Effective Heavy Metals Removal from Water Using Nanomaterials: A Review

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Abstract:

The discharge of toxic heavy metals including zinc (Zn), nickel (Ni), lead (Pb), copper (Cu), chromium (Cr), and cadmium (Cd) in water above the permissible limits causes high threat to the surrounding environment. Because of their toxicity, heavy metals greatly affect the human health and the environment. Recently, better remediation techniques were offered using the nanotechnology and nanomaterials. The attentions were directed toward cost-effective and new fabricated nanomaterials for the application in water/wastewater remediation, such as zeolite, carbonaceous, polymer based, chitosan, ferrite, magnetic, metal oxide, bimetallic, metallic, etc. This review focused on the synthesis and capacity of various nanoadsorbent materials for the elimination of different toxic ions, with discussion of the effect of their functionalization on the adsorption capacity and separation process. Additionally, the effect of various experimental physicochemical factors on heavy metals adsorption, such as ionic strength, initial ion concentration, temperature, contact time, adsorbent dose, and pH was discussed.

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Effective Heavy Metals Removal from Water Using Nanomaterials: A Review

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Abstract: The discharge of toxic heavy metals including zinc (Zn), nickel (Ni), lead (Pb), copper (Cu), chromium (Cr), and cadmium (Cd) in water above the permissible limits causes high threat to the surrounding environment. Because of their toxicity, heavy metals greatly affect the human health and the environment. Recently, better remediation techniques were offered using the nanotechnology and nanomaterials. The attentions were directed toward cost-effective and new fabricated nanomaterials for the application in water/wastewater remediation, such as zeolite, carbonaceous, polymer based, chitosan, ferrite, magnetic, metal oxide, bimetallic, metallic, etc. This review focused on the synthesis and capacity of various nanoadsorbent materials for the elimination of different toxic ions, with discussion of the effect of their functionalization on the adsorption capacity and separation process. Additionally, the effect of various experimental physicochemical factors on heavy metals adsorption, such as ionic strength, initial ion concentration, temperature, contact time, adsorbent dose, and pH was discussed.

Keywords: water treatment; nanomaterials; heavy metals; functionalization

1. Introduction

Healthy peoples require clean drinking water as one of the essential life requirements [1–3]. However, due to the increased industrialization and the excessive use of chemicals all over the world, unwanted pollutants released into drinking water have became a major concern. One of the major noxious water pollutants are heavy metal ions that cause serious side effects to human and living organisms. Toxic heavy metals are the comparatively high-density metallic elements that can cause toxicity also at lower doses. In the recent years, heavy metals pollution was increased significantly by several folds, resulting from the continuous development of urban, industrial, and agricultural activities. Generally, the main sources of heavy metals toxicity are sewage sludge, pesticides, metallic ferrous ores, fertilizers, municipal wastes, and fossil fuels burning [4,5]. As advised by the Environmental Protection Agency (EPA), there is a standard quality for drinking water, which depends on the

level of the present pollutants and the harmful effects on health which could occur when pollutants levels exceed the permitted levels [6]. Industrial contaminants commonly include zinc (Zn), nickel (Ni), lead (Pb), copper (Cu), chromium (Cr), and cadmium (Cd) over other metals. These toxic metals have many poisoning symptoms, with impacts on human and living organisms through their accumulation inside the food chain [7]. The progress and excessive activities of humans has caused the environmental pollution by toxic metals even though these metals naturally exist in the crust of earth. These activities include wood and dyes preservation, photographic materials, electroplating and steel industries, smelting, printing pigments, pesticides, leather tanning, explosive industrial, coating, mining biosolids, atmospheric accumulation, sewage irrigation, textiles, alloys fabrication, fertilizers manufacturing, and batteries construction [8]. Nevertheless, many physiological and biochemical processes require some heavy metals usage in trace amounts, such as molybdenum (Mo), nickel (Ni), manganese (Mn), selenium (Se), zinc (Zn), magnesium (Mg), iron (Fe), chromium (Cr), copper (Cu), and cobalt (Co). These trace metals are considered essential while others are non-essential. However, high concentrations of these trace metals become harmful for humans and the environment. Many harmful effects such as nervous disorders, anemia, renal failure, and cancer are associated with high lead levels in drinking water. Many metals such as mercury [9], lead [10], chromium [11], cadmium [12], and arsenic [13] are classified as having the greatest importance for public health, due to their high toxicity, as exposure to these metals even at small levels can cause several organs damage. According to the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (U.S. EPA), several metals such as lead, arsenic, cadmium, chromium, and mercury are known to be carcinogenic depending on their experimental and epidemiological tests. Therefore, the elevated toxic metals contamination has motivated scientists to develop several remediation methods, such as flocculation and coagulation [14], photocatalysis [15], ion exchange [16], adsorption [17], membrane filtration [18], and chemical precipitation [19]. Because of diverse factors related to economic and technological considerations, a limited number of wastewater treatment processes are universally used by various industries to treat their effluents. In spite of their availability to remove different pollutants from wastewaters, these processes represent some limitations (high cost, process complexity, low efficiency, etc.). Interestingly, the adsorption technique was considered as the most effective one for heavy metals removal from wastewater since is considered as safe, clean, efficient and technical feasible process [20]. Absorbent materials are characterized by their high surface area and porosity, resistance to toxic substances with high effectiveness and simple design and easy operation, making this technology the most worldwide method for heavy metals removal from wastewater [20]. Many adsorbents have been used for toxic metals in wastewater treatment, such as nanocomposites [21], nanofilteration [22], engineered nanomaterials [23], chelating minerals [24], activated carbon [25], and biopolymers [26]. Because the old technologies are conventional and limited, in the past few years nanotechnology science has been applied for heavy metals removal from waters. Nanoparticles (NPs) size-dependent properties provide various opportunities in diverse applications. Interestingly, this science has gained tremendous international interest with the increasing request for nanomaterials in which materials are transferred from the micro- to the nano-scale [27]. Additionally, the existence of the high number of functional groups over their surfaces, availability, and lesser flocculation allowed their wide application for the remediation of wastewater containing toxic metals [28]. Interestingly, the developed nanomaterials provided different geometries with various new characteristics which cannot be observed in bulk materials. These nanomaterials with different geometries have demonstrated high heavy metals removal efficiency. This fact is related to their exceptional properties including high surface area, porosity, specific surface charge, surface functionality, and ions binding capabilities [27,28]. Furthermore, nanomaterials are attractive and cost effective due to their reusability for several cycles. However, these nanomaterials have some limitations hindering their industrial applications, such as their removal from treated water [29]. This problem is overcome through nanomaterials functionalization by the link with biomolecules [30], carbon [31], polymers [32], and inorganic compounds [33], which allow easy separation from treated

water as well as enhancing their adsorption power. In this review, we briefly discuss the use of various nanomaterials for the efficient removal of toxic metals from water/wastewater via the adsorption technique. We also discuss the effect of different conditions on the adsorption process, such as the initial metal concentration, temperature, contact time, adsorbent dosage, and pH. Additionally, we summarize the adsorption isotherms used for heavy metals adsorption through different nanomaterials.

2. Nanomaterials for Heavy Metals Removal

In the recent years, heavy metals removal from wastewater has been achieved using different types of nanomaterials such as zeolite, carbonaceous, polymer based, chitosan, ferrite, magnetic, metal oxide, bimetallic, metallic, etc. The heavy metals scavenging from wastewater using nanomaterials is achieved through the adsorption technique over their surfaces. Based on their basic material being used as absorbents and their importance for heavy metal removal, various types of nanomaterials are listed and discussed in detail in the next sections.

2.1. Carbon Based Nanomaterials

Functionalized carbon nanomaterials are considered one of the most promising adsorbents for toxic metals due to their unique chemical and physical features that allow their usage at large scales for wastewater purification. They have attracted much attention in the scientific community and engineering due to their extraordinary physical, chemical, optical, mechanical and thermal properties. In recent years, different types of contaminants were removed using several constructed carbon-based nanomaterials such as graphene, carbon-based nanocomposite, and carbon nanotubes. One of the most important carbon-based nanomaterials used for water treatment is graphene. It is the thinnest two-dimensional material comprised of a one-atom-thick planar sheet of sp²-bonded carbon atoms, while carbon nanotubes have a cylindrical nanostructure which also consist of sp²-bonded carbon atoms. Graphene has a high dispersity in aqueous solution, resulting from its high hydrophilic tendency due to the existence of oxygen functional groups on the graphene oxide (GO) surface. The large surface area and existence of functional groups over the GO surface makes it a promising material for water detoxification. Several pollutants are found to be removed with high efficiency from water using graphene-based nanomaterials. The adsorption of toxic metals from water via graphene occurs through the complexation of oxygen functional groups in the graphene and cationic metal. For organic dyes the interaction occurs through the π -electron delocalized arrangement of graphene. Zeng et al. [34] functionalized reduced GO hydrogel by MnO₂ nanotubes to produce 3D nanomaterial with a size of 20 nm used for the high adsorption of zinc, copper, silver, cadmium, and lead ions with the adsorption capacity of 83.9, 121.5, 138.2, 177.4 and 356.37 mg/g, respectively. This high adsorption capacity resulted from the synergetic action between MnO₂ nanotubes and reduced GO of the porous 3D nanostructures. Another research group, prepared the nanosheets of GO for the elimination of cobalt ions with the adsorption capacity of 68.2 mg/g and cadmium ions with an adsorption capacity of 106.3 mg/g [35]. Interestingly, another form of carbon material called carbon nanotubes (CNTs) are the most attractive materials for environmental engineers due to their electrical conductivity, cylindrical hollow structure, small size, and large surface area. Multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) are the two main classes of CNTs. Wastewater treatment from toxic heavy metals via adsorption over CNTs was designated by several researchers. For instance, CNTs allowed the removal of Mn (II), Zn (II), Co (II), Pb (II), and Cu (II) [36]. In another study, the lead ions removal from water with an adsorption capacity equal 70.2 mg/g was reported [37]. Furthermore, MnO₂ was used to coat oxidized multi-walled CNTs, allowing an efficient scavenging of cadmium ions from water with an adsorption capacity equal 41.7 mg/g [38]. Lately, researchers synthesized the nanocomposite of carbon layered silicate that has developed features compared to conventional carbon nanomaterials that attracted the scientists' attention. Interestingly, an environmentally-safe composite, nanoadsorbent montmorillonite/carbon, was synthesized and used for the elimination of lead ions with an adsorption capacity of 247.86 mg/g [39].

2.2. Zeolites Nanoparticles

The high porosity of zeolites allows their use for the removal of toxic metals from wastewater. The negative charge between silicon and aluminum ions can be balanced by the movement of alkaline earth and alkali metals in their framework. However, nanoparticles of zeolites are used for adsorption efficiently due to their active and large surface areas. Recently, the adsorbent NaX nanozeolite/polyvinyl alcohol was synthesized and used efficiently for the removal of cadmium and nickel ions from water with an adsorption capacity for nickel lower than cadmium ions [40]. In another work, zeolite immobilized over alumina nanoparticles was used for the removal of Co (II) and Cr (III). Compared with immobilized nanoparticles, the adsorption power of zeolite and alumina nanoparticles was found to be enhanced by 17.3% for Co (II) and 31.77% for Cr (III) [41]. Additionally, zeolite nanoparticles used to fill ploysulfone membrane to remove lead and nickel ions from water via a combined treatment of filtration and adsorption. The capacity of adsorption of this fabricated membrane reached 122 mg/g for nickel and 682 mg/g for lead [42]. Recently, clinoptilolite zeolite nanoparticles were modified using pentetic acid and characterized then tested for the removal of Cd (II) from water. The modified clinoptilolite zeolite nanoparticles offered an excellent elimination of cadmium pollutants from water showing an adsorption capacity of 138.9 mg/g. The cadmium ion chelation occurred through ion exchange with raw clinoptilolite zeolite nanoparticles and by complexation with functional groups of pentetic acid indicating the important role of functionalization in the enhancement of adsorption capacity. The adsorption process occurred through monolayer and multilayered adsorption [43].

2.3. Polymer Based Nanomaterials

Many factors enhance the application of nanofibrous membranes filled with polymers (such as cellulose, chitosan, etc.) in environmental remediation, such as high surface area, small interfibrous pore size, and high gas penetrability that improve their chelation adsorption capacity. They are an excellent choice for the adsorption process due to their simple degradation behavior, adaptable surface functional groups, and excellent strength skeleton. Nanomembranes filled with polymers have a high selectivity and adsorption capacity resulting from existing functional moieties such as SO₃H, COOH, and NH₂, by which the permeated toxic metals are chelated. Materials used in the polymer-based nanomaterials can be used for their classification.

2.3.1. Cellulose Based Nanomaterials

Scientists tested the removal of toxic heavy metals using biopolymers-based adsorbents such as cellulose. Abou-Zeid et al. [44] synthesized 3 bio adsorbents: tetramethyl piperidine oxide oxidized 2, 3, 6-Tricarboxy cellulose nanofiber (T-CNFs) and TPC-cellulose nanofiber (TPC-CNFs) with and without polyamide-amine-epichlorohydrin crosslinker (PAE) and used for the treatment of water containing calcium, lead, and copper ions. For both lead and copper ions, the adsorption capacities were 82.19, 97.34, and 92.23 mg/g, respectively for Crosslinked TPC-CNFs, TPC-CNFs, and T-CNFs. In another study, phosphoric acid was used to functionalize cellulose nanofibers with a phosphate group to form CNF/P useful for the removal of copper ions from water [45]. Recently, Choi et al. synthesized cellulose nanofibers through electrospun cellulose acetate nanofibers deacetylation process that followed by functionalization of nanofibers with thiol group through esterification reaction. This polymer-based adsorbent used for the removal of Pb (II), Cd (II), and Cu (II) ions with adsorption capacity has been determined via Langmuir isotherm equal to 22.0, 45.9, and 49 mg/g, respectively. The metal ions removal occurred via the complexation reaction between the two surface thiol groups and divalent metals to approve the success of this synthesized functionalized nanomaterial for water remediation process [46]. Additionally, the previous method was used for the synthesis of cellulose nanofibrous mats that are then modified using citric acid. The citric acid modified cellulose nanofibrous were tested for the removal of chromium ions through a batch adsorption experiment. This synthesized nanoadsorbent offered an efficient removal of Cr (VI) from aqueous solution [47].

The removal of toxic metals has been achieved efficiently using organic polymers with functional groups to greedily chelate these toxics [48]. This system is composed of polymeric support with functional arms. On this basis, different ratios of acrylamide and acrylic acid were used for the synthesis of superadsorbent polymer hydrogel for the elimination of Co (II), Cu (II), Ni (II), and Cd (II) with high adsorption capacity from water. The adsorption efficiency toward cadmium and nickel ions was lower than that of copper and cobalt ions due to the easy penetration of small cations from polymeric support and easily chelated by functional arms [48]. In another study, nanofibers with ion-selectivity behavior including diethylenetriamine, ethyleneglycol, and ethylenediamine supported over a base polymer of polyacrylonitrile showed efficient removals of Zn (II), Pb (II), and Cd (II), with an adsorption capacity of 7.2, 8.8, and 6.1 mmol/g, respectively. Its high adsorption capacity may be attributed to the high surface area of the three nanofibers that allowed large numbers of functional groups for the scavenging of toxic metals [49]. Additionally, two new polymers were prepared by the reaction between 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione with pentaethylenehexamine and diethylenetriamine to form polymeric nanomaterials with ethyleneamine arms to capture metallic ions through complexation reaction. The long amine chains in the nanoadsorbent were prepared using pentaethylenehexamine, which allowed a higher capture of divalent copper, chromium, cobalt, and cadmium ions than that prepared using diethylenetriamine [50]. A co-electro spinning technique was used for the fabrication of nanofibers membranes from metal-organic frameworks (MOF-808) and polyacrylonitrile to produce PAN/MOF-808 nanoadsorbent, offering an efficient removal of heavy metals from water according to the order Hg (II) < Pb (II) < Cd (II) < Zn (II). This removal efficiency order is in line with the metals ionic size, which indicates that the steric effect of metals hampers the access of metals to complex with active sites [51]. In another study, researchers synthesized poly-(ethylene-co-vinyl alcohol) nanofibers that efficiently removed hexavalent chromium pollutants from wastewater with the adsorption capacity of 90.75 mg/g obtained at less than 100 min [52]. In a similar study, nanofibers of polyacrylonitrile were functionalized using amidoxime to enhance its adsorption capacity for metals elimination. This nanoadsorbent efficiently removed lead and copper divalent ions from water [53]. A quantity of 1, 2-diaminoethane or 1, 3-diaminopropane was used to modify the resin of synthesized poly (styrene-alt-maleic anhydride) with 3-aminobenzoic acid. The synthesized nanoadsorbent was used for the elimination of Pb (II), Zn (II), Cu (II), and Fe (II) from water [54]. Sohail et al. [55] synthesized polyamidoamine (PAMAM) dendrimers via a divergent method. The functionalization occurred via two steps: Michael addition reactions of amino groups on methyl acrylate to produce shell of ester then linked to ethylene diamine to form the new developed surface. The characterization indicated that these zero generation dendrimers have 200-400 nm of size. These higher generation dendrimers have more outer functional groups on the external side that allowed the efficient removal of nickel ions from water [55].

2.3.3. Chitosan Based Nanomaterials

Chitosan is a linear polysaccharide composed of randomly distributed β -(1 \rightarrow 4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, like sodium hydroxide. Chitosan is biocompatible, non-toxic, and hydrophilic polymer that able to interact with different metals via complexation reaction. This complexation reaction easily occurred due to the existence of amino functional groups over chitosan surface. This functionalization of chitosan occurs via connection with different materials to improve its adsorption capacity, selectivity, mechanical properties, and stability at low pH. For example, chitosan was used as a carbon and nitrogen source for the synthesis of nitrogen-doped carbon materials with a 3D hierarchically porous structure, which was tested for the elimination of cadmium and lead ions from water via the electrostatic interactions between surface oxygen and nitrogen functional groups and metallic ions. Therefore, the chelation process is chemisorption over this nanoadsorbent [56]. In another study, chitosan was combined

with zinc oxide nanoparticles to produce core shell nanocomposite of ZnO/chitosan that showed to remove effectively Cu (II), Cd (II), and Pb (II) ions from water [26]. Additionally, the same coupling was made using titanium dioxide nanoparticles to fabricate a nanocomposite of chitosan/TiO₂ that allowed to adsorb efficiently lead and copper divalent ions [57]. Moreover, the chitosan nanoparticles were functionalized using alginate to form alginate/chitosan nanocomposite that permit the removal of 94.9% of nickel ions from aqueous solution [58]. The nanocomposite of chitosan alginate was fabricated and tested for the removal of divalent mercury from water. Here, alginate is negatively charged while chitosan is positively charged allowing the interaction with different charged pollutants in water as calcium and tripolyphosphate ions. This nanocomposite showed high adsorption capacity of 217.40 mg/g toward mercury ions [59]. Recently, Hussain et al. synthesized chitosan modified with salicylaldehyde in the size of 80 nm for the efficient removal of Pb (II), Cd (II), and Cu (II) from water. The nanocomposite showed high adsorption capacity toward Pb (II), Cd (II), and Cu (II) equal to 63.71, 84.60, and 123.67 mg/g, respectively. Additionally, this nanocomposite was tested for lead removal from tap water of 4.88 ppb [60]. In a separate study, Khalil et al. synthesized two novel chitosan nanocomposites. One was prepared via the functionalization of chitosan using cinnamaldehyde to produce chitosan-cinnamaldehyde (CTS-Cin) and the other nanocomposite was magnetic chitosan cinnamaldehyde (Fe₃O₄@CTS-Cin). These nanocomposites are promising for the treatment of water containing toxic metals. The two nanocomposites effectively removed hexavalent chromium Cr (VI) from water at 298 K with adsorption capacity of 61.35 mg/g for CTS-Cin and 58.14 mg/g for Fe₃O₄@CTS-Cin [61].

2.4. Magnetic Nanomaterials

Advanced nanomaterials have several classes in which magnetic nanomaterials are the main class that save the easily magnetic separation as well as the improved removal of toxic metals. This class of nanomaterials introduces excellent recyclability after separation that gives this class ecological benefits and wide applications in environmental remediation. With size decrease, the properties of these nanomaterials change significantly. The efficiency of non-magnetic nanomaterials in water treatment is lower than magnetic nanomaterials due to their hard separation and small surface area. However, the magnetic nanomaterials are easily dispersed, less toxic, with inert chemical behavior, and have a large surface area. These properties of magnetic nanomaterials make them cost effective, efficient, and faithful for water purification. Thus, heavy metals removal is effectively achieved by using these nanomaterials. A vital member of this class is iron oxide nanomaterials that provide ease of reusability, separation, and quick and high adsorption capacity. In this context, Fe₃O₄ nanoparticles were synthesized and used for the efficient adsorption of lead divalent ions from water with 36 mg/g of adsorption capacity [62]. In addition, Mn (II), Zn (II), Cu (II), and Pb (II) were removed using nanoparticles of Fe₃O₄ prepared by Giraldo et al. with a minimum adsorption capacity toward Mn (II) and maximum adsorption capacity toward Pb (II), which is related to the different hydrated ionic radius of these metals. This differentiation of metals size affects the electrostatic attraction between adsorption sites and toxic metals [63]. In another study, the nanoparticles of Fe_3O_4 were synthesized and their adsorption capacity of toxic metals Cu (II) and As (II) was compared with commercial iron oxide. The lower adsorption capacity of commercial iron oxide toward metals adsorption indicated the improved properties of synthesized nanoparticles [64]. Interestingly, nanorods, nanowires, and nanotubes provided great efficiency toward heavy metals removal from water/wastewater due to their higher surface area than other structured nanomaterials. For example, Cu (II), Cd (II), Ni (II), Zn (II), Pb (II), and Fe (II) were efficiently removed from water via adsorption over Fe₃O₄ nanorods with adsorption capacity of 76, 88, 95, 107, 113, and 127 mg/g, respectively [65]. The real applications of bare magnetic nanoparticles are limited due to their easy aggregation in water, which results from their tendency toward oxidation. Additionally, it is very important to prevent the magnetic nanoparticles from precipitation or aggregation alongside their synthesis development. A functionalization process of bare magnetic nanoparticles was followed to overcome these problems. The selectivity, stability, and adsorption capacity of magnetic nanoparticles

increased via surface functionalization. The existence of different functional groups over magnetic surfaces offers different types of interactions between surfaces and metals including Van der Waals, electrostatic, ligand combination, chemical binding, and complex formation. Additionally, surface metal electrostatic interactions can be enhanced via functionalization using charged moieties. Thus, the selectivity of surfaces toward different metals resulted mainly through enhanced electrostatic attraction. Based on this, preventing the aggregation of magnetic nanoparticles can be achieved using capping hydrophilic coatings such as poly vinyl pyrollidine, poly vinyl alcohol, and polyethylene glycol. In addition, magnetic nanoparticles homogeneity and high surface area were enhanced through functionalization. Tailoring the magnetic surfaces caused alteration of magnetic nanoparticles toward toxic pollutants depend mainly on their surface area and size that are decided significantly by surface modification. Surface modification of magnetic nanoparticles occurred through many trials, including different modifiers such as carbonaceous, biomolecules, inorganic, organic, and polymers materials, etc.

2.4.1. Nanocomposite Magnetic Nanoparticles

Several metal oxides magnetic nanocomposites have been engineered and applied for heavy metals removal from water. For example, nanocomposite of Fe₃O₄/MnO₂ was fabricated with flower shape for the adsorption of Zn (II), Pb (II), Cu (II), and Cd (II). The adsorption of prepared nanocomposite was compared with that of iron oxide NPs that found to be enhanced by modification process [66]. Researchers coupled ferrite molecules with many metals to produce metal ferrite magnetic nanomaterials to allow its ease magnetic separation for the recyclability. The general formula of metal ferrite nanocomposite is $M(Fe_xO_y)$, where M is the metal atom. Many metal ferrites have been synthesized for heavy metals removal such as ZnFe₂O₄, CuFe₂O₄, and Mn_{0.67}Zn_{0.33}Fe₂O₄ [29,67]. ZnFe₂O₄ removed lead divalent ions while CuFe₂O₄ removed molybdenum divalent ions from aqueous solution with high adsorption capacity. Mn_{0.67}Zn_{0.33}Fe₂O₄ efficiently removed lead, cadmium divalent ions, and arsenic pentavalent ions. In another study, the co-precipitation method used for the synthesis of manganese and cobalt spinel ferrites (MnFe₂O₄ and CoFe₂O₄) resulted in nanoparticles in the size range of 20-80 nm. The synthesized nanoparticles removed divalent zinc ions with the adsorption capacity of 384.6 and 454.5 mg/g for CoFe₂O₄ and MnFe₂O₄, respectively [68]. Vamvakidis et al. synthesized the magnetic nanocomposite cobalt ferrite ($CoFe_2O_4$) that was further modified by coating with octadecylamine. The synthesized magnetic nanocomposite removed copper divalent ions with high adsorption capacity of 164.2 mg/g. The nanocomposite showed very easy separation via a magnet and simple regeneration via acidic treatment [69].

2.4.2. Inorganic Functionalized Magnetic Nanoparticles

Magnetic nanoparticles can be functionalized with inorganic materials including silica, metal, nonmetal, metal oxides, etc. These coatings improve the stability of the nanoparticles in solution and provide sites for covalent binding with specific ligands to the nanoparticle surface. For example, amorphous oxide shells of Mn-Co were used for the modification of magnetic nanoparticles surface allowing the exhibition of strong negative charge on their surfaces at various pHs. Interestingly, the obtained absorbent allowed the removal of Pb(II), Cu(II) and Cd(II) with adsorption capacity of 481.2, 386.2 and 345.5, respectively [70]. Additionally, magnetic nanoparticles functionalized with aluminosilicate displayed the higher adsorption capacity of Hg²⁺ [71]. In another study, silica was used to coat magnetic nanoparticles modified by 1, 2, 3-triazole for the removal of toxic divalent metals such as zinc, copper, and lead, allowing a maximum removal for lead ions and a minimum for zinc ions. This order is matching the atoms electronic properties that derive the complexation reaction. Metals with high ionic potentials will tend to acquire ligand electrons and stable alliances will be established. Thus, when the metals have the same charge, the hydrated ionic radius will derive the complexation reaction and the bigger cation will form the less stable complex. Therefore, in this

study, the adsorption order followed the metals hydrated ionic radius [72]. Another class of inorganic materials used for the functionalization of magnetic nanoparticles is carbonate. In this context, calcium carbonate is a promising material for the modification of magnetic nanoparticles used for heavy metal removal from water due to its non-toxicity, low price, and high solubility that enhance the precipitation reaction of toxic species. However, their use is limited in water/wastewater remediation due to problematics of separation, sludge generation, and low efficacy. These limitations can be avoided by the combination with magnetic nanomaterials to enhance their adsorption capacity and ease their separation from experimental media. In this direction, Wang et al. synthesized magnetic mesoporous calcium carbonate-based nanocomposites via solvothermal method followed by annealing treatment to produce irregular sphere morphology nanocomposite with a size of 50 nm. This nanoadsorbent caused the removal Cd (II) and Pb (II) from water with maximum adsorption capacity of 821 and 1179 mg/g, respectively [73].

2.4.3. Carbon Materials Magnetic Nanoparticles

Nanoadsorbents efficiency for the adsorption of heavy metals from aqueous solutions can be improved by functionalization with carbon materials, such as activated carbon and graphene oxide. Subsequently, the adsorption capacity of graphene oxide/iron oxide/EDTA (EDTA: ethylenediaminetetraacetic acid) toward lead ion removal was tested. The capacity of adsorption improved with high degree due to the existence of hydroxyl and carboxyl groups over graphene oxide surface that chelate metal ions in addition to the existence of EDTA coordination power. All these functional groups over the surface interact with toxic metals through electrostatic interactions and hence, enhance the modified surface adsorption capacity [31]. In another study, Li et al. [74] synthesized environmentally benign nanocomposite of thiol (SH) functionalized Fe_3O_4 nanoparticles modified with activated carbon ($Fe_3O_4@C-SH$ NPs) via one-step fabrication. The nanocomposite removed divalent copper ions from aqueous solutions with a maximum adsorption capacity of 28.8 mg/g. The nanocomposite showed high adsorption capacity and selectivity to copper ions over co-existing ions [74].

2.4.4. Organic Functionalized Magnetic Nanoparticles

The adsorption capability of magnetic nanomaterials toward heavy metals is believed to be improved via functionalization with functional groups provided from organic molecules. For example, EDTA was used to functionalize magnetic nanoparticles coated with silica for their application for toxic metals removal. In this context, the added dithiocarbamate groups were used for the removal of divalent mercury at trace concentrations, showing high adsorption removal capacity [75]. Likewise, glutathione was used for the modification of magnetic nanoparticles coated with silica to produce the nanoadsorbent of Fe₃O₄/SiO₂/GSH useful for the removal of divalent lead ions from water. Interestingly, the temperature enhanced the adsorption of lead ions over the adsorption sites of synthesized nanoadsorbent. Additionally, the magnetic properties of this adsorbent allowed its ease of separation from the reaction medium via a magnet [76]. Furthermore, iron oxide nanoparticles were modified with amine and metformine and applied for copper ions removal from water. The highest elimination reached 92% of copper ions over Fe₃O₄ coated with silica modified with 0.1 wt % metformine [77]. In another research, Fe₃O₄ nanoparticles modified with 3-aminopropyltriethoxysilane were linked with crotonic acid and acrylic acid for the removal of divalent ions of Cd, Zn, Cu, and Pb. The highest adsorption capacity was reached for lead while the lowest adsorption capacity was found for cadmium due to different complexation affinity of metals with carbonyl group [78]. Recently, Zhang et al. used humic acid to modify nitrogen-doped Fe₃O₄ magnetic porous carbon for the removal of hexavalent chromium ions from water. The existence of functional groups over surfaces enhanced their complexation with Cr (VI) allowing the high adsorption capacity of adsorption equal to 130.5 mg/g [79]. Additionally, magnetic nanoparticles modified with amino groups showed efficient removal of toxic metals. Li et al. synthesized ternary amino-functionalized magnetic nano-sized

illite-smectite clay for the effective removal of Pb⁺² ions from water with the high adsorption capacity of 227.8 mg/g due to the complexation of metals with amino groups on the surfaces [80]. Wang et al. modified the nanocomposites of hollow Fe₃O₄/SiO₂/chitosan with triethylenetetramine for the removal of hexavalent chromium ions from water. The modification of the surface with the ligand triethylenetetramine provided more and stronger sites for the chromium complexation. This modified nanocomposite showed high adsorption capacity of Cr (VI) of 254.6 mg/g within only 15 min [81]. Likewise, triethylenetetramine was used for the modification of mesoporous Fe_3O_4 nanoparticles for the removal of Cu (II) from water with an efficiency of 86% [82]. Tetraethylene pentamine was used to functionalize magnetic polymer surfaces for the adsorption of hexavalent chromium via the reduction of Cr (VI) to non-toxic Cr (III) and via electrostatic interactions as confirmed by experimental data [83]. Similarly, many core-shell magnetic nanoparticles were functionalized with multi amino groups for the chelation of hexavalent chromium and divalent copper ions in water. The adsorption of two metals was found depending on electrostatic interactions and depending on medium pH. The pH value of 2-4 enhanced the adsorption capacity due to the availability of amino binding sites but at lower pH these sites protonated and loss its availability that negatively affect the adsorption process of copper ions. Precipitation of copper ions occurred at pH higher than 4. At the same pH range 2-4, the higher adsorption of chromium occurred via electrostatic interaction while at higher pH the adsorption process retarded due to active sites competitions between hydroxyl ions and chromium ions. In co-metals systems the competition occurred at low pH and high metals concentration while high pH and low metals concentration did not influence the adsorption removal capacity in co-metals systems [84].

2.4.5. Biomolecules Functionalized Magnetic Nanoparticles

Many investigations have been reported for the environmentally-safe use of biomolecules in the functionalization of magnetic nano-scaled particles to develop their chelation capability toward toxic metals removal from water/wastewater. Triazinyl- β -cyclodextrin was used for the modification of magnetic nanoparticles to enhance its adsorption capacity toward divalent ions such as of cobalt, zinc, copper, and lead. The existence of triazinyl- β -cyclodextrin azinyl nitrogen and hydroxyl groups over magnetic nanoparticles surfaces improved their chelation power toward above mentioned metals. The minimum adsorbed metal was cobalt ions while the maximum adsorbed metal was lead ions due to different chelation ability of surface nitrogen and oxygen [85]. In several studies, biopolymer cellulose was used to functionalize magnetic nanoparticles. Carboxy methyl cellulose-immobilized magnetic nanoparticles were prepared and tested for the removal of divalent lead ions with an enhanced adsorption capacity of 152.1 mg/g. The cellulose chains over magnetic nanoparticles exhibit many functional groups responsible for electrostatic interactions and chelation of lead ions over the nanoadsorbent. It was found that at pH over zero point charge the adsorption capacity was increased while at pH below zero point charge the adsorption capacity was decreased [86]. Phanerochaete chrysosporium pellets biomass strain loaded with Ca-alginate and magnetic nanoparticles for the efficient adsorption of divalent lead ions showed an enhanced adsorption capacity of 167.37 mg/g [87]. In another investigation, magnetic nanoparticles bounded in alginate polymer were modified with amino acid glycine in order to improve the removal of lead ions from water due to complexation ability of COOH- and NH₂- groups of glycine toward the toxic metal [28,88].

2.4.6. Polymers Functionalized Magnetic Nanoparticles

In order to get a high adsorption capacity for heavy metals adsorption from water, magnetic nanoparticles were also modified with polymers for many benefits like bio-compatibility, better mechanical strength, and higher chemical stability. Several studies reported the linkage of magnetic nanoparticles and polymers for the improvement of thermal and mechanical properties of nanoadsorbent. Fe₃O₄ nanoparticles were modified using diethylenetriamine and polyacrylic acid for the removal of hexavalent chromium and divalent copper from water with higher adsorption

capacity toward copper ions than chromium ions [89]. Additionally, magnetic nanoparticles were coated by the mercaptoethylamino polymer for the removal of divalent cadmium, lead, and mercury ions in addition of monovalent silver ions [90]. Interestingly, divalent zinc and cadmium ions were efficiently removed from water when hydroxyapatite was used to modify magnetic nanoparticles [91]. A green method of synthesis was used for the Fe_3O_4 nanoparticles synthesis via eucalyptus extract. Then, these nanoparticles were modified using chitosan polymer in order to enhance the removal of pentavalent arsenic ions from water. These modified magnetic nanoparticles showed great adsorption capacity of arsenic ions at natural pH and short duration time [32]. Glycidylmethacrylatemaleic anhydride linked iminodiacetic acid was embedded in the fabrication of magnetic nanocomposite for the efficient elimination of divalent cadmium and lead ions from water [92]. In a recent study, the facile hydrothermal method was used for the synthesis of polyethylenimine functionalized magnetic montmorillonite clay (MMT-Fe₃O₄-PEI) for the adsorption of Cr (VI) from aqueous solution [93]. Interestingly, the nanoadsorbent removed chromium ions from water with high adsorption capacity of 62.89 mg/g. The removal mechanism occurred via partial reduction of Cr (VI) to Cr (III) and electrostatic attractions between protonated amino groups with Cr (VI) anions. This nanoadsorbent was reused several times for chromium uptake from water [93].

2.5. Metal Oxides and Metal Based Nanomaterials

Recently, the heavy metals removal from water was successively achieved using metal oxides and metals. However, the bare metals which are unstable, aggregate, and their separation from the processed media is very difficult, so their use is not common in water remediation. These problems are overcome via the functionalization process to ease their separation and enhance their stability to prevent aggregation problems. One of the most important nanoparticles for water treatment is the zero valent nano iron Fe⁰ due to its high capacity of adsorption, reducing properties, non-toxicity, high surface area, and high stability. Many studies reported the use of Fe^{0} for toxic metals remediation from water. Zero valent nano iron Fe^0 was synthesized for efficient removal of 99% of pentavalent arsenic from water [94]. Similarly, Fe⁰ was prepared from ferric chloride using Syzygium jambos for the efficient scavenging of hexavalent chromium with an adsorption capacity of 983.3 mg/g [95]. Sometimes, zero valent nano iron Fe⁰ was more stabilized by combination with other stabilizing agents. For example, chitosan carboxymethyl β-cyclodextrin complex is a biodegradable non-toxic stabilizer used to envelop Fe⁰ for the removal of divalent copper and hexavalent chromium ions from water. The mechanism of heavy metals removal included the reduction of Cu⁺² to Cu⁰ and Cr⁺⁶ to Cr⁺³ while the Fe⁰ oxidized to Fe⁺³ [96]. Additionally, heavy metals elimination has been reported through bimetallic nanoparticles. In this context, kaolinite embedded Fe/Ni nanoparticles were synthesized for the excellent removal of divalent copper ions with efficiency of 99.8% [97]. Furthermore, the metal oxides have been demonstrated for the treatment of water containing heavy metals pollutants. Metal oxides nanoparticles were classified according to their magnetism into magnetic and non-magnetic metal oxides nanoparticles. Heavy metals remediation from water over non-magnetic nanoparticles metal oxides includes the oxides of Mn, Cu, Fe, Al, Ce, Zn, etc. For example, sodium titanate was used for the synthesis of nanofibrous adsorbent useful for the removal of many toxic ions from water including Zn, Pb, Ni, Cd, and Cu. The metals' removal from single and coexisting systems was compared and found higher in the case of single system adsorption owing to the competition among several adsorbates on the adsorption locations [98]. MnO₂ nanofiber was coated by polypyrrole and polyacrylonitrile and aimed at the capture of divalent lead species, with a high adsorption removal capacity of 251.90 mg/g [99]. Likewise, CeO₂ nanofibers were coated with 3-mercaptopropyltrimethoxysilane and vinylpyrrolidone for the removal of divalent ions of lead and copper with higher adsorption to lead ions than copper ions [100]. Additionally, polyvinyl alcohol was used for the coating of ZnO nanofibers for the removal of U (VI), Ni (II), and Cu (II) allowing a minimum adsorption capacity for Ni (II) and maximum adsorption capacity for U (VI) [101]. The deriving factors of this order of adsorption are metallic hydrated ionic radius, electronegativity, and atomic mass. U (VI) has the highest atomic mass, highest

hydrated ionic radius and lowest electronegativity that influence the adsorption order over these nanofibers. α -Fe₂O₃ nanofibers were synthesized for the removal of hexavalent chromium from water with an adsorption capacity of 16.18 mg/g [102]. In another study, α -Fe₂O₃ nanoparticles were coated with volcanic rock for the elimination of divalent cadmium toxics from H₂O at 30 °C showing a capacity of adsorption equal to 146.42 mg/g [103]. In separate studies, magnetron sputtering was used for the synthesis of CuO nanoparticles for the elimination of Pb (II) and Cr (VI) from H₂O with adsorption capacity of 37.02 and 15.62 mg/g, respectively [28,87,104]. Additionally, nanoparticles of alkaline metal oxides were reported for the heavy metals' removal. Compared to previously mentioned nanoparticles of metal oxides, these nanoparticles of alkaline metal oxides are eco-friendly and less toxic. The nanoparticles of magnesium oxide MgO are important members of this group, that were studied for heavy metals removal by many researchers. MgO was synthesized for toxic metals removal in addition to bacterial disinfection. The synthesized nanoadsorbent inactivated Escherichia coli in addition to the removal of divalent lead and cadmium ions [105]. In another work, flowerlike MgO nanoparticles were synthesized with high surface area for the removal of divalent ions of cadmium and lead with the adsorption capacity of 1500 and 1980 mg/g, respectively. The high adsorption occurred via a dissimilar cation exchange mechanism among metal and magnesium ions [106].

Alumina (Al₂O₃) is another important metal oxide nanoadsorbent for heavy metals removal. Alumina has many structural forms χ , θ , γ , β , and α that are naturally exist in soils [107]. Natural α -Al₂O₃ adsorbent possesses high stability in conventional methods [108]. Al₂O₃ has interesting characteristics such as high electrical insulation, corrosion and water resistance, compressive strength, and thermal conductivity, as well as its strong interatomic bonding which allowed its use as excellent adsorbent [109]. Dehghani et al. [110] benefited from nano γ -alumina properties for the removal of heavy metals from aqueous solution. The synthesized γ -alumina caused the uptake of Co (II) ions from wastewater by maximum adsorption capacity of 75.78 mg/g. This synthesized nanoadsorbent can effectively remove cobalt ions from aqueous solutions within a shorter time and with lower adsorbent dosage than others reported in the literatures. New works indicated the aptitude of alumina nanoparticles to emulate nano-membranes for pollutants adsorption. In this study, the pores of the spent alumina catalyst were filled with 2-amine-1-methyl benzimidazole and dithizone aimed to the efficient elimination of divalent zinc, cadmium, and nickel toxics from aqueous wastes. The adsorption removal capacity over 2-amine-1-methyl benzimidazole/alumina was found 1.01, 0.55, 0.38 mmol/g for Cd (II), Zn (II), and Ni (II), respectively. The adsorption of these mentioned toxic metals occurred via chemical reaction and physisorption over 2-amine-1-methyl benzimidazole/alumina nanosorbents [109]. Polyethersulfone membranes were filled with alumina nanoparticles by several dosages to improve its efficiency toward Cu (II) ions removal. It was concluded that the increased alumina nanoparticles, increased the metal ions elimination from water [111]. The alumina adsorption capacity can also be improved via combination with metallic nanoparticles. In a recent study, Kumari et al. [112] used green synthesized nanoparticles of silver to be stabilized over alumina nanoparticles for heavy metals removal from pharmaceutical effluents. They used bio-based reductant Bacillus cereus cell extracts for the green synthesis process environmentally-safe. This nanocomposite caused the removal of Pb and Cr from pharmaceutical effluent with efficiency of 99.5% and 98.44%, respectively [112]. Metal oxides adsorption capacities can be improved through modification with surfactants. Thus, the modification of alumina nanoparticles with surfactants was improved by inhibiting nanoparticles agglomeration and therefore increasing their surface area for better adsorption capacity. γ -Al₂O₃ NPs was modified using sodium dodecyl sulfate (SDS) and sodium tetra decyl sulphate for the elimination of divalent cadmium ions allowing high effect of surfactant on the adsorption process [113]. The adsorption efficiency was found improved by modification from 67% to 95%. Additionally, SDS was used to modify alumina surfaces for better adsorption of Mn (II) ions from manganese-bearing real industrial wastewater and Mn(II)-spiked wastewater. The removal occurred via adsolubilization of manganese ions in the admicelle formed by SDS on the alumina surface. The adsorption of Mn (II) over this modified nanoadsorbent occurred with efficiency of 92% [114].

2.6. Silica Based Nanomaterials

The exceptional properties of silica-based nanomaterials such as definite pore size, manageable surface characters, and high surface area has made these nanomaterials an important metal oxides class for the detoxification of water from heavy metals. Additionally, these nanoadsorbents possess advanced selectivity and adsorption capacity to metals when modified with thiol and amino groups. Additionally, they are eco-friendly and non-toxic that increased their applications in water remediation. The adsorption capacity of functionalized and non-functionalized silica nanoadsorbents toward the chelation of divalent ions of lead, nickel, and cadmium are studied and compared in the literature [115]. The comparison occurred between NH₂-silica gel, non-functionalized nanosilica spheres, and NH₂silica nano hollow spheres showed higher adsorption capacity of functionalized materials equal to 96.80, 31.40, 40.74 mg/g for the removal of lead, nickel, and cadmium ions, respectively. Additionally, silica nanospheres were modified with phenyl groups and 3-amino propyl in order to enhance the adsorption removal capacity toward divalent copper ions. Interestingly, as the number of amino groups increased, the adsorption efficiency toward copper ions was increased [116]. In a similar research, nitrilotriacetic acid was used to modify silica gel that applied for treatment of wastewater containing divalent ions of lead, cadmium, and copper. The modified nanoadsorbent removed the Pb (II), Cd (II), and Cu (II) with adsorption capacity of 76.23, 53.15, 63.6 mg/g, respectively within only 2–20 min [117]. Recently, Yang et al. used kerf loss silicon waste for the synthesis of 3-aminopropylethoxysilane (APTES)-functionalized nanoporous silicon (NPSi) hybrid materials via nanosilver-assisted chemical etching. The functionalized nanoadsorbent examined for the adsorption of hexavalent chromium Cr (VI) from aqueous solution with a maximum adsorption of 103.75 mg/g within one hour. The adsorption mechanism occurred via the reduction of Cr (VI) to Cr (III) over protonated amino groups. This functionalized nanoadsorbent maintains its efficiency after 5 cycles of adsorption [118]. The several nanomaterials applied for the elimination of toxic metallic ions from wastewater were summarized in Table 1.

Metal Ions	Adsorbent	Contact Time (min)	Initial Metal Conc. (mg/L)	Dosage of Adsorbent (mg/L)	pН	Temp. (K)	Ref.
Cd (II)	Graphene Oxide Nanosheets	-	20	1000	10	303	[35]
	(PVA)/NaX nanozeolite	60	50	500	5	318	[40]
	SPH	-	100	2	7	298	[48]
	HDI-IC-DETA	30	58.9, 112.4	1000	6	333	[50]
	Nitrogen-doped carbon materials	120	40	400	5	298	[56]
	Fe ₃ O ₄ /MnO ₂	30	10	1000	3	298	[66]
	SNHS, NH2-SNHS, (NH2-SG)	1440	140	15	14	298	[115]
	MnO ₂ /oMWCNTs	150	15	500	5	323	[105]
	NTA-silica gel	720	20	1000	2.9	298	[117]
	DTZ-Al ₂ O ₃ and MAB-Al ₂ O ₃)	720	44.9-865.4	3330	11	298	[109]
	SMA (SDS and STS @ Al ₂ O ₃)	120	-	-	6	298	[113]
	Polystyrene-poly(N-isopropylmethacrylamide-acrylic acid	100	50	0.0011 g	9	298	[119]
	Fe ₃ O ₄ /HA	15	0.1	10	6	298	[120]
Co (II)	Graphene Oxide Nanosheets	-	20	1000	10	303	[35]
	Al ₂ O ₃ NPs in zeolite	240	50	-	7	318	[41]
	SPH	-	100	2	7	298	[48]
	HDI-IC-DETA	30	58.9, 112.4	1000	6	333	[50]
Pb (II)	CNTs	360	10	500	6	308	[37]
	MMT/C	50	100	400	5	308	[39]
	PAN nanofibers	30	100	1000	6	298	[49]
	Nitrogen-doped carbon materials	120	40	400	5	298	[56]
	Fe ₃ O ₄	30	100	10,000	5.5	298	[62]

Table 1. Nanomaterials for heavy metals removal from water.

Metal Ions	Adsorbent	Contact Time (min)	Initial Metal Conc. (mg/L)	Dosage of Adsorbent (mg/L)	pН	Temp. (K)	Ref.
	$(CMC-Fe_3O_4)$	120	200	1000	6	298	[86]
	CuFe ₂ O ₄	220	10	20	4.5	298	[29]
	Fe ₃ O ₄ -SiO ₂ -GSH MNPs	120	100	100	5.5	308	[76]
	MNPs-Ca-alginate	60	500	1800	5	308	[87]
	Glycine-MNPs (GF MNPs)	100	10	10,000	2	298	[88]
	PAN/PPy/MnO ₂) nanofiber	120	400	60	6	298	[99]
	SNHS, NH2-SNHS, (NH2-SG)	1440	140	15	14	298	[115]
	NTA-silica gel	720	20	1000	2.9	298	[117]
	TEMPO	-	-	-	-	298	[109]
	Polystyrene-poly(N-isopropylmethacrylamide-acrylic acid	100	50	0.0011 g	9	298	[119]
	NH ₂ MNPs	60	10	100	5	298	[121]
	Fe ₃ O ₄ @C	120	50	1000	5.5	293	[122]
	Fe ₃ O ₄ /HA	15	0.1	10	6	298	[120]
Ni (II)	(PVA)/NaX nanozeolite	60	50	500	5	318	[40]
	SPH	-	100	2	7	298	[48]
	HDI-IC-PEHA	30	58.6, 63.8, 51.9	1000	6	333	[50]
	Alg-CS	30	70	3000	3	298	[58]
	(PVA)/zinc oxide (ZnO) nanofiber	300	50	1000	5	318	[101]
	$DTZ-Al_2O_3$ and $MAB-Al_2O_3$)	720	17.5-368.5	3330	7	298	[109]
	SNHS, NH ₂ -SNHS, (NH ₂ -SG)	1440	140	15	14	298	[115]
Cr (III)	Al_2O_3 NPs in zeolite	240	50	-	7	318	[41]
	HDI-IC-PEHA	30	58.6, 63.8, 51.9	1000	6	333	[50]
	Polystyrene-poly(N-isopropylmethacrylamide-acrylic acid	100	50	0.0011 g	9	298	[119]
Cr (VI)	TEPA-NMPs	180	50	5000	3	318	[83]
	EVOH nanofiber membranes	100	150	100	2	318	[52]
	SJA-Fe	90	50	500	5.5	298	[95]
	PAA-coated amino-functionalized Fe ₃ O ₄	-	600	20,640	5	298	[89]
	α -Fe ₂ O ₃ nanofibers	5	200	2000	-	298	[102]
	CuO	10	20	1600	3	298	[104]
	BiOBr/Ti ₃ C ₂	80	20	40	-	298	[123]
Cu (II)	SPH	-	100	2	7	298	[48]
	PAN nanofibers	30	100	1000	6	298	[49]
	HDI-IC-PEHA	30	58.6, 63.8, 51.9	1000	6	333	[50]
	Fe ₃ O ₄	30	2	10	7	298	[82]
	PAA-coated amino-functionalized Fe ₃ O ₄	-	600	20,640	5	298	[89]
	Kaolinite (K-Fe/Ni)	30	200	-	4.7	298	[97]
	(PVA)/zinc oxide (ZnO) nanofiber	300	50	1000	5	318	[101]
	NH ₂ -silica	150	-	1000	5	298	[116]
	NIA-silica gei	720	20	1000	2.9	298	[11/]
	(IFC-CINFS) Cohalt formita Titanata NTa alginata	-	-	0.15	-	290	[109]
	Polyatyrona poly(N isopropylmathaemilamida acmilia acid	120	10 50	0.15	0	290	[124]
	GA-APTES	100	15.88	1250	4	290	[119]
7 (11)		20	100	1200		200	[10]
Zn (11)	PAIN nanotibers	30	100	1000	6	298	[49]
M- (II)		720	38.8-117.6	3330	2	298	[109]
NIO (II)	$ZnFe_2O_4$	-	110	2000	3	298	[07]
Hg (II)	Fe ₃ O ₄ /SiO ₂ /APTES	-	50×103	-	-	298	[75]
	re ₃ 0 ₄ /nA	15	0.1	10	0	298	[120]
As (V)	NZVI	720	1	100	6.5	298	[94]
As (III)	Cobalt territe, Iitanate NTs, alginate	120	10	0.15	6	298	[124]
Fe (III)	Cobalt territe, litanate N Is, alginate	120	10	0.15	6	298	[124]
U (VI)	(PVA)/zinc oxide (ZnO) nanofiber	300	50	1000	5	318	[101]

Table 1. Cont.

3. Factors Affecting Adsorption Process

The adsorption process of heavy metals ions over different surfaces is controlled by various factors including the initial ion concentration, the temperature, the contact time, the adsorbent dosage, and the pH of reaction medium. Thus, in the following sections the effect of the mentioned factors on the heavy metals removal from water/wastewater will be discussed.

3.1. Ionic Strength Effect

The adsorption process over the adsorbate surface is greatly affected by the existence of extra ions in the solution. So, the ionic strength of solution plays a vital role in the adsorption efficiency.

The extra added ions affected significantly the adsorption efficiency through their competition with the main adsorbed ions on the adsorbent chelation sites. Commonly, the influence of experimental ionic strength on chelation performance was studied by the addition of Cl⁻ and Na⁺ ions to the solution. Additionally, the adsorbent affinity toward added ions and their concentrations affected the adsorption efficiency. Sometimes, the effect of ionic strength on the adsorption process is neglected due to the low attraction of adsorbent to the extra ions compared to the target metal ions as reported in several studies. For example, in the study of the adsorption of lead divalent ions over the surface of $Fe_3O_4/SiO_2/GSH$ nanocomposite [76], the adsorption was increased when sodium chloride concentration in the solution was 0.025 mM that enhances the dispersion of functional groups on the adsorbent surfaces. However, when the sodium chloride concentration reached 0.2 mM there was a decrease in the adsorption of lead ions due to the competition on the chelation sites. In another study [92], during the adsorption of divalent cadmium and lead ions over magnetic nanocomposite, the addition of sodium chloride ions up to 3 mol/L has no effect on the adsorption of toxic metals This indicates the great attraction of metal ions over the nanocomposite surface more than the added ions. Consequently, the influence of ionic strength on the adsorption reaction may be significant or neglected depending on the attraction between the target adsorbate and the adsorbent in addition to sodium chloride concentration.

3.2. Initial Ion Concentration Effect

Generally, it is recognized that the increasing of toxic species concentration increases the adsorption process to a certain point after which the adsorption decreases due to the metal ions optimum concentration that must be exist in the reaction medium for the applied adsorbent. Low numbers of toxic metals are available at low concentration allowing the decrease of the scavenging efficiency, but at a higher metallic concentration the available ions for adsorption process are increased leading to the enhancement of the removal efficiency. Nevertheless, above a certain initial concentration, ions with the equal amount of adsorption locations are available, which therefore decreases their elimination adsorption capacity. For instance, nanofibrous adsorbent PVA/ZnO adsorption capacity was improved for the chelation of Ni (II), Cu (II), and U (VI) when the metallic initial concentration increased from 90 to 500 mg/L [101]. Similarly, the adsorption of divalent mercury ions over chitosan-alginate nanoparticles (CANPs) surface enhanced when initial metallic concentration elevated from 4 to 12 mg/L then reduces successively [59].

3.3. Temperature Effect

The adsorption process is greatly influenced by the temperature of the solution. Generally, the increasing of the temperature reduced the solution viscosity and, consequently, improved the ions diffusion to reach the adsorption allowing the enhancement of the adsorption competence. Therefore, the adsorption process of metal ions from aqueous solution can be affected by solution temperature in two ways depending on heat emitted or absorbed. The increasing temperature causes the increase of the adsorption rate for endothermic adsorption while causing the decrease of the adsorption rate for exothermic adsorption. Moreover, the adsorption study under temperature change introduces many thermodynamic parameters about the adsorption process including entropy changes (Δ S), enthalpy change (Δ H), and Gibbs free energy change (Δ G). In the literature [59], for the CANPs adsorption of divalent mercury ions, the adsorption process was exothermic. So, when the temperature is raised from 10 to 20 °C there is an enhancement of adsorption process, but over this temperature the adsorption process decreased significantly due to the increased kinetic energy that caused the desorption of metallic ions from adsorbent sites. Hence, the increased temperature decreased the chelated ions over CANPs surface. Another reason for adsorption decrease is the weak electrostatic interactions between mercury and adsorbent at increased temperature as it is exothermic adsorption. The process is known to be endothermic and spontaneous when $\Delta H = \text{positive value and } \Delta G = \text{negative value } [126-131].$ In another work, Fe₃O₄ nanoparticles chelated divalent lead ions through endothermic adsorption

process. So, the increasing of the temperature increased the mobility of ions to reach a large number of binding sites that enhanced the adsorption capacity to lead ions [62].

3.4. Contact Time Effect

The water/wastewater economical remediation from toxic heavy metals significantly depends on the contact time between nanosorbent and metal ions. The adsorption efficiency greatly increases by increasing the time of contact between pollutants and adsorbent due to the increase of interaction time between active sites of chelation and metals. Normally, at the beginning of the adsorption the removal efficiency occurs quickly and then increases gradually. This occurs because of the availability of the free active sites at initial adsorption that are gradually occupied with time by chelated metals. This phenomenon was reported for the adsorption of divalent mercury ions on surfaces of CANPs. When the contact time increased from 0 to 90 min, the adsorption greatly increased. At the first half-hour the adsorption increased rapidly then delayed with reaching equilibrium at 90 min [59]. Similarly, the study reported the chelation of divalent cadmium and lead ions over surfaces of MNCPs [92]. The adsorption efficiency within 20 min reached 91% and 100% of maximum adsorption (48.54 and 53.35 mg/g) for Cd (II) and Pb (II) ions respectively. Subsequently, the adsorption becomes independent on the contact time when the equilibrium reached between desorption and adsorption.

3.5. Adsorbent Dosage Effect

The dosage of the added adsorbent plays a vital role in the removal of pollutants via adsorption. Increasing the adsorbent dosage caused an increase in the number of existing active sites to chelate toxic metals, and greatly enhances the adsorption capacity. So, the amount of nanoparticle dosage efficiently improves the adsorption capacity. Nonetheless, the active sites decrease as a result of surface area decrease by additional increase in the nanoparticles amount due to the agglomeration of the adsorbent that greatly reduces the adsorption capacity. The adsorbent dosage effect on the heavy metals removal from the aqueous solution has been studied in several studies. For instance, nanofibrous TiO₂ coated chitosan was used for the elimination of divalent copper and lead ions from water with an optimal dosage of 2000 mg/L. After this optimal dosage of nanosorbent, there were nanoparticles agglomerations and the decrease of surface area caused a reduction of adsorption capacity toward toxic metals [57]. In another study, Fe₃O₄@C nanoadsorbent used for the removal of lead ions from water improved the efficiency from 41% to 92% when the adsorbent dosage increased from 0.5 to 2 g/L, due to the increase of the active site number and to the simple contact of lead ions with these sites. However, the increase of the adsorbent dosage reduced the removal efficiency from 41% to 22% due to the adsorbent agglomeration that reduces the existed active sites to chelate lead ions [123].

3.6. pH Effect

The adsorption reaction and adsorption capacity greatly depend on the reaction medium pH. So, the effect of pH on metal ions scavenging must be determined. In a study of Hg (II) divalent ions removal via CANPs nanoparticles, there was an increase in the adsorption capacity when the pH changed from 2 to 5. However, at lower pH, the functional groups over nanoparticles surfaces became protonated, which led to electrostatic repulsion that prevents the adsorption of the target heavy metal. Additionally, there was a competition between the heavy metal and H_3O^+ for the active sites of the adsorbent. Sometimes, the adsorption enhanced at moderate values of pH due to the deprotonation of functional groups and to the decrease of repulsion forces that enhances the adsorption capacity [59].

Similarly, chromium reached its highest adsorption on functionalized magnetic polymer at pH 2. This adsorption exhibited a dependence on the electrostatic interactions related to the presence of functional groups. However, it is very important to take into consideration the speciation chromium oxidation state in order to determine the adsorption mechanism [82–84,132]. The heavy metals adsorption, as determined in several studies, is favored at moderate pH values than at lower pH values. For instance, nanofiber chitosan/TiO₂ chelated divalent ions of copper and lead with minimum

removal at 2–4 pH values and maximum removal at 6 pH values [57]. Similarly, the cadmium ions removal increased by increasing the pH from 4 to 6, then remained constant at pH 9. However, the increase of pH to 11 decreased the removal of cadmium to 80%, indicating that cadmium removal is favored at moderate pH values due to the deprotonation of functional groups that reduces repulsion forces and increases the attraction between metal ions and functional active sites [88]. Though, at low pH the protonated active sites numbers increase and caused a great repulsion with positive charged toxic pollutants that greatly reduces the adsorption capacity of the nanoadsorbent [87]. At very high pH values, several complexes between metal species and OH groups formed that blocked the large numbers of adsorbent active sites and reduced their adsorption capacity.

4. Desorption and Recyclability of the Nanoadsorbents

The viability of adsorbents in practical applications is depending on their evaluation for the reusability due to the reduced cost of adsorption by the successful successive use of the adsorbent [133–135]. The reusability of nanoadsorbents occurred by the successful separation from the experimental medium using several methods, as reported in the literatures. For example, ion-selective polyacrylonitrile nanofibers were used for the removal of divalent ions of zinc, lead, and copper in a reusability study with up to four cycles of excellent efficiency of more than 90%, by using $0.5 \text{ M} \text{ H}_3\text{PO}_4$ and $1.0 \text{ M} \text{ HNO}_3$ [49]. Stable adsorption results were found for the removal of zinc and lead using these nanoadsorbents indicating the ease of reusability and recyclability, while the adsorption results decreased for copper ions with the reusability. Additionally, CMC-Fe₃O₄ used for the removal of divalent lead ions was tested for reusability through cleaning with 0.1 M Na₂ HPO₄ and H_2O [84]. The adsorption capacity of this nanosorbent was slightly decreased during the reusability cycles. After 5 cycles the adsorption capacity was still more than 85%. This nanoadsorbent has a great tendency for reusability, as shown in a magnetism study in which the magnetization before and after five cycles was still the same that made these nanomaterials valued for water treatment. In another study, diluted HNO₃ solution as a desorbent was used to study the reusability of HNC-3 for lead ions removal. The results indicated excellent reusability even after 5 cycles for lead removal. This complete recovery with nitric acid indicated that the lead ions were completely desorbed from the nanomaterial active sites, due to the competition between lead ions and protons for the active sites on the nanoadsorbent surface [56]. Additionally, core/shell gel particles of polystyrene-poly (N-isopropylmethacrylamide-acrylic acid) used for the adsorption of Cr (III), Cd (II), Cu (II), and Pb (II) ions were reused via washing with 0.5 M HCl. The reusability of these core/shell gel particles was successful up to 3 repetitive cycles, but with a small noted decrease in the Cr (III), Cd (II), and Cu (II) removal in the 3rd cycle [119]. MnO₂ nanotubes@reduced graphene oxide hydrogel (MNGH) nanoadsorbent was applied for the removal of divalent lead ions from water in a reusability study. The desorption of metal ions from adsorbent was conducted using 0.5 M HNO₃. Pb (II) adsorption capabilities decrease somewhat with reuse cycles. After eight cycles of reusability, the adsorbent retained 87% of its adsorption capacity. Thus, this nanoadsorbent is suitable for toxic metals removal with ease reusability [34].

5. Conclusions

Recently, great developments have been observed in the field of nanotechnology and nanoscience that produce environmentally-safe, economical, and efficient materials for environmental engineering. These engineered nanomaterials are promising for water treatment due to their unique physicochemical properties that enable the heavy metals scavenging with high adsorption capacity and selectivity even at very low concentrations. Efficient heavy metals removal from water was reached via the simple adsorption technique. The current review discussed the heavy metals removal using different nanomaterials like zeolite, polymers, chitosan, metal oxides, and metals under different conditions. The new studies focused on nanomaterials functionalization in order to enhance properties of separation, stability, and adsorption capacity. The functionalization process was reached using different molecules such as biomolecules, polymers, inorganic materials etc. By providing the magnetic properties to the adsorbent, its separation becomes easier via magnetic separation techniques. The effect of various experimental conditions like ionic strength, initial concentration of metal, contact time, temperature, adsorbent dosage, and pH of the solution on the adsorption was discussed. For initial metal concentration, the increased metal ion concentration initially increases the adsorption process then decreases due to the occupation of adsorbent active sites. For the effect of time, the adsorption occurs rapidly at the beginning of adsorption then slows down at equilibrium. Additionally, the temperature greatly affects the metal ions capture from water. For endothermic adsorption, the increase of the temperature caused an increase of the adsorption capacity while for exothermic adsorption the increase of the temperature caused a decrease of adsorption capacity. The metal/binding sites ratio that showed the adsorbent dosage effect on adsorption was found to greatly affect the adsorption capacity. The metals removal was found greatly depending on the pH solution. Maximum metals removal was reached at moderate pH. However, at low or high pH values, the removal was lower. This review provided precious information regarding the use of engineered nanomaterials for the removal of toxic heavy metals that will guide the researchers intending to fabricate new nanomaterials for water/wastewater remediation. It should be noted, that all experiments are conducted at lab-scale for toxic metals in aqueous solutions and studies are needed to evaluate the process efficiency at pilot and large scale using real wastewater.

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