

Nano adsorbents review: a method for the separation of heavy metals from waste water.

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Abstract

Owing to their capacity to create toxic havoc in the metabolism of flora and fauna alike, removal of heavy metals from polluted waters is of paramount importance. The use of sophisticated micro methods, such as creative variations of surface chemistry, basic concepts of chemistry and nanotechnology, opens up especially attractive horizons for the management of water supplies polluted by heavy metals. In order to eliminate a wide range of defiant heavy metal pollutants in waste water, the acquired result of surface engineered nano adsorbent developed has successfully shown to demonstrate rapid adsorption rate and superior sorption performance. The use of these materials in water treatment results in dramatically enhanced performance characteristics such as wide surface area, good volumetric capacity, extra shelf-life, less mechanical tension, reliability with excellent sorption activity under operating conditions, no secondary emissions, solid chelating capability and fast recovery and reuse. This analysis aims to act as a one-stop-reference by pulling together all recent research work on the synthesis of nanoparticles and their advantages as adsorbents in the treatment of contaminated heavy metal wastewater so far, providing researchers with a deep perspective and bridging the gap between past, pre-polluted wastewater.

Key words: MWCNTs , Nano Adsorbents , MNPs

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I. Introduction

In different bodies of water, such as river streams and seas, humongous volumes of waste water are released. There are several organic and inorganic elements in urban waste water. While the former contains sugars, lignin, fats, proteins, etc., arsenic, cadmium, chromium, copper, lead, mercury, zinc and so on are found in the latter [1]. The effect of its release into the atmosphere is extreme and due to this release, which in turn impacts the food chain, the sea life is directly impacted. It is therefore important to treat water prior to its release into the environment [2]. A major improvement in effort was made to build a productivity. The removal from water emitted from tanneries, electroplating systems, metal and wood processing industries of hazardous heavy metals such as Cr(VI), Cd(II), Cu(II), As(I), Pb(II) and Zn(II) is a prime necessity as discharge of untreated effluents results in serious environmental and public health problems.

Presently, a variety of methods for water management, such as,

The WHO has developed precipitation [4], ion exchange [5], reverse osmosis [6], membrane filtration [7] and oxidation [8] as standard controlled protocols for the release of effluent into the setting. However, these traditional methods have several flaws, such as the creation of poisonous sludge, high pH sensitivity, corrosion issues, and even some of the processes that make the heavy metal removal process unproductive [3, 9-14]. On the other hand, due to its low cost, high performance and ease of operation, the adsorption technology is considered to be the most promising way of extracting even trace quantities of heavy metal ions from effluents [3, 9-15]. While conventional sorbents are able to extract heavy metals from wastewater, their subtle ability and efficiency of sorption restrict their applications in concentrated solutions, which it called for the creation of different cost-effective adsorbents to eliminate heavy metals from metal-contaminated waste water [9, 13]. Nanomaterials have been developed as a novelty to allow effective removal of heavy metal ions from waste water [10, 14, 16] in order to resolve the problems posed by the use of these traditional sorbents. As possible adsorbents for environmental remediation, emission control and a broad variety of other bioprocess-based industrial applications, nifty nanocomposites of metal oxides, cement, and polymers were formed [10, 14, 16, 17]. Their specific characteristics, such as high surface-to-volume ratio, surface alteration, biocompatibility, reversibility and relatively low cost, have allowed them to gain increasing prominence as effective adsorbents [10, 14, 16-21]. The bulk of metal nano adsorbents analyzed are nanoparticles of iron oxide, generally referred to as magnetic nanoparticles (MNPs) [18, 19]. The presence of iron provides them with magnetic properties that

allow them to be easily isolated using simple magnetic fields from waste water. They are also relatively less toxic and inexpensive. However, if these MNPs are too limited in number, there are some limits where the separation can require strong external magnetic fields. This adds up to the expense of the whole procedure [18, 19]. Other metal oxide nanoparticles, including titanium, cerium, and zinc, are present. They are cheaper and, when reduced to the nanoscale, have larger surface area. The metals, though, appear to be brittle at such a small scale and begin to agglomerate, which could impair their ability to adsorb other heavy metals in waste water. Several applications have seen the use of activated carbon as an effective adsorbent. Carbon nanotubes (CNTs) are now being tested for their ability to strip heavy metals from waste water as an adsorbent [20–22]. They have high-energy carbon binding sites in them, which are useful for the purpose of adsorption [20]. However, questions have been raised about the toxicity of CNTs and their effects on human health. There is a detrimental effect on the atmosphere and restricted selectivity of different adsorbates [21, 22]. In order to solve these issues, new nano adsorbents are being researched in order to introduce less toxic carbon adsorption power. Polymer nano sorbents have also been used for wastewater treatment applications and have strong adsorption properties, such as good pore sizes and compact functional groups that improve their selectivity. However, there are drawbacks due to certain inadequacies in their molecular structure. It is difficult to mix them with reasonable selectivity with the target adsorbate and to recycle them laboriously if they are of low purity [14].

Bare nanoparticles, vulnerable to atmospheric oxygen oxidation, are easily aggregated in aqueous environments that have undergone surface modification of these nanoparticles for stabilization and subsequent adsorbent applications [23]. In such surface-modified adsorbents, the molecular composition is substantially different from the center of the nanoparticles. Modifications of the surface layer of nanoparticles impart properties that promote enhanced adsorption [10, 14, 16–19]. Size regulation and polydispersity control are also essential parameters that need to be considered during the creation of novel separation methods, as these measurements play a significant role in deciding the properties of nanoparticles [20–22]. This paper provides a study of recent scientific advances in the usage of different heavy metal removal nanoparticles As(V), Cu(II), Hg(II), Co(II), Cr(VI), Pb(II) and Cd(II) (II) from Water/wastewater.

II. For the removal of various metals, nanoparticles

2.1 Arsenic Elimination

Natural waters typically contain low amounts of total arsenic in two distinct ionic states, pentavalent arsenate [As(V)] and/or trivalent arsenite [As(III)] in the 1–10 µg/L [24] concentration range. Because of agricultural processes such as mining and smelting, arsenic pollution occurs and can also be found in coal-fired power plants. Arsenic contamination can lead to cancers of the lungs, skin, kidney and bladder and to neurological abnormalities, lack of appetite, fatigue, changes in pigmentation and human hyperkeratosis [24, 25]. Provides up-to-date descriptions of the metal nano adsorbents for arsenic removal in water/wastewater provided in table 1. The use of MNPs for the separation of heavy metal ions from waste water has been thriving. This further facilitates fast isolation using a simple magnetic field from the reaction mixture. Haematite (alpha-Fe₂O₃), magnetite (Fe₃O₄) and goethite (alpha-FeOOH) nanoparticles synthesized by ferrihydrate precipitation methods have been shown to be pH-dependently efficient in extracting As(V) ions [26]. Chen et al. [25] prepared, on the surface, porous ultrafine alpha-Fe₂O₃ nanoparticles with high-affinity hydroxyl groups used for As(V) removal in wastewater. Problems of weak aggregation and isolation of adsorbents, however, were present. The preparation of the mesoporous magnetic γ -Fe₂O₃ nanostructures by atmospheric calcination of composite Fe₃O₄/phenol-formaldehyde resin structures [27] resolved these problems. Ghosh et al. [28] modified goethite nanoparticles with synthesized hydrazine sulphate to extract As(V) from waste water. With an adsorbent dosage of 6 g/L, 99 percent of As(V) could be extracted from an initial As(V) concentration of 50 mg/L with a contact time of 240 min. The desorption analysis showed that when treated with dilute sodium hydroxide solution of pH 13.0, the loaded adsorbent could be regenerated well without loss of adsorption ability.

Fe₃O₄ nanoparticles coated with ascorbic acid were synthesized and assessed as an adsorbent to extract arsenic from waste water. The removal percentage for As(III) is 50 percent at an initial arsenic concentration of 0.1 mg/L, while that for As(V) is 30 percent during the initial adsorption period of 30 min [29]. The use of binary metal oxide nanoparticles is another example of arsenic removal by adsorption. The synthesis of ultrafine superparamagnetic magnesium ferrite nanocrystallites by doping Mg(II) into alpha-Fe₂O₃ using a solvothermal method has achieved simple magnetic separation. Increased As(III) and As(V) adsorption was observed at a low magnesium concentration of 10 percent. Arsenic equilibrium concentration due to modification of the alpha-Fe₂O₃ microstructure by Mg(II) [30].

Nabi et al. [31] synthesized, by the sol-gel process, pure and iron-doped TiO₂ particles and tested them for arsenic removal from water. By avoiding the increase in its grain size and thereby preserving the necessary surface area for the adsorption process, iron-doping helps to increase the adsorption potential of the TiO₂ nanoparticles. Titanium nanoparticles with a high affinity to arsenic ions were synthesized with certain modifications by the liquid impregnation method [32]. For both forms of pure and metal-doped titania

nanoparticles with 2 mg/L as the initial metal concentration in solution, over 90 percent of As(III) removal was observed in batch experiments. Consequently, under different operating conditions, the impact of fixed bed columns of nanoparticles coated on glass beads was also analyzed for As(III) elimination. It is possible to recycle nanoparticles simply and effectively by regenerating the column using a 10 percent NaOH solution. Martinson et al.[33] synthesized and examined CuO nanoparticles in order to extract As(III) and As(V) from waste water. In addition to the full adsorption potential for As(III) and As(V), 90% of As(III) and 99% of As(V) were extracted within 30 and 5 minutes, respectively, at an initial concentration of 0.9 mg/L with a 2 g/L load of CuO nanoparticle. Studies of X-ray photoelectron spectroscopy (XPS) have shown that As(III) is oxidized and then adsorbed on the surface of CuO in the form of As(V).

As a nano sorbent for the removal of As(III) and As(V) from water[34], hydrous cerium oxide (HCO) nanoparticles were used. Within 30 minutes, about 87 percent of As(III) and 83 percent of As(V) were extracted from water samples containing initial concentrations of 124 µg/L As(III) and 92 µg/L As(V) when the loading concentration of the HCO nanoparticle is 0.02 g/L. Liu et al. [35] synthesized and used porous nanoflakes of magnesium oxide (MgO) to extract As(III) from aqueous solutions. By the interaction of MgO nanoflakes with water, the elevated As(III) sorption potential was based on the in situ formation of Mg(OH)₂. These nanoflakes were also able to react with As(III) to form a compound of magnesium-arsenite, which in turn contributes to MgO nanoflakes' high As(III) sorption power. With an initial As(III) concentration of 94.9 mg/L and an equivalent load of 0.5 g/L of MgO nanopowders and industrial MgO powders, 92% of As(III) was withdrawn using the former within 360 minutes, although only one third of As(III) was withdrawn using the latter. This suggests that for the elimination of arsenic from polluted water, MgO nanoflakes may be used as possible adsorbents. The possible impact on the removal of arsenic by CuO nanoparticle was calculated and the maximum sorbent was extracted at a contact period of 300 min at a wider pH range of 25 °C[36]. Approximately 100% of Cu(II) was extracted and the nano adsorbent could be regenerated and reused using NaOH effectively. Hang et al. [37] carried out a simple hydrothermal process followed by heat treatment to synthesize 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. Within 10 min of contact with 0.15 g/L of ZrO₂·xH₂O, roughly 66 percent of arsenic was eliminated when the equilibrium concentration of As(III) was 6.55.

A µg/L. In a related analysis by Cui et al.[38], the amount of arsenic adsorbed by ZrO₂·xH₂O nanoparticles under low equilibrium arsenic concentrations was approximately 0.92 mg/g for As(III) and 5.2 mg/g for As(V), respectively. Around 92 percent of As(V) was adsorbed with a ZrO₂ loading concentration of 0.02 g/L in 30 minutes with an initial As(V) concentration of 0.089 mg/L. For the separation of As(III) and As(V) from waste water [39], a composite of multi-wall CNTs and manganese dioxide (MWCNT/MnO₂) was made. The presence of MnO₂ in the nanocomposite enables As(III) to As(V) to be transformed, and can then be quickly consumed by the MWCNT. The MnO₂ oxidizes As(III) during the arsenic removal process and itself is lowered from Mn(IV) to Mn(II). This nanoadsorbent blends, thus, Oxidative properties of MnO₂ with MWCNT adsorption properties for the efficient separation from waste water of arsenic[39]. MWCNT-zirconia nanohybrid (MWCNT-ZrO₂) has been synthesized and researched for the isolation of arsenic from waste water as a potential adsorbent. A noteworthy benefit of this adsorbent is that the adsorption mechanism is independent of pH and the adsorption potential for both As(III) and As(V) is much higher compared to that of MWCNTs coated with iron oxide[40]. With Chen et al.[41] stated that for adsorption of arsenic at pH 6.9 and room temperature, multi-walled boron nitride nanotubes (BNNTs) functionalized with MNPs were used. It was hypothesized that the mechanism for As(V) adsorption was an interplay of chemical complexation and physical electrostatic attraction with a chemisorption preference. The removal potential shows only minor variations in the pH range from 5.0 to 11.0, suggesting that the functionalized BNNT could be used for As(V) adsorption at a broad pH range and could be ideal for realistic applications at near-neutral pH under normal waste water conditions [41].

2.2 Copper elimination

Copper plays a significant part in the production of hormones, muscles, and bones in humans. It also, though, exhibits toxic effects and, when ingested in excess, is a carcinogen. It may also lead to liver deposition, which in turn results in vomiting, fever, nausea, trouble breathing, stomach pain, liver and kidney failure, and eventually human gastrointestinal bleeding [42]. 50 µg/L has been defined by the US EPA (1991) as the permitted limit for copper in water. Table 1 lists the numerous nano adsorbents analyzed for Cu(II) elimination. For the adsorption of copper from aqueous solutions, synthetic nanoFe₃O₄ particles have been studied. With a contact time of 60 min, a total of 97.8 percent of Cu(II) was extracted at an initial copper concentration of 1.07 g/L [43]. To generate amino-functionalized MNPs, primary amino groups were formed over the MNP surface using aminopropyl triethoxysilane. The functionalized nano adsorbents generated were able to extract 98% of copper from both tainted river water and tap water [44]. Li et al.[45] addressed the preparation, using the sol-gel process, of amine functionalized magnetic silica nanoparticles. At lower PH, amine

group protonation decreases the efficiency of adsorption, while heavy complexation occurs between Cu(II) and the free amine group at higher pH, thus increasing adsorption. This then makes MNPs attractive for the reduction of heavy metals in waste water.

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

Adsorbent	Preparation	Size	Surface area	Adsorbate	Adsorption capacity	Time (min)	pH	Temperature	Kinetic model	Isotherm	References
		range (nm)	(m ² /g)		(mg/g)						
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]
Multiwalled 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 K	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	[50]
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 Polymerization	~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 adsorption ability, while at higher pH, Cu(II) and the free amine group form a strong matrix, increasing adsorption. As a result, MNPs are appealing for heavy metal removal of wastewater. Copper removal from water was studied using Fe₃O₄ nanoparticles coated with sodium dodecyl sulphate (SDS–Fe₃O₄ NPs).

Because of the presence of charges in the particles, the heavy metal was likely removed through electrostatic attraction and ion exchange. The rate of adsorption was also found to be fast [46]. Neeraj and his colleagues [47] used cMNPs to sequester 99 percent of 100 mg/L Cu(II) ions in aqueous solution using an adsorbent dose of 2.0 g/L and a contact time of 30 minutes. The saturated cMNPs have the potential to be

conveniently regenerated using 0.1 N HCl and 0.1 N NaOH in a sequential acid base treatment, with the regenerated adsorbent exhibiting exceptional reusability (>95%) over five consecutive cycles.

Zhou et al. [48] investigated cMNPs modified with -ketoglutaric acid in order to improve adsorption performance and achieve a maximum adsorption potential for Cu(II) ions. For an initial Cu(II) concentration of 200 ppm and a 7 g/L dosage of the adsorbent, the Cu(II) elimination percentage was found to be 89.75 percent. The solvothermal approach was used to make porous ZnO nanoplates, which were then annealed. [49] Ethylene glycol was used to improve its morphology. Cu(II) ions were found to have a high adsorption potential on the nanoplates. For the use of

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 Titanium oxide Iron oxide	–	–	–	Cd(II)	49.1 101.1 12.2	4320	–	–	Pseudo second order	Freundlich	[99]

Rafiq et al. [50] prepared magnesium and zinc oxide nanoadsorbents to remove copper from electroplating industrial wastewater. With adsorbent dosages of 0.3 and 0.2 g for zinc and MgO nanoadsorbents, respectively, both adsorbents were capable of extracting 92–98 percent of copper. When the two nanoadsorbents were matched, MgO outperformed the other.

Because of the hollow, layered cylindrical structure of graphene material, which provides them with usually high specific surface areas, superior mechanical power, thermal and chemical stabilities, and respectively elevated sorption capacity for various heavy metals removal [20–22], the use of CNTs as nanosorbent has recently attracted a lot of interest. CNTs were made using the chemical vapour deposition process, which included the use of acetylene gas.

The carbon source was carbon, and the oxidation safety gas was argon. The nanotubes were then functionalized using nitric acid oxidation. The CNTs treated with nitric acid serve as an efficient adsorbent, with a cumulative removal of Cu(II) of 98.39 percent in wastewater. Salam et al. [51] created a chitosan/ MWCNTs composite for water adsorption of Cu(II) ions. Copper ions are highly adsorbed even in the presence of other heavy metals such as Cd(II), Zn(II), and Ni(II). This is attributed to the copper ion's tendency to quickly reduce into the nanoadsorbent's carbonaceous surface after being drawn to the active site. The reduced copper then leaves the rock, making room for other ions to adsorb. Sheng et al. [52] used MWCNTs for copper adsorption and investigated the role of humic acid (HA) and fulvic acid (FA) in the process. Both of these acids were observed to increase copper adsorption at lower pH while showing less adsorption at higher pH. Because of the high complexation potential of the surface adsorbed HA/FA at low pH, both HA and FA, which are negatively charged, get adsorbed on to the positively charged MWCNTs, resulting in stronger copper adsorption [52]. The removal of heavy metals, especially copper, from waste water was fabricated and tested using a radiation-induced chitosan/(acrylamidoglycolic acid-co-acrylic acid) magnetic nanopolymer. The MNPs are encapsulated in a hydrogel network that aids in the adsorption process and is easily isolated due to their magnetic properties [53].

2.3 Cobalt removal

Electroplating, petrochemical, dye and ink industries, as well as alloys of iron and other metals, have all used cobalt. As a result, water pollution of cobalt is more common in these industries. Coal burning releases it into the atmosphere as well [63]. Cobalt is less harmful than the majority of other metals used in wastewater. It induces fatigue, asthma, stomach disorders, and thyroid and liver damage at higher concentrations [63, 64]. For the removal of cobalt from aqueous solution, a variety of nanoadsorbents have been used, the adsorption conditions of which are described in Table 1.

Co(II) ion elimination from aqueous fluids was achieved using MNPs [19, 43, 65–67]. At pH 5.4, 99.2 percent of Co(II) was removed in 10 minutes with a dose rate of 2.57 g of adsorbent/L of aqueous solution [43]. Huang et al. [67] used a simple two-step method to make Ag/Fe bimetallic nanoparticles, and polyvinyl pyrrolidone was used to protect the nanoparticles from oxidation. These nanoparticles were used as adsorbents to strip 99 percent Co(II) from an aqueous solution in less than 5 minutes. The borohydride reduction process was used to make nanosized zero-valent iron for removing aqueous Co(II) ions at concentrations ranging from 1

to 1000 mg/L [68]. The rapid absorption of Co(II) ions was observed. With these nanoparticles, rapid absorption of Co(II) ions was observed as the pH increased. Because of their high adsorption potential, the nanoparticles can be regenerated and found to be useful for the removal of Co(II). In the presence of zero valence iron (ZVI) nanoparticles, Zari et al. [69] investigated the impact of sonication time on the removal of Co(II) from wastewater. With sonication, the overall removal efficiency for Co(II) is about 59 percent after 30 minutes, which is higher than the nanoparticle's removal efficiency without sonication. This is because sonication breaks down zero valence nanoclusters into an ideal scale with a higher surface to volume ratio for Co(II) ion adsorption. The nanoparticles, on the other hand, appear to cluster and grow in size at very high sonication times. The kinetic mechanism of electron transfer from ZVI nanoparticles to Co(II) ions necessitates a 30-minute sonication period. Siva et al. [70] used *Cyperus rotundus* grass extract to synthesise silver nanoparticles (AgNPs), which were then used to prepare phenol–formaldehyde resin (PFR) encapsulated silver nanocomposites (PFR–AgNPs). Experiments were conducted in a column with a fixed-bed glass column. For the elimination of Co(II) ion solution, a column of 3.5 g PFR–AgNPs was used. The adsorption mechanism was exothermic, and the expended adsorbent could be regenerated with a solution of 5 percent (w/w) NaCl. The highest adsorbent rate of 8.27 mg/g of cobalt was extracted using alkaline treated sol–gel precipitation approach compared to the other methods [71]. Nano-zirconium vanadate ions are prepared to extract cobalt using three strategies: homogeneous precipitation, hydrothermal synthesis, and sol–gel precipitation.

2.4 Lead abatement

If Pb(II) concentrations in drinking water exceed the 5 ng/mL level, it is one of the most dangerous heavy metals, causing anaemia, encephalopathy, hepatitis, nephritic syndrome, and other health problems. As a result, the Pb(II) ions in wastewater must be removed before it can be used again [81]. The nanosorbents investigated for the reduction of lead ions in wastewater are mentioned in Table 1.

MNPs are low-cost adsorbents with a high potential for adsorption of Pb(II) ions from water, a quick adsorption rate, easy separation aided by a magnetic field, and easy regeneration [81–84]. Chemical co-precipitation was used to make superparamagnetic polyethylene glycol coated MNPs for the removal of Pb(II) from wastewater. Magnetic nanosorbents adsorb quickly, and equilibrium was reached at pH 6.0 in less than 10 minutes [82]. The rate of adsorption increased with increasing temperature, indicating endothermic adsorption, and the optimum pH for Pb(II) adsorption was about 5.5. The researchers created magnetically separable alginate nanobeads, which were found to be capable of extracting 92.5 percent Pb(II) from wastewater at pH 7.0 [83]. For an initial Pb(II) concentration of 400 mg/L, the optimum pH was found to be 7.0, at which maximal adsorption was 92.5 percent. Desorption experiments demonstrate that the adsorbent can be regenerated up to the fifth cycle with no decrease in adsorption volume. Pb(II) ions were isolated from magnetic chitosan nanocomposites based on amine functionalised MNPs with a maximum efficiency of 94.6 percent. However, as opposed to MNPs, the nanocomposites had a lower adsorption. The adsorption increases as the pH rises until it reaches 6.0 [84]. The maximum efficiency of 94.6 percent Pb(II) ions was extracted from magnetic chitosan nanocomposites based on amine functionalised MNPs. In comparison to MNPs, though, the nanocomposites had a lower adsorption. Up to pH 6.0, adsorption improves. Cheraghali et al. [86] produced alginate-Santa Barbara Amorphous-15 by encapsulating the nanoporous SBA-15 in a calcium alginate biopolymeric matrix. The endothermic and random existence of adsorption was suggested by the measured values of enthalpy, entropy, and Gibbs free energy (G, H, and S). HMO nanoparticles were made by a redox reaction of potassium permanganate and hydrogen peroxide and were used as adsorbents to remove Pb(II) from wastewater effectively [87]. The adsorption mechanism was random and endothermic, with a measured activation energy of 38.23 kJ/mol for Pb(II) adsorption by HMO. PbOH⁺ was found to be the most often adsorbed speciation, and the final chemical state of Pb(II) on the surface of HMO was found to be identical to PbO. Researchers also concentrated on impregnating HMO nanoparticles onto porous cation exchange resins to increase the applicability of nanoparticles in heavy metal removal [87, 88]. Kanchana et al. [89] used chitosan, methyl cellulose, and kaolin clay nanocomposites to extract Pb(II) ions from simulated wastewater. As compared to methyl cellulose composites, nanochitosan kaolin clay composites were found to be a more efficient adsorbent. It was clear that a 6 g/L adsorbent concentration was used to treat wastewater with a 300-minute contact period at pH 6.0. Encapsulation of ZrO₂ nanoparticles into spherical macroporous polystyrene beads covalently bound with surface groups such as charged sulfonate groups resulted in hybrid nanomaterials. [number 90] Zr-MPS, Zr-MPN, Zr-MPC, and Zr-GAC are the acronyms for these elements. The sorption capacities of these nanomaterials for the removal of Pb(II) were investigated, and it was discovered that the declining capacities were Zr-MPS > Zr-MPN > Zr-GAC > Zr-MPC. The optimal pH for Zr-MPS adsorption is between 5 and 6.5

Due to their suitable functional groups and wide surface area, the combination of magnetic chitosan and graphene oxide was used to isolate Pb(II) from polluted waste water.

The above incorporated adsorbent could be reused successfully for six consecutive cycles, lowering the cost and improving the nanosorbent's regeneration property [91]. To investigate the adsorption potential of Pb(II) from waste water, researchers created mesoporous silica-coated particles that were chemically treated with o-vanillin. It was discovered that 80–90% of adsorption occurs in 60 minutes [92]. The overall removal of Pb(II) by the combination of polyacrylic acid/acrylonitrile-attapulgitic nanoparticles prepared by polymerisation reaction is 96.6 percent Pb(II) removal with a power of 109.9 mg/g at their optimum pH 5.0– 6.0, respectively [93].

MWCNTs with an alumina coating is designed to remove lead from wastewater. The van der Waals interaction between carbon atoms in MWCNT sheets and Pb(II) or the electrostatic attraction between positive lead ions and the negative surface of the MWCNT portion of the adsorbent may be the mechanism of adsorption. The electrostatic interaction between Pb(II) and the negatively charged pairs of atoms enhances the adsorption even further. On the alumina surface, there are charged oxygen atoms [94]. Manganese dioxide-coated MWCNT nanocomposite for Pb(II) removal from wastewater was studied by Saleh and Gupta [95]. Again, the removal process is dependent on interactions between the lead ions and the active sites on the composite adsorbent's surface. The manganese oxides on the adsorbent surface make it strongly negative, allowing the positive lead ions to quickly attract them and thereby enhancing the adsorption mechanism.

2.5 Chromium removal

Electroplating, leather tanning, pigment, photographic, and cement industries are the most important causes of chromium emission. Several manufacturing effluents contain chromium, which accumulates in the food chain and can cause serious health problems ranging from skin irritation to lung cancer. As a result, it is important to remove Cr(VI) from industrial effluents until they are discharged into the atmosphere [19]. For the reduction of chromium ions in wastewater, various forms of nanoadsorbents have been investigated, as seen 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, In a batch adsorption method, ethylenediamine-modified cMNPs resin removes ions from aqueous solution. The sorbents were successfully regenerated using 0.1 N NaOH solutions, and the maximal adsorption was observed at pH 2.0. Cao et al. [73] used a template-free, microwave-assisted aqueous hydrothermal technique to make ceria hollow nanospheres made of CeO₂ nanocrystals. It is a low-cost and environmentally friendly synthesis process. This ceria hollow nanospheres have a significantly higher adsorption capability for heavy metal ions than other ceria-based nanomaterials. Solvent casting was used to make chitosan/clay nanocomposites with the hydrophilicity of an organic polycation and the adsorption potential of an inorganic polyanion [74]. Limited quantities of montmorillonite-Na⁺ were also found in the chitosan matrix. With an adsorbent dosage of 50 mg/L and a contact time of 180 minutes, 93.5 percent of the Cr(VI) was extracted with an initial Cr(VI) concentration of 100 ppm at a small pH range.

[75] Bhaumik et al. polypyrrole (PPy)–polyaniline synthesis(PANI) nanofibers by polymerizing their monomers in the presence of FeCl₃ oxidant and combining PPy.⁺ and PANI.⁺ free radicals. The isolation of Cr(VI) from wastewater was then investigated using these nanoadsorbents. A mixture of anion exchange and Cr(VI) reduction to Cr was discovered to be the metal removal method (III). MWCNTs were investigated by Hu et al. [76] for the elimination of chromium from water.

The separation of Cr is aided significantly by redox reactions at the adsorbent's surface (VI). MWCNTs were also investigated by Gupta et al. [77] for the adsorption of chromium from aqueous solution. Its adsorption properties were found to be superior to those of normal activated charcoal, which has issues with the adsorption of hydrophilic compounds. To boost adsorption, MWCNT/nanoiron oxide composites were prepared and adsorption tests were carried out. After a 60-minute contact cycle, the MWCNT/nanoiron oxide showed a nearly 90% adsorption capability.

Parida et al. [78] immobilised TiO₂ nanoparticles on MCM-41 mesoporous mesoporousmesoporousmesoporousmesoporousmesoporousmesoporousmesoporousmesoporousmesoporous (VI). Cr(VI) adsorption into 20% TiO₂-MCM-41 at pH 5.5 and 323 K was 91 percent in 80 minutes at 100 mg/L Cr(VI) ion concentration. With higher intra-particle diffusion rates, the adsorption pursued a second-order kinetics. Thermodynamic parameters indicated that the adsorption mechanism is endothermic, and desorption experiments indicated that the adsorption mode is chemisorption. The adsorbent in the removal of Cr(VI) is a copolymer of the polyglycidyl methacrylate graft with functionalised iron oxide, with maximum adsorbent capacities of 132.5 and 162.9 mg/g, respectively, at their effective pH 4.0. The treatment of metal Cr(III) ions from waste contaminants has been achieved using a mesoporous silica nanoadsorbent surface modified with two distinct classes of nitrogen and sulphur [80]. The above synthesised nanoadsorbent extracts Cr(III) in 30 minutes

at pH 5.2 with a 98 percent adsorption rate and a maximum adsorption potential of 30 mg/g using a co-condensation technique [80].

2.6 Mercury removal

Mercury is a particularly radioactive chemical that can be present in the atmosphere both naturally and as an added contaminant. It induces neurological, nephrological, immunological, cardiac, motor, developmental, and even genetic abnormalities in humans [54]. The numerous nanoadsorbents investigated for mercury recovery from wastewater are mentioned in Table 1. Shan et al. [55] created poly(1-vinylimidazole) oligomer coated magnetite silica nanospheres (FSPV) as a nanoadsorbent for the removal of Hg(II) from water. FSPV spheres with a diameter of 10–20 nm have a saturation magnetisation of 44.7 emu/g and can be conveniently isolated from water in 5 minutes using a simple magnetic method. The adsorbent could maintain 94 percent of its initial adsorption potential after five consecutive cycles of adsorption followed by desorption with HCl.

For rapid and effective Hg(II) removal, thiol-functionalised mesoporous (2.1 nm) silica-coated magnetic nanospheres were used [56]. Transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDXS), and XPS were used to characterise the particles, and the results show that the SiO₂ and thiol groups surround the surface of the Fe₃O₄ particles. Hg(II) was quickly desorbed using thiourea in a 3 M HCl solution, and the nanospheres could be reused in repeated adsorption cycles without losing their operation. Kyzas et al. [57] investigated two modified chitosan derivatives for Hg(II) removal: one was chitosan cross-linked with glutaraldehyde and functionalized with MNPs, and the other was chitosan cross-linked with glutaraldehyde and functionalized with MNPs. Adsorption and desorption maximal pHs were discovered to be 5.0 and 2.0, respectively. The adsorbent's reusability was so high that it could maintain 90% of its original adsorption capability even after four cycles. Nasirimoghaddam et al. [58] confirmed the covalent binding of carboxymethyl chitosan to MNP through carbodiimide activation. The developed adsorbents removed Hg(II) ions from aqueous solutions quickly, with a maximum removal of 92.4 percent at room temperature. 0.1 M sulfuric acid desorbed 85 percent of the removed mercury from nanoparticles, allowing the adsorbents to be reused for subsequent cycles.

MWCNTs were used by Tawabini et al. [59] to separate Hg(II) ions from wastewater. When used at a pH between 4.0 and 8.0 and when the solution to be handled was agitated at a speed of 150 rpm, these nanosorbents were more effective at extracting Hg(II) from polluted water. Functionalised MWCNTs were made by adding amine and thiol groups to the side walls of the tubes via the reaction of ethylenediamine, cyanuric chloride, and sodium 2-mercaptoethanol one after the other to improve the adsorption mechanism [60]. Hg(II) was removed from wastewater using polymeric nanosorbents such as poly(aniline (AN)-co-5-sulfo-2-anisidine (SA) and poly(1-amino-5-chloroanthraquinone) (PACA) [61, 62]. The reactive ratio of these comonomers was observed to be 2.05 (AN) and 0.02 (SA) when monomers of AN and SA were used to make copolymeric nanoparticles [61].

2.7 Cadmium removal

Cadmium is also widely used in a wide range of technologies. However, since the factories that use this metal do not properly drain their effluents, cadmium is gradually being contained in water. Cadmium is a radioactive heavy metal that poses a significant risk to live species that consume this water [9]. Nickel–cadmium electrodes, phosphate fertilisers, pigments, alloys, and metal plating are all made of it [97]. Cadmium is found in water from a variety of sources, including metal refinery spill, fossil fuel burning ash, and waste batteries and paints. Kidney injury, stomach complications, diarrhoea, and death have all been linked to cadmium ingestion [96].

The tests for cadmium removal using nanoadsorbents are summarised in Table 1. By coating a shellac layer on the surface of MNPs, a natural biodegradable and reusable resin with abundant hydroxyl and carboxylic groups, a new and efficient adsorbent for Cd(II) removal from aqueous solution was developed. Cd(II) could be quickly desorbed from nanoparticles using mild organic acid solutions at low concentrations, according to desorption studies [98]. Cadmium removal from wastewater was investigated using inorganic nanoparticles of cerium oxide [99]. The adsorption concentrations of Cd were also compared using nanoparticles of iron oxide and titanium dioxide (II). MNPs is observed to have the highest Cd(II) adsorption of the three nanoparticles with the same contact period. The adsorption ability of nanotitanium dioxide for Cd(II) ions was investigated using various crystal structures such as anatase, rutile, mix crystal, and amorphism [100]. On the adsorbent base, kinetic tests showed both chemisorption and physisorption. Because of its higher surface energy, rough surface, and unsaturated oxygen bond, anatase TiO₂ powder had the highest chemisorption potential of all the other samples. The formation of complexes with the ions that are later separated from water is dependent on electrostatic interactions and soft acid/soft base interactions [100]. TiO₂ Degussa P25 nanopowder/fly ash was manufactured by Visa and Duta [101] for the adsorption of heavy metals like cadmium from wastewater.

The adsorption process was similar to that of titanium dioxide nanopowder, which was previously discussed. Hydrous manganese dioxide-001 is a hybrid adsorbent made by impregnating HMO nanoparticles into a polystyrene cation exchanger resin (D-001) and tested for Cd(II) ion elimination from water [102]. The pH at which Cd(II) adsorption occurs is optimally around 7.0. These adsorbents can then be regenerated with a 2 percent HCl solution, with minimal nanoparticle degradation. Ion exchange with the D-001 polymeric exchanger and innersphere complexation with HMO nanoparticles are the mechanisms of adsorption. Al-Khaldi et al. [103] contrasted the elimination of Cd(II) from waste effluents using various carbon nanoadsorbents such as fly ash, CNTs, carbon nanofibres, and activated carbon, finding that fly ash with pH 7.0 eliminated 95 percent of pollutants in 2 hours, while activated carbon removed 38 percent, carbon nanofibers 34 percent, and CNTs 27 percent, respectively. The overall adsorbent rate of 98 percent was reached at their optimum conditions of pH 7.0 with a contact period of 90 minutes [104]. Nanosilica spheres adjusted with sulphur and nitrogen groups were used to adsorb Cd(II). For cadmium adsorption, Vukovi et al. [105] used oxidised and ethylenediamine-functionalized MWCNTs. Using O-(7-azabenzotriazol-1-yl)-N, N, N, N-tetramethyluronium hexafluorophosphate, this adsorbent was made by chemically modifying carboxyl classes. The adsorption mechanism was discovered to be endothermic and random.

III. Heavy metal reduction with other nanoparticles.

The removal of a particular heavy metal with higher adsorption efficiencies has been studied using the nanoparticles discussed thus far. Other nanoparticles are being investigated for their ability to remove several metals from waste water simultaneously and with greater effectiveness (Table 2).

Cd(II) and Zn(II) were removed from wastewater using magnetic hydroxyapatite (MNHAP) as an adsorbent [106]. The adsorbents were found to be nanosized (28 nm in diameter) and extremely stable under both oxidising and reducing conditions using scanning electron microscopy.

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

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

MNHAP had a higher adsorption affinity for Cd(II) than Zn (II). In comparison to other desorption agents, EDTA performed best in the desorption step [106]. The removal of Cu²⁺, Zn²⁺, and Pb²⁺ from water was effectively studied by synthesising magnetic maghemite nanotubes using microwave radiation technique, with the highest adsorption rates of 111.11, 84.95, and 71.42 mg g⁻¹, respectively.

At a temperature of 25°C and a touch time of 60–90 minutes, the maximal pH was discovered to be 6.0 [107]. Tofighy and Mohammadi [108] looked into the possibility of CNTs removing heavy metals like Cu²⁺, Zn²⁺, Pb²⁺, Co²⁺, and Cd²⁺. The above carbon nanoadsorbent extracts the heavy metal with varying adsorption concentrations and capacities, according to kinetic studies of adsorption. Some metals have been adsorbed more preferentially than Pb²⁺.

Because of their high specific surface area to volume ratio, nanoparticles of aluminium oxide (Al₂O₃) were used to efficiently remove Cd, Zn, and other heavy metals from wastewater and soil solutions [109]. Zn and Cd adsorption was studied in mono and binary systems at a pH of 6.5. The presence of phosphate or HA, and to a lesser degree the presence of citrate at low concentrations, greatly increased adsorption. Phosphate and humic acid increased Zn and Cd adsorption in both systems, while citrate reduced Zn adsorption by 25% in the mono-metal system. It was discovered that when Zn or Cd was removed from the structures, the removal of phosphate and HA was increased, which may mean improved adsorption due to ternary complex formation or metal-ligand precipitation.

Among the three ligands, phosphate was found to be the most efficient in increasing Zn and Cd adsorption [109]. SDS-coated MNPs have been investigated as a possible nanosorbent for removing Cu(II), Ni(II), and Zn(II) ions from wastewater [110]. The use of SDS coated MNPs for the removal of heavy metal ions demonstrated a high adsorption potential and a fast adsorption operation, as well as the ability to quickly isolate the adsorbents using a magnet. It was also discovered that methanol can be used to desorb the nanoadsorbents, allowing for three adsorption–desorption periods.

Another form of nanoadsorbent used to research heavy metal removal is γ -Alumina (γ -Al₂O₃) nanofibres modified with functional groups that have a good affinity for the pollutants. Pb(II), Cd(II), Cr(III), Co(II), Ni(II), and Mn(II) have all been removed from water using 2,4-dinitrophenylhydrazine (DNPH) immobilised on SDS coated nanoalumina [111]. Even after three adsorption–desorption cycles, desorption tests with a mixture of nitric acid and methanol revealed that the modified alumina nanoparticles could be reused without substantial loss of their original properties, including their activity as an adsorbent. As a result, modified nanoalumina with DNPH has a high adsorption potential and can be used to remove these multi-cations [111].

Hg(II), Pb(II), and Cd(II) metal ions are effectively removed from wastewater using a poly-methacrylic acid grafted chitosan–bentonite nanocomposite (MACB) synthesised by γ -irradiation polymerisation [112]. The experimental findings revealed that the MACB nanocomposite's adsorption potential is in the following order: Hg(II) > Pb(II) > Cd(II). The PEG aided hydrothermal process was used to synthesise nickel ferrite (NiFe₂O₄) and copper ferrite (CuFe₂O₄) nanoparticles, which were then tested for the removal of Cu(II), Ni(II), and Zn(II) from wastewater [113]. Cu(II), Ni(II), and Zn(II) removal efficiencies using CuFe₂O₄ nanoparticles were found to be 83.50, 98.85, and 99.80 percent, respectively, and Cu(II), Ni(II), and Zn(II) removal efficiencies using NiFe₂O₄ nanoparticles were found to be 92.55, 36.56, and 99.91 percent, respectively. At a contact period of 280 minutes and a pH of 9, MgO nanoparticles (MON) were used to strip both lead Pb(II) and chromium Cr(VI), with maximal efficiency of 94.78 and 81.25 percent, respectively [114]. The synthesis of magnetic nanoadsorbent with their transformed amino groups on dithiocarbonate (DTC) on the polymer chains has eliminated another pollutant of Hg(II) from pollutants. As compared to a single-layer nanoadsorbent of 3-aminoethoxy silane modified on the surface of Fe₃O₄ particles, the above nanoadsorbent performed better. At 40°C, polymer-based nanoadsorbent has a high potential of adsorbent rate with 100% performance, while monolayer adsorbent only extracted 77% [115]. Yang et al. [11] used diamine functionalized mesoporous silica on MWCNT to remove heavy metals Cu(II), Ni(II), Pb(II), and Zn(II). Due to the combined adsorption capability of the diamine modified mesoporous silica and the CNTs, this adsorbent has a much higher adsorption potential than normal MWCNTs.

IV. Opportunities for the Future

The nanoparticles can be used as effective adsorbents for removing different heavy metals from dirty water, as discussed above. The ease of synthesis, economic viability, and ease of surface alteration are only a few of the main characteristics that have contributed to the advancement of this novel technology. Low concentrations of heavy metals have been extracted with high selectivity and adsorption potential so far. However, the need for larger-scale wastewater treatment remains, and the application of these nanomaterials is unclear. Scaling up laboratory size tests to wider scales, enhancing the biocompatibility of nanoparticles, making the process eco-friendly, and making the whole process cost efficient are all things that need to be worked on. For researchers in this area, the use of nanoparticles to remove heavy metals from wastewater has become a game-changer. However, there are a few technological issues that must be addressed in order for this system to become a viable wastewater treatment option in the future. The first issue is the lack of available methods for desorption of the nanosorbents in use. If we want to make this procedure cost efficient, we need to recover these adsorbents, which can be achieved using the desorption process. There has been no research performed on this so far, and there is a need to find effective ways to return nanosorbents to their active state. Furthermore, for effective adsorption, this method necessitates a wide surface area of nanoparticles. Obtaining nanoparticles of the ideal size and surface area would require optimising the synthesis protocol under optimal conditions, the composition of surface coatings, and their corresponding geometric structure on the nanoparticles.

Any of the nanoparticles that have been addressed so far have been created using chemical processes, which may have toxic effects on the treated water. Greener methods for the synthesis of these nanoadsorbents should be investigated to prevent such issues. Nanoadsorbents have been made from coal, fly ash, wood, silica gel, clay products, agricultural wastes such as bagasse pith, maize cob, coconut shell, rice husk, and so on, cotton wastes, and cellulose-based wastes. These adsorbents are often difficult to come by at a reasonable price. However, if there is an uptick in market demand for those goods, this issue can be solved. As a result, a broader use of such particles would increase their use and make their processing more cost-effective.

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