (CMCs) and montmorillonite were used as adsorbents for Pb(II) removal [85]. The montmorillonite was used as nanofiller and water was used as a medium for dissolving and dispersing CMCs and montmorillonite. The TEM results showed that the composite nanoparticle generated without the use of a cross-linker has a good uniform distribution of particle morphology compared to those with a cross-linker agent. Cheraghali *et al.* [86] synthesised alginate-Santa Barbara Amorphous-15 by the encapsulation of the nanoporous SBA-15 in the biopolymeric matrix of calcium alginate. The calculated values of enthalpy, entropy and Gibb's free energy (ΔG° , ΔH° and ΔS°) indicated the endothermic and spontaneous nature of adsorption. Hydrous manganese dioxide (HMO) nanoparticles fabricated by a redox reaction of potassium permanganate and hydrogen peroxide and were used as adsorbents for effective Pb(II) removal from wastewater [87]. The adsorption process was spontaneous and endothermic and the activation energy for Pb(II) adsorption by HMO was calculated to be 38.23 kJ/mol. The main adsorbed speciation was PbOH⁺ and the final chemical state of Pb(II) on the surface of HMO was found to be similar to PbO. To improve the applicability of nanoparticles in heavy metal elimination, researchers have focused on impregnating HMO nanoparticles onto porous cation exchange resins [87, 88]. Kanchana *et al.* [89] synthesised nanocomposites of chitosan with methyl cellulose and kaolin clay to remove the Pb(II) ions from simulated wastewater. Nanochitosan kaolin clay composites were found to be a more effective adsorbent compared to methyl cellulose composites. It was evident that an adsorbent concentration of 6 g/L was used to treat wastewater with a contact time of 300 min at the pH 6.0. Hybrid nanomaterials were synthesised by the encapsulation of ZrO₂ nanoparticles into spherical macroporous polystyrene beads covalently bound with surface groups like charged sulfonate group (SO₃⁻), and others like N(CH₃)₃⁺/CH₂Cl and activated carbon [90]. These are denoted as Zr-MPS, Zr-MPN, Zr-MPC, Zr-GAC, respectively. The sorption capacities of these nanomaterials for Pb(II) removal were studied and it was found that the decreasing capacities were in the order Zr-MPS > Zr-MPN > Zr-GAC > Zr-MPC. The optimum pH of adsorption using Zr-MPS ranges 5–6.5.

The integration of magnetic chitosan with graphene oxide was used to remove Pb(II) from contaminated waste water due to their appropriate functional groups and large surface area. The above integrated adsorbent could be reused effectively for six consecutive cycles, which reduces the cost and enhances the regeneration property of the above nanosorbent [91]. Mesoporous silica-coated particles which were chemically modified with o-vanillin has been produced to study the adsorption capacity of Pb(II) from the waste water. It was found that 80–90% of adsorption takes place in 60 min [92]. Potential removal of Pb(II) by the hybrid of poly acrylic-acid/acrylonitrile-attapulgitic nanoparticles that has been prepared by polymerisation reaction, has the maximum removal of 96.6% Pb(II) with the capacity of 109.9 mg/g at their optimum pH 5.0–6.0, respectively [93].

Alumina-coated MWCNTs were built for the extraction of lead from wastewater. The mechanism of adsorption could be due to the van der Waals interaction between carbon atoms in the MWCNT sheets and Pb(II) or due to the electrostatic attraction between the positive lead ions and the negative surface of the MWCNT part of the adsorbent. The adsorption is further enhanced by the electrostatic interaction between Pb(II) and the pairs of negatively

charged oxygen atoms on the alumina surface [94]. Saleh and Gupta [95] studied manganese dioxide-coated MWCNT nanocomposite for Pb(II) removal from wastewater. Here again the removal mechanism is based on the interactions between the lead ions and the active sites on the surface of the composite adsorbent. The manganese oxides on the adsorbent surface make it highly negative, which easily attracts the positive lead ions and hence, enhance the adsorption process.

2.7 Removal of cadmium

Cadmium has been increasingly used in various technologies nowadays. The industries using this metal, however, do not efficiently discharge its effluents, due to which cadmium is now increasingly found to enter water. Cadmium is a toxic heavy metal and poses severe threat to living organisms consuming this water [96]. It is used in the manufacture of nickel–cadmium batteries, phosphate fertilisers, pigments, alloys and metal plating [97]. Cadmium exposure in water comes from sources like discharge from metal refineries, fossil fuels combustion ash and from waste batteries and paints. The problems caused by cadmium consumption include kidney damage, stomach problem, diarrhoea and sometimes, death [96]. Table 1 summarises the experiments carried out for cadmium removal using nanoadsorbents.

A new and effective adsorbent for Cd(II) removal from aqueous solution was synthesised by coating a shellac layer, a natural biodegradable and a renewable resin with abundant hydroxyl and carboxylic groups, on the surface of MNPs. The desorption studies showed that Cd(II) could easily be desorbed from the nanoparticle using mild organic acid solutions at low concentration [98]. Inorganic nanoparticles of cerium oxide, were studied for the removal of cadmium from wastewater [99]. Nanoparticles of iron oxide and titanium dioxide were also used to compare the adsorption rates of Cd(II). It was found that among the three nanoparticles, MNPs showed higher adsorption of Cd(II) for the same contact time. The adsorption efficiency of nanotitanium dioxide with different crystal structures such as anatase, rutile, mix crystal and amorphism for Cd(II) ions was explored [100]. Kinetic studies revealed both chemisorption and physisorption on adsorbent surface. Among all the other samples, anatase TiO₂ powder showed a highest chemisorption capacity because the structure has higher surface energy, rough surface and unsaturated oxygen bond. The process of adsorption depends on the

electrostatic interactions and the soft acid/soft base interactions to form complexes with the ions that later get removed from water [100]. Visa and Duta [101] fabricated TiO₂ Degussa P25 nanopowder/fly ash for the adsorption of heavy metals like cadmium from wastewater. The mechanism of adsorption was similar to that of the previously discussed titanium dioxide nanopowder. Hydrous manganese dioxide-001 is a hybrid adsorbent fabricated by the impregnation of HMO nanoparticles onto a polystyrene cation exchanger resin (D-001) and checked for the removal of Cd(II) ion from water [102]. The optimum pH at which the adsorption of Cd(II) takes place is around 7.0. These adsorbents can then be regenerated with 2% HCl solution with negligible loss of the nanoparticle. The mechanism of adsorption is ion exchange with the D-001 polymeric exchanger and the innersphere complexation with HMO nanoparticles. Al-Khaldi *et al.* [103] compared the different carbon nanoadsorbents such as fly ash, CNTs, carbon nanofibres, activated carbon on the removal of Cd(II) from waste effluents, from which 95% of contaminants was removed by fly ash with pH 7.0 at the speed of 150 rpm in 2 h, whereas 38% was removed by activated carbon, 34% with carbon nanofibers and 27% with CNTs, respectively. A nanosilica spheres modified with sulphur and nitrogen groups was used to adsorb Cd(II) where, the maximum adsorbent rate of 98% has been achieved at their optimum conditions of pH 7.0 with the contact time of 90 min [104]. Vuković *et al.* [105] used oxidised and ethylenediamine-functionalised MWCNTs for the adsorption of cadmium. This adsorbent was prepared by the chemical modification of carboxyl groups, using O-(7-azabenzotriazol-1-yl)-N, N, N, N-tetramethyluronium hexafluorophosphate. The adsorption process was found to be spontaneous and endothermic in nature.

3 Other nanoparticles for heavy metals removal

The nanoparticles discussed so far have been investigated for the removal of a specific heavy metal with higher adsorption efficiencies. There are other nanoparticles also explored for their capability of removing more than one metal from waste water, simultaneously with higher efficiency (Table 2).

Magnetic hydroxyapatite (MNHAP) was used as an adsorbents for the removal of Cd(II) and Zn(II) from wastewater [106]. Scanning electron microscopy results showed that adsorbents size in nanorange (28 nm in diameter) and highly stable under both

Table 2 Nanoadsorbents for the removal multi-metal ions from wastewater

Adsorbent	Preparation	Size range, nm	Surface area, m ² /g	Adsorbate	Adsorption capacity, mg/g	Time, min	pH	Temperature	Kinetic model	Isotherm	References	
MNPs	Co-precipitation method	54	—	Zn(II)	13.95	—	—	—	—	Langmuir	[110]	
		54	—	Cd(II)	22.42	—	—	—	—	Langmuir		
MNPs	Cocprecipitation with further modification	—	—	Ni(II)	41.2	1	4.0	—	—	Langmuir	[46]	
		—	—	Zn(II)	59.2	1	4.0	—	—	Langmuir		
		—	—	Cu(II)	24.3	1	4	—	—	Langmuir		
MONs	—	20	103.5	Pb(II)	16.44	280	9.0	298	—	Langmuir, Freundlich,	[114]	
				Cr(VI)	21.78	—	—	—	—	—		
Magnetic maghemite nanotubes	Microwave radiation method	10–12	321.638	Cu(II)	111.11	60–90	6.0	298	Second order reaction	Langmuir	[107]	
				Zn(II)	84.95	—	—	—				—
				Pb(II)	71.42	—	—	—				—
Nano-alumina	—	75	42.62	Cd(II)	83.33	90	5	RT	—	Langmuir, Freundlich	[111]	
				Pb(II)	100.0	90	5	RT	—	Langmuir, Freundlich		
				Cr(III)	100.0	90	5	RT	—	Langmuir, Freundlich		
				Pb(II)	100.0	90	5	RT	—	Langmuir, Freundlich		
Magnetic nanoadsorbent	Conventional radical polymerisation	~80	—	Hg(II)	59.45	360	—	298 K	Pseudo-second order	—	[115]	

oxidising and reducing conditions. The MNHAP showed better adsorption affinity to Cd(II) better than Zn(II). Desorption process was carried better with EDTA compared to other desorption agents [106]. The removal of Cu²⁺, Zn²⁺ and Pb²⁺ from water was studied efficiently by synthesising magnetic maghemite nanotubes using microwave radiation technique, where the above metals was removed with the maximum adsorption rate of 111.11, 84.95 and 71.42 mg g⁻¹, respectively. The optimum pH was found to be 6.0 at the temperature of 25°C with the contact time of 60–90 min [107]. Tofighy and Mohammadi [108] have studied the potential effect of CNTs on the removal of heavy metals such as Cu²⁺, Zn²⁺, Pb²⁺, Co²⁺ and Cd²⁺. The kinetic studies of adsorption results that the above carbon nanoadsorbent removes the heavy metal with different adsorption rates and capacities. Pb²⁺ has been more preferably adsorbed than other metals.

Nanoparticles of aluminium oxide (Al₂O₃) were used for the efficient removal of Cd, Zn, and other heavy metals from wastewater and soil solutions due to their high specific surface area to volume ratio [109]. Adsorption of Zn and Cd was performed at a pH of 6.5 both in mono and binary systems. Adsorption was found to be significantly enhanced by the presence of phosphate or HA and to a lesser extent by the presence of citrate at low concentrations. Phosphate and humic acid, enhanced Zn and Cd adsorption in all systems, whereas, there was a reduction in Zn adsorption in the mono-metal system by 25% when citrate was used. It was found that enhanced the removal of phosphate and HA accompanies removal of Zn or Cd from the systems, which may indicate enhanced adsorption due to ternary complex formation or metal-ligand precipitation. Phosphate was found to be the most effective among the three ligands in enhancing Zn and Cd adsorption [109]. SDS coated MNPs explored as potential nanosorbent for the removal of Cu(II), Ni(II) and Zn(II) ions from wastewater [110]. Use of SDS coated MNPs for the removal heavy metal ions showed great adsorption capacity with rapid adsorption process and also the adsorbents were easily separated by magnet. It was also seen that desorption can be done with methanol and the nanoadsorbents can be used for three adsorption–desorption cycles, consequently.

γ-Alumina (γ-Al₂O₃) nanofibres modified with functional groups with a strong affinity to the contaminants are another type of nanoadsorbent used to study heavy metal removal. 2,4-dinitrophenylhydrazine (DNPH) immobilised on SDS coated nanoalumina was developed for the removal of metal cations such as Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Mn(II) from water [111]. Desorption experiments by elution with a mixture of nitric acid and methanol showed that the modified alumina nanoparticles could be reused without significant losses of its initial properties including its activity as an adsorbent, even after three adsorption–desorption cycles. Thus, modified nanoalumina with DNPH having a high adsorption capacity is very useful for the removal of these multi-cations [111].

Poly-methacrylic acid grafted chitosan–bentonite nanocomposite (MACB) synthesised by γ-irradiation polymerisation for the effective removal of Hg(II), Pb(II) and Cd(II) metal ions from wastewater [112]. The experimental results indicated that the order of adsorption capacity of MACB nanocomposite was found to be: Hg(II) > Pb(II) > Cd(II). Nanoparticles of nickel ferrite (NiFe₂O₄) and copper ferrite (CuFe₂O₄) were synthesised by the PEG assisted hydrothermal method and studied for the removal of Cu(II), Ni(II) and Zn(II) from wastewater [113]. The removal efficiencies of Cu(II), Ni(II) and Zn(II) by using CuFe₂O₄ nanoparticles were found to be 83.50, 98.85 and 99.80%, respectively, and the removal efficiencies of Cu(II), Ni(II) and Zn(II) by using NiFe₂O₄ nanoparticles were found to be 92.55, 36.56 and 99.91%, respectively. MgO nanoparticles (MON) was used to remove both lead Pb(II) and chromium Cr(VI), with the maximum efficiency of 94.78 and 81.25% at the contact time of 280 min and pH 9, respectively [114]. Another pollutant of Hg(II) has been removed from contaminants by the synthesis of magnetic nanoadsorbent with their transformed amino groups on dithiocarbonate (DTC) on the polymer chains. When the above nanoadsorbent was compared

with single-layer nanoadsorbent of 3-aminoethoxy silane modified on the surface of Fe₃O₄ particles, polymer-based nanoadsorbent provides a high capacity of adsorbent rate with 100% efficiency at 40°C, whereas only 77% was removed with monolayer adsorbent [115]. Yang *et al.* [11] prepared diamine functionalised mesoporous silica on MWCNT for the removal of the heavy metals Cu(II), Ni(II), Pb(II), and Zn(II). The adsorption capacity for this adsorbent is much higher than that of the regular MWCNTs due to the combined adsorption capabilities of the diamine modified mesoporous silica and the CNTs.

4 Future prospects

As discussed above, the nanoparticles can be used as effective adsorbents for removing various heavy metals from contaminated water. The ease of synthesis, economic feasibility, easy surface modifications are a few vital features which have led to development of this novel technology. So far, lower concentrations of heavy metals have been removed with high selectivity and adsorption capacity. However, requirement for wastewater treatment at a larger level still persists and the implementation of these nanomaterials is uncertain. Work has to be done on scaling up the laboratory scale experiments to larger scale, improving the biocompatibility of nanoparticles, making it eco-friendly and making the entire process cost effective.

The use of nanoparticles for the removal of heavy metals from wastewater has been a breakthrough for researchers in this field. However, there are a few technical glitches involved, which have to be overcome to make this technology an efficient method for wastewater treatment in the future. The first of the problems is the lack of available methods to do a desorption of the used nanosorbents. It is necessary to recycle these adsorbents if we need to make this technique cost effective and this can be done through the method of desorption. At present, limited research has been done on this and there is a need to find efficient methods to get back the nanosorbents in their active form. Also, this technique requires the surface area of nanoparticles to be large for efficient adsorption. Optimising the protocol of synthesis under optimum conditions, nature of surface coatings and their subsequent geometric arrangement on the nanoparticles will help in obtaining nanoparticles of the ideal size and surface area.

At present, most of the nanoparticles that have been discussed are made of chemical methods which may have possible toxic effects on the treated water. In order to avoid such problems, greener methods for the synthesis of these nanoadsorbents could be studied. Coal, fly ash, wood, silica gel, clay materials, agricultural wastes like bagasse pith, maize cob, coconut shell, rice husk and so on, cotton wastes and cellulose based wastes have been used to synthesise nanoadsorbents. These adsorbents are also not available at economical prices. However, this problem can be rectified when there is an increase in the demand for such materials in the market. Hence, a wider application of such particles will enhance its use and makes its production economical.

5 References

- [1] Muga, H.E., Mihelcic, J.R.: 'Sustainability of wastewater treatment technologies', *J. Environ. Manage.*, 2008, **88**, (3), pp. 437–447
- [2] Wuana, R.A., Okieimen, F.E.: 'Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation'. *ISRN Ecology*, 2011, pp. 1–20
- [3] Gorchev, H.G., Ozolins, G.: 'WHO guidelines for drinking-water quality', *WHO Chronicle*, 1984, **38**, pp. 104–108
- [4] Fu, F., Xie, L., Tang, B., *et al.*: 'Application of a novel strategy-advanced fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater', *Chem. Eng. J.*, 2012, **189**, pp. 283–287
- [5] Da,browskia, A., Hubicka, Z., Podkošcielnyia, P., *et al.*: 'Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method', *Chemosphere*, 2004, **56**, (2), pp. 91–106
- [6] Chan, B.K.C., Dudeney, A.W.L.: 'Reverse osmosis removal of arsenic residues from bioleaching of refractory gold concentrates', *Miner. Eng.*, 2008, **21**, (4), pp. 272–278
- [7] Song, J., Oh, H., Kong, H., *et al.*: 'Polyrhodanine modified anodic aluminum oxide membrane for heavy metal ions removal', *J. Hazard. Mater.*, 2011, **187**, (1–3), pp. 311–317
- [8] Barakat, M.A.: 'New trends in removing heavy metals from industrial waste water', *Arab. J. Chem.*, 2011, **4**, (4), pp. 361–377

- [9] Fu, F., Wang, Q. 'Removal of heavy metal ions from wastewaters: a review', *J. Environ. Manage.*, 2011, **92**, (3), pp. 407–418
- [10] Hua, M., Zhang, S., Pan, B., *et al.*: 'Heavy metal removal from water/wastewater by nanosized metal oxides: a review', *J. Hazard. Mater.*, 2012, **211**, pp. 317–331
- [11] Yang, W., Ding, P., Zhou, L., *et al.*: 'Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution', *Appl. Surf. Sci.*, 2013, **282**, pp. 38–45
- [12] Badruddoza, A.Z.M., Shawon, Z.B.Z., Tay, W.J.D., *et al.*: 'Fe₃O₄/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater', *Carbohydr. Polym.*, 2013, **91**, (1), pp. 322–332
- [13] Lakherwal, D.: 'Adsorption of heavy metals a review', *Int. J. Environ. Res. Dev.*, 2014, **4**, (1), pp. 41–48
- [14] Ray, P.Z., Shipley, H.J.: 'Inorganic nano-adsorbents for the removal of heavy metals and arsenic: a review', *RSC Adv.*, 2015, **5**, (38), pp. 29885–29907
- [15] Peralta-Videa, J.R., Lopez, M.L., Narayan, M., *et al.*: 'The biochemistry of environmental heavy metal uptake by plants: implications for the food chain', *Int. J. Biochem. Cell Biol.*, 2009, **41**, (8), pp. 1665–1677
- [16] Wang, X., Guo, Y., Yang, L., *et al.*: 'Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment', *J. Environ. Anal. Toxicol.*, 2012, **2**, (7), pp. 1–7
- [17] Qu, X., Alvarez, P.J., Li, Q., *et al.*: 'Applications of nanotechnology in water and wastewater treatment', *Water Res.*, 2013, **47**, (12), pp. 3931–3946
- [18] Dave, P.N., Chopda, L.V.: 'Application of iron oxide nanomaterials for the removal of heavy metals', *J. Nanotechnol.*, 2014, **2014**, pp. 1–14
- [19] Shen, Y.F., Tang, J., Nie, Z.H., *et al.*: 'Preparation and application of magnetic Fe₃O₄ nanoparticles for wastewater purification', *Sep. Purif. Technol.*, 2015, **68**, (3), pp. 312–319
- [20] Tian, Y., Gao, B., Morales, V.L., *et al.*: 'Methods of using carbon nanotubes as filter media to remove aqueous heavy metals', *Chem. Eng. J.*, 2012, **210**, pp. 557–563
- [21] Inyang, M., Gao, B., Wu, L., *et al.*: 'Filtration of engineered nanoparticles in carbon-based fixed bed columns', *Chem. Eng. J.*, 2013, **220**, pp. 221–227
- [22] Gangopom, H.R., Sattler, M.L., *et al.*: 'Carbon nanotubes for air pollutant control via adsorption: A review', *Rev. Nanosci. Nanotechnol.*, 2014, **3**, (2), pp. 149–160
- [23] Maity, D., Agrawal, D.C.: 'Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media', *J. Magn. Magn. Mater.*, 2007, **308**, (1), pp. 46–55
- [24] Choong, T.S.Y., Chuah, T.G., Robiah, Y., *et al.*: 'Arsenic toxicity, health hazards and removal techniques from water: an overview', *Desalination*, 2007, **217**, (1), pp. 139–166
- [25] Chen, L., Xin, H., Fang, Y., *et al.*: 'Application of metal oxide heterostructures in arsenic removal from contaminated water', *J. Nanomater.*, 2014, **2**, pp. 1–10
- [26] Adegoke, H.I., Adekola, F.A., Fatoki, O.S., *et al.*: 'A comparative study on sorption of As(V) ions on hematite, goethite and magnetite nanoparticles', *Nanotechnology*, 2014, **1**, pp. 184–187
- [27] Lin, Y.F., Chen, J.L.: 'Synthesis of mesoporous maghemite (gamma-Fe₂O₃) nanostructures with enhanced arsenic removal efficiency', *RSC Adv.*, 2013, **3**, (35), pp. 15344–15349
- [28] Ghosh, M.K., Poinern, G.E.J., Issa, T.B., *et al.*: 'Arsenic adsorption on goethite nanoparticles produced through hydrazine sulfate assisted synthesis method', *Korean J. Chem. Eng.*, 2012, **29**, (1), pp. 95–102
- [29] Feng, L., Cao, M., Ma, X., *et al.*: 'Superparamagnetic high-surface-area Fe₃O₄ nanoparticles as adsorbents for arsenic removal', *J. Hazard. Mater.*, 2012, **217**, pp. 439–446
- [30] Tang, W., Su, Y., Li, Q., *et al.*: 'Mg-doping: a facile approach to impart enhanced arsenic adsorption performance and easy magnetic separation capability to alpha-Fe₂O₃ nanoadsorbents', *J. Mater. Chem. A*, 2013, **1**, (3), pp. 830–836
- [31] Nabi, D., Aslam, I., Qazie, I.A.: 'Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal', *J. Environ. Sci.*, 2009, **21**, (3), pp. 402–408
- [32] Danish, M.I., Qazi, I.A., Zeb, A., *et al.*: 'Arsenic removal from aqueous solution using pure and metal-doped titania nanoparticles coated on glass beads: adsorption and column studies', *J. Nanomater.*, 2013, **69**, pp. 1–17
- [33] Martinson, C.A., Reddy, K.J.: 'Adsorption of arsenic(III) and arsenic(V) by cupric oxide nanoparticles', *J. Colloid Interf. Sci.*, 2009, **336**, (2), pp. 406–411
- [34] Li, R., Li, Q., Gao, S., *et al.*: 'Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part A. Adsorption capacity and mechanism', *Chem. Eng. J.*, 2012, **185**, pp. 127–135
- [35] Liu, Y., Li, Q., Gao, S., *et al.*: 'Exceptional As(III) sorption capacity by highly porous magnesium oxide nanoflakes made from hydrothermal synthesis', *J. Am. Ceram. Soc.*, 2011, **94**, (1), pp. 217–223
- [36] Goswami, A., Raul, P.K., Purkait, M.K.: 'Arsenic adsorption using copper (II) oxide nanoparticles', *Chem. Eng. Res. Des.*, 2012, **90**, (9), pp. 1387–1396
- [37] Hang, C., Li, Q., Gao, S., *et al.*: 'As(III) and As(V) adsorption by hydrous zirconium oxide nanoparticles synthesized by a hydrothermal process followed with heat treatment', *Ind. Eng. Chem. Res.*, 2012, **51**, (1), pp. 353–361
- [38] Cui, H., Li, Q., Gao, S., *et al.*: 'Strong adsorption of arsenic species by amorphous zirconium oxide nanoparticles', *J. Ind. Eng. Chem.*, 2012, **18**, (4), pp. 1418–1427
- [39] Al-Saleh, A.A., Tawfik, A., Agarwal, S., *et al.*: 'Synthesis of MWCNT/MnO₂ and their application for simultaneous oxidation of arsenite and sorption of arsenate', *Appl. Catal. B, Environ.*, 2011, **106**, (1), pp. 46–53
- [40] Ntim, S.A., Mitra, S.: 'Adsorption of arsenic on multiwall carbon nanotube-zirconia nanohybrid for potential drinking water purification', *J. Colloid Interf. Sci.*, 2012, **375**, (1), pp. 154–159
- [41] Chen, R., Zhi, C., Yang, H., *et al.*: 'Arsenic(V) adsorption on Fe₃O₄ nanoparticle-coated boron nitride nanotubes', *J. Colloid Interf. Sci.*, 2011, **359**, (1), pp. 261–268
- [42] Bilal, M., Shah, J.A., Ashfaq, T., *et al.*: 'Waste biomass adsorbents for copper removal from industrial wastewater – a review', *J. Hazard. Mater.*, 2013, **263**, (2), pp. 322–333
- [43] Kanthimathi, G., Kotteeswaran, P., Muthuraman, M., *et al.*: 'Atomic absorption and vibrational spectral magnetic studies on the removal of Cu(II) and Co(II) ions using synthetic nano adsorbent Fe₃O₄', *Soft Nanosci. Lett.*, 2013, **3**, (4), pp. 75–78
- [44] Hao, Y.M., Man, C., Hu, Z.B.: 'Effective removal of Cu(II) ions from aqueous solution by amino-functionalized magnetic nanoparticles', *J. Hazard. Mater.*, 2010, **184**, (1), pp. 392–399
- [45] Li, H., Xiao, D.L., He, H., *et al.*: 'Adsorption behavior and adsorption mechanism of Cu(II) ions on amino-functionalized magnetic nanoparticles', *T. Nonferr. Metal. Soc.*, 2013, **23**, (9), pp. 2657–2665
- [46] Adeli, M., Yamini, Y., Faraji, M.: 'Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples', *Arab. J. Chem.*, 2012 DOI: 10.1016/j.arabjc.2012.10.012
- [47] Neeraj, G., Krishnan, S., Kumar, P.S., *et al.*: 'Performance study on sequestration of copper ions from contaminated water using newly synthesized high effective chitosan coated magnetic nanoparticles', *J. Mol. Liq.*, 2016, **214**, pp. 335–346
- [48] Zhou, Y.T., Nie, H.L., White, C.B., *et al.*: 'Removal of Cu²⁺ from aqueous solution by chitosan-coated magnetic nanoparticles modified with α -ketoglutaric acid', *J. Colloid Interf. Sci.*, 2009, **330**, (1), pp. 29–37
- [49] Wang, X., Cai, W., Lin, Y., *et al.*: 'Mass production of micro/nanostructured porous ZnO plates and their strong structurally enhanced and selective adsorption performance for environmental remediation', *J. Mater. Chem.*, 2010, **20**, (39), pp. 8582–8590
- [50] Rafiq, Z., Nazir, R., Durr-e-Shahwar, *et al.*: 'Utilization of magnesium and zinc oxide nano-adsorbents as potential materials for treatment of copper electroplating industry wastewater', *J. Environ. Chem. Eng.*, 2014, **2**, (1), pp. 642–651
- [51] Salam, M.A., Makki, M.S.I., Abdelaal, M.Y.A.: 'Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution', *J. Alloy. Compd.*, 2009, **509**, (5), pp. 2582–2587
- [52] Sheng, G., Li, J., Shao, D., *et al.*: 'Adsorption of copper (II) on multiwalled carbon nanotubes in the absence and presence of humic or fulvic acids', *J. Hazard. Mater.*, 2010, **178**, (1), pp. 333–340
- [53] Abou El-Fadl, F.I., Abd El-Mohdy, H.L.: 'Removal of heavy metal ions from aqueous solutions by radiation-induced chitosan(acrylamidoglycolic acid-co-acrylic acid) magnetic nanopolymer', *Polym. Eng. Sci.*, 2015, **55**, (6), pp. 1441–1449
- [54] Zahir, F., Rizwi, S.J., Haq, S.K., *et al.*: 'Low dose mercury toxicity and human health', *Environ. Toxicol. Pharmacol.*, 2005, **20**, (2), pp. 351–360
- [55] Shan, C., Ma, Z., Tong, M., *et al.*: 'Removal of Hg(II) by poly(1-vinylimidazole)-grafted Fe₃O₄@SiO₂ magnetic nanoparticles', *Water Res.*, 2014, **69**, pp. 252–260
- [56] Hakami, O., Zhang, Y., Banks, C.J.: 'Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of Hg from water', *Water Res.*, 2012, **46**, (12), pp. 3913–3922
- [57] Kyzas, G.Z., Deliyanni, E.A.: 'Mercury (II) removal with modified magnetic chitosan adsorbents', *Molecules*, 2013, **18**, (6), pp. 6193–6214
- [58] Nasirimoghaddam, S., Zeinali, S., Sabbaghi, S.: 'Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples', *J. Ind. Eng. Chem.*, 2015, **27**, pp. 79–87
- [59] Tawabini, B., Al-Khaldi, S., Atieh, M., *et al.*: 'Removal of mercury from water by multi-walled carbon nanotubes', *Water Sci. Technol.*, 2010, **61**, (3), pp. 591–598
- [60] Hadavifar, M., Bahramifar, N., Younesi, H., *et al.*: 'Adsorption of mercury ions from synthetic and real wastewater aqueous solution by functionalized multi-walled carbon nanotube with both amino and thiolated groups', *Chem. Eng. J.*, 2014, **237**, pp. 217–228
- [61] Li, X.G., Feng, H., Huang, M.R.: 'Strong adsorbability of mercury ions on aniline/sulfoanisidine copolymer nanosorbents', *Chemistry*, 2009, **15**, (18), pp. 4573–4581
- [62] Huang, S., Ma, C., Liao, Y., *et al.*: 'Removal of Mercury (II) from aqueous solutions by adsorption on poly (1-amino-5-chloroanthraquinone) nanofibrils: Equilibrium, kinetics, and mechanism studies', *J. Nanomater.*, 2016, **2016**, pp. 1–11
- [63] Imran, A.: 'New generation adsorbents for water treatment', *Chem. Rev.*, 2012, **112**, (10), pp. 5073–5091
- [64] Beckera, F.L., Rodríguez, D., Schwab, M.: 'Magnetic removal of cobalt from waste water by ferrite co-precipitation', *Procedia Mater. Sci.*, 2012, **1**, pp. 644–650
- [65] Sharma, Y.C., Srivastava, V., Singh, V.K., *et al.*: 'Nano-adsorbents for the removal of metallic pollutants from water and wastewater', *Environ. Technol.*, 2009, **30**, (6), pp. 583–609
- [66] Chang, Y.C., Chang, S.W., Chen, D.H.: 'Magnetic chitosan nanoparticles: Studies on chitosan binding and adsorption of Co(II) ions', *React. Funct. Polym.*, 2006, **66**, (3), pp. 335–341
- [67] Huang, J., Fang, F., Wang, L., *et al.*: 'Removal of cobalt ions from aqueous solution by Ag/Fe bimetallic nanoparticles', *Desalin. Water Treat.*, 2015, **56**, (8), pp. 2127–2134

- [68] Uzum, C., Shahwan, T., Eroglu, A.E., *et al.*: 'Application of zero-valent iron nanoparticles for the removal of aqueous Co^{2+} ions under various experimental conditions', *Chem. Eng. J.*, 2008, **144**, (2), pp. 213–220
- [69] Zari, H., Ghasem, R.B., Yousef, G.: 'Sonication enhanced removal of nickel and cobalt ions from polluted water using an iron based sorbent', *J. Chem.*, 2013, **2013**, pp. 1–5
- [70] Siva, S., Sudharsan, S., Sayee, K.R.: 'Selective Co(II) removal from aqueous media by immobilizing silver nanoparticles within a polymer matrix through a formaldehyde cross linking agent', *RSC Adv.*, 2015, **5**, (30), pp. 23340–23349
- [71] El-Latif, M.A., Elkady, M.F.: 'Kinetics study and thermodynamic behavior for removing cesium, cobalt and nickel ions from aqueous solution using nano-zirconium vanadate ion exchanger', *Desalination*, 2011, **271**, (1), pp. 41–54
- [72] Gollavelli, G., Chang, C.C., Ling, Y.C.: 'Facile synthesis of smart magnetic graphene for safe drinking water: heavy metal removal and disinfection control', *ACS Sustain. Chem. Eng.*, 2013, **1**, (5), pp. 462–472
- [73] Cao, C.Y., Cui, Z.M., Chen, C.Q., *et al.*: 'Ceria hollow nanospheres produced by a template-free microwave-assisted hydrothermal method for heavy metal ion removal and catalysis', *J. Phys. Chem.*, 2010, **114**, (21), pp. 9865–9870
- [74] Pandey, S., Mishra, S.B.: 'Organic-inorganic hybrid of chitosan/organoclay bionanocomposites for hexavalent chromium uptake', *J. Colloid. Interf. Sci.*, 2011, **361**, (2), pp. 509–520
- [75] Bhaumik, M., Maity, A., Srinivasu, V.V., *et al.*: 'Removal of hexavalent chromium from aqueous solution using polypyrrole-polyaniline nanofibers', *Chem. Eng. J.*, 2012, **181**, pp. 323–333
- [76] Hu, J., Wang, S.W., Shao, D.D., *et al.*: 'Adsorption and reduction of chromium (VI) from aqueous solution by multi-walled carbon nanotubes', *Open Environ. Pollut. Toxicol. J.*, 2009, **1**, pp. 66–73
- [77] Gupta, V.K., Agarwal, S., Saleh, T.A.: 'Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes', *Water Res.*, 2011, **45**, (6), pp. 2207–2212
- [78] Parida, K., Mishra, K.G., Dash, S.K.: 'Adsorption of toxic metal ion Cr(VI) from aqueous state by TiO_2 -MCM-41: Equilibrium and kinetic studies', *J. Hazard. Mater.*, 2012, **241**, pp. 395–403
- [79] Duranoğlu, D., Kaya, I.G., Beker, U., *et al.*: 'Synthesis and adsorption properties of polymeric and polymer-based hybrid adsorbent for hexavalent chromium removal', *Chem. Eng. J.*, 2012, **181**, pp. 103–112
- [80] Gervas, C., Mubofu, E.B., Mdoe, J.E., *et al.*: 'Functionalized mesoporous organo-silica nanosorbents for removal of chromium (III) ions from tanneries wastewater', *J. Porous Mat.*, 2016, **23**, (1), pp. 83–93
- [81] Khayat, S.Z., Khayat, S.F.: 'Selective removal of lead (II) ion from wastewater using superparamagnetic monodispersed iron oxide (Fe_3O_4) nanoparticles as a effective adsorbent', *Int. J. Nanosci. Nanotechnol.*, 2013, **9**, (2), pp. 109–114
- [82] Nassar, N.N.: 'Rapid removal and recovery of Pb(II) from wastewater by magnetic nanoadsorbents', *J. Hazard. Mater.*, 2010, **184**, (1), pp. 538–546
- [83] Idris, A., Ismail, N.S.M., Hassan, N., *et al.*: 'Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution', *J. Ind. Eng. Chem.*, 2012, **18**, (5), pp. 1582–1589
- [84] Liu, X., Hu, Q., Fang, Z., *et al.*: 'Magnetic chitosan nanocomposites: a useful recyclable tool for heavy metal ion removal', *Langmuir*, 2009, **25**, (1), pp. 3–8
- [85] Khedr, M.A., Waly, A.I., Hafez, A.I., *et al.*: 'Synthesis of modified chitosan-montmorillonite nanocomposite', *Aust. J. Basic Appl. Sci.*, 2012, **6**, (6), p. 216
- [86] Cheraghali, R., Tavakoli, H., Sepehrian, H.: 'Preparation, characterization and lead sorption performance of alginate-SBA-15 composite as a novel adsorbent', *Sci. Iran.*, 2013, **20**, (3), pp. 1028–1034
- [87] Meng, X., Hongjie, W., Di, L., *et al.*: 'Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: adsorption behavior and mechanism', *J. Environ. Sci.*, 2012, **25**, (3), pp. 479–486
- [88] Qing, S., Bingcai, P., Bingjun, P., *et al.*: 'Fabrication of polymer-supported nanosized hydrous manganese dioxide (HMO) for enhanced lead removal from waters', *Sci. Total Environ.*, 2009, **407**, (21), pp. 5471–5477
- [89] Kanchana, V., Gomathi, T., Geetha, V., *et al.*: 'Adsorption analysis of Pb(II) by nanocomposites of chitosan with methyl cellulose and clay', *Der Pharm. Lett.*, 2012, **4**, pp. 1071–1079
- [90] Zhang, Q., Du, Q., Hua, M., *et al.*: 'Sorption enhancement of lead ions from water by surface charged polystyrene-supported nano-zirconium oxide composites', *Environ. Sci. Technol.*, 2013, **47**, (12), pp. 6536–6544
- [91] Sun, W., Leilei, L., Chuannan, L., *et al.*: 'Synthesis of magnetic graphene nanocomposites decorated with ionic liquids for fast lead ion removal', *Int. J. Biol. Macromol.*, 2016, **85**, pp. 246–251
- [92] Culita, D.C., Simonescu, C.M., Patescu, R.E., *et al.*: 'o-Vanillin functionalized mesoporous silica-coated magnetite nanoparticles for efficient removal of Pb (II) from water', *J. Solid State Chem.*, 2016, **238**, pp. 311–320
- [93] Jin, X., Yu, C., Li, Y., *et al.*: 'Preparation of novel nano-adsorbent based on organic-inorganic hybrid and their adsorption for heavy metals and organic pollutants presented in water environment', *J. Hazard. Mater.*, 2011, **186**, (2), pp. 1672–1680
- [94] Gupta, V.K., Agarwal, S., Saleh, T.A.: 'Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal', *J. Hazard. Mater.*, 2011, **185**, (1), pp. 17–23
- [95] Saleh, T.A., Gupta, V.K.: 'Column with CNT/magnesium oxide composite for lead (II) removal from water', *Environ. Sci. Pollut. Res.*, 2012, **19**, (4), pp. 1224–1228
- [96] Jyoti, C., Rajeev, K.: 'Removal of cadmium ion from water/wastewater by nano-metal oxides: A review', *Water Qual. Expo. Health*, 2014, **5**, (4), pp. 215–226
- [97] Khan, S., Cao, Q., Zheng, Y.M., *et al.*: 'Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China', *Environ. Pollut.*, 2008, **152**, (3), pp. 686–692
- [98] Gong, J., Chen, L., Zeng, G., *et al.*: 'Shellac-coated iron oxide nanoparticles for removal of cadmium(II) ions from aqueous solution', *J. Environ. Sci.*, 2012, **24**, (7), pp. 1165–1173
- [99] Ada, R.C., Ana, G., Edgar, G., *et al.*: 'Potential use of CeO_2 , TiO_2 and Fe_3O_4 nanoparticles for the removal of cadmium from water', *Desalin. Water Treat.*, 2012, **41**, (1-3), pp. 296–300
- [100] Xie, X., Gao, L.: 'Effect of crystal structure on adsorption behaviors of nanosized TiO_2 for heavy-metal cations', *Curr. Appl. Phys.*, 2009, **9**, (3), pp. S185–S188
- [101] Visa, M., Duta, A.: ' TiO_2 /fly ash novel substrate for simultaneous removal of heavy metals and surfactants', *Chem. Eng. J.*, 2013, **223**, pp. 860–868
- [102] Wan, S., Zhao, X., Lv, L., *et al.*: 'Selective adsorption of Cd(II) and Zn(II) ions by nano-hydrous manganese dioxide (HMO)-encapsulated cation exchanger', *Ind. Eng. Chem. Res.*, 2010, **49**, (16), pp. 7574–7579
- [103] Al-Khaldi, F.A., Abu-Sharkh, B., Abulkibash, A.M., *et al.*: 'Cadmium removal by activated carbon, carbon nanotubes, carbon nanofibers, and carbon fly ash: a comparative study', *Desalination Water Treat.*, 2015, **53**, (5), pp. 1417–1429
- [104] Ali, Z., Ahmad, R., Khan, A.: 'Functionalized nanospheres for efficient sequestration of cadmium ions', *RSC Adv.*, 2014, **4**, (91), pp. 50056–50063
- [105] Vuković, G.D., Marinković, A.D., Čolić, M., *et al.*: 'Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes', *Chem. Eng. J.*, 2010, **157**, (1), pp. 238–248
- [106] Feng, Y., Gong, J.L., Zeng, G.M., *et al.*: 'Adsorption of Cd(II) and Zn(II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents', *Chem. Eng. J.*, 2010, **162**, (2), pp. 487–494
- [107] Roy, A., Bhattacharya, J.: 'Removal of Cu (II), Zn (II) and Pb (II) from water using microwave-assisted synthesized maghemite nanotubes', *Chem. Eng. J.*, 2012, **211**, pp. 493–500
- [108] Tofighy, M.A., Mohammadi, T.: 'Adsorption of divalent heavy metal ions from water using carbon nanotube sheets', *J. Hazard. Mater.*, 2011, **185**, (1), pp. 140–147
- [109] Stetiya, M.H., Wang, J.J.: 'Zinc and cadmium adsorption to aluminum oxide nanoparticles affected by naturally occurring ligands', *J. Environ. Qual.*, 2014, **43**, (2), pp. 498–506
- [110] Huang, W., Zhou, M.: 'SDS coated Fe_3O_4 magnetic nanoparticles for adsorption of Cd^{2+} and Zn^{2+} in aqueous solution', *J. Environ. Eng.*, 2012, **6**, (4), pp. 1251–1256
- [111] Alkhami, A., Tehrani, M.S., Bagheri, H.: 'Simultaneous removal of heavy metal ions in wastewater samples using nano-alumina modified with 2, 4-dinitrophenylhydrazine', *J. Hazard. Mater.*, 2010, **181**, (1), pp. 836–844
- [112] Khalek, M.D., Mahmoud, G.A., Kelesh, N.A.E.: 'Synthesis and characterization of poly-methacrylic acid grafted chitosan-bentonite composite and its application for heavy metals recovery', *Chem. Mater. Res.*, 2012, **2**, pp. 1–12
- [113] Sezgin, N., Sahin, M., Yalcin, A., *et al.*: 'Synthesis, characterization and the heavy metal removal efficiency of MFe_2O_4 (M=Ni, Cu) Nanoparticles', *Ekol*, 2013, **22**, (89), pp. 89–96
- [114] Dargahi, A., Golestanifar, H., Darvishi, P., *et al.*: 'An investigation and comparison of removing heavy metals (lead and chromium) from aqueous solutions using magnesium oxide nanoparticles', *Pol. J. Environ. Stud.*, 2016, **25**, (2), pp. 557–562
- [115] Farrukh, A., Akram, A., Ghaffar, A., *et al.*: 'Design of polymer-brush-grafted magnetic nanoparticles for highly efficient water remediation', *ACS Appl. Mater. Interf.*, 2013, **5**, (9), pp. 3784–3793