Similarity Removal of Heavy Metals from Aqueous Solutions Using Advanced Materials, with Emphasis of Synthetic and Nanomaterials

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Abstract

Contaminated water with heavy metals is considered to be a serious threat to human health as well as to the environment. Heavy metals get a great attention owing to their toxicity and persistence in the environment. Different techniques for elimination of heavy metal have discussed in literature. Adsorption, the most extensively used method; plays vital role in wastewater treatment. Many research studies have been taken place during the last decade for the preparation of effective and economically suitable adsorbents. More recently, nanotechnology and material science have opened a new way for the buildup of new materials that can be used for the elimination of different pollutants. This review includes analyzing and discussion of different research studies and research papers published during last ten years, concerning the usage of nanomaterials for omitting heavy metals from aqueous solutions.

Keywords: *Heavy metals; nanomaterials; nanoadsorbents; metal oxide; carbon nanotubes*

Contents

Nomenclature

MCL	Maximum Concentration Limit	TNW	Titanate NanoWires
USEPA	United States Environmental Protection Agency	CNTs	Carbon Nano Tubes
		SWCNTs	Single-Walled Carbon NanoTubes
NMOs	Nano Metal Oxides	MWCNTs	Multi-Walled Carbon NanoTubes
M-MIONPs	Modified Magnetic Iron Oxide Nanoparticles	MWCNT-COOHs	
			Carboxylic Multi-Walled Carbon NanoTubes
GOF/Fe_3O_4	Graphene oxide foam/Fe_3O_4 nanocomposite	MWCNT-HAP	
SPIONs	Superparamagnetic iron oxide nanoparticles		Multi-Walled Carbon NanoTube-HydroxyAPatite
PMMA	Poly methylmethacrylate	S-MWCNTs	Sulfur containing Multi-Walled Carbon NanoTubes
EDTA	EthyleneDiamine Tetra Acetic acid		
ACC	Activated Carbon Cloth	SWCNT-SH	Thiol-derivatized Single-Walled Carbon NanoTubes
HMO	Hydrous Manganese Oxide		
ZnO-UF	Zinc Oxide -Urea Formaldehyde	CS/SWCNTs	Chitosan/ Single-Walled Carbon NanoTubes
LPTNs	Layered Protonated Titanate Nanosheets		
		C-β-CD	Carboxymethyl-β-CycloDextri
TNF	Titanate NanoFlowers		
TNT	Titanate NanoTubes		

1. Introduction

Heavy metals found their ways to the environment through wastewater streams of the modern industrial activities such as batteries, pesticides, fertilizers and paper industries, metal plating, and mining operations (Table 1) [1-2]. Heavy metal contamination has got great attention since they are known to be toxic and non-biodegradable [3]. They can cause serious health effects, including organ damage, nervous system damage, reduce growth and development, cancer and death in extreme cases. So regulations for wastewater discharge were developed to control human exposure to heavy metals. The MCL standards for those heavy metals, established by USEPA [4] are listed in Table 2.

Table 1: Anthropogenic sources of heavy metals [2]

Metal	sources
Lead (Pb)	lead acid batteries, paints, Smelting operations, coal-based thermal power plants, ceramics
Copper (Cu)	Mining, electroplating, smelting operations
Cadmium (Cd)	Zinc smelting, waste batteries, paint sludge, incinerations and fuel combustion
Nickel (Ni)	Smelting operations, thermal power plants, battery industry
Zinc (Zn)	Smelting, electroplating
Chromium(Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning

Many treatment methods have been reported in the literature which can be used to treat contaminated water with heavy metals. Among these methods are; the chemical precipitation, ion exchange, coagulation, and electrochemical removal but these methods led to incomplete elimination, usage of high-energy, and creation of toxic sludge [5]. Other methods such as solvent extraction, biological, photo catalysis, membrane filtration, floatation, and adsorption are employed for taking away metal ions from aqueous solutions. Among of all these methods, adsorption was found to be the most persuasive method [6]. The adsorption process is affected by the characterizations of the adsorbent materials such as the surface morphology, adsorbent surface area, the pore volume, mean particle size and the functional groups attached to the adsorbent

surface [7]. Huge numbers of adsorbents have been reported in several recent studies including activated carbon [8-13], synthetic polymers [14-17] and silica-based adsorbents [18]. These types of adsorbents suffer from intra-particle diffusion that decreases the adsorption rate due to the size of the adsorbents. To overcome this limitation, preparation of nanoadsorbents has taken place. These nanoadsorbents have small diffusion resistance that increased the importance of using nanoparticles as adsorbent [19].

Table 2: The MCL standards for heavy metals, established by USEPA [4]

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.2
Zinc	Depression, lethargy, neurological signs and increased thirst	0.8
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

2. Nanomaterials as adsorbent

Clearly, the progress in nanotechnology and nanomaterial science recently has shown remarkable potential for the heavy metal elimination from wastewater [20-21].

Nanotechnology uses materials that have at least one dimension in the ranges from 1 to 100 nm [22, 23]. At this scale, nanomaterials possess some unique physical properties, chemical properties and morphologies due to the enhanced surface area which allows more sites for surface chemistry [24]. Nanoparticles can be easily aggregated in aqueous systems which could decrease their adsorption efficiency so it is important to modify the surface by the attachment with suitable functional groups such as carboxylic acids, phosphoric acid, silanol, thiol, and amine as well as small organic molecules, biomolecules and polymer [25]. In the last twenty years, some attempts were achieved in order to prepare and use these nanosized materials for omitting heavy metals from aqueous solutions due to their large surface area, ease and ability to functionalize their surfaces in order to increase adsorption capacity [26]. Nanomaterials used as adsorbents that will be surveyed within this review, include metal oxide nanomaterials, carbon nanomaterials, and polymer-based nanomaterials.

2.1 Metal oxide nanomaterials

Nanosized metal oxides (NMOs) are characterized by their large surface areas, high adsorption capacities and surface functional groups that can interact with heavy metal ions [27-29]. Many recent researches classified the nanosized metal oxides (NMOs) as powerful adsorbents for heavy metals from aqueous systems [30-31]. But nanosized metal oxides suffer from their poor stability because the surface energy increases as the particle size cut down to nanometer dimensions. Also,

the nano metal oxides are tending to agglomerate because of Van der Waals forces; this will lead to decrease the high adsorption capacity and selectivity of NMOs [32]. Many recent studies for the adsorption of heavy metals from wastewater have taken place; the most widely studied nano metal oxides include iron oxides, manganese oxides, aluminum oxides, CuO, NiO, ZnO and TiO$_2$ [33-39]. Nanoparticles can be prepared by many efficient routes, including the use of mechanical attrition, in particular, high-energy ball milling [40-43], ultrasonic shot peening [44-46], inert gas condensation (IGC) [47-48], reverse micelle (or microemulsion) [49-50], controlled chemical co-precipitation [51-53], chemical vapor condensation [54-55], pulsed electrodeposition [56-57], liquid flame spray [58], the sol-gel method [59-61] and hydrothermal reactions [62]. Metal oxides nanoparticles dominated minimal environmental impact, low solubility and they do not lead to any secondary pollution; they have also been widely adopted as sorbents to remove heavy metals. Summary for the most recent NMOs used for heavy metal removal from wastewater are devoted in the following sections.

2.1.1 Iron Oxide/Hydroxides Nanoparticles

Methods that used for the preparation of iron oxide nanoparticles playing an important role because of the presence of sixteen pure phases of the iron oxides such as oxides, hydroxides and oxy-hydroxides, that can be obtained [63]. Among the different phases of Iron Oxide/ hydroxides; the magnetic phase-magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$) and non-magnetic, hematite (α-Fe$_2$O$_3$) are the most widely used iron-based nanoadsorbents [64]. It is easy to control the shape, size and compositions of the nanoparticles prepared by chemical methods by controlling the temperature and pH of the reaction as well as the nature of precursor salts [65]. Magnetic iron oxides have got great attentions in wastewater treatment because it enables a rapid and effective method for solid-liquid separation using a magnetic field [66]. Numbers of research groups have been working with magnetic iron oxides as an adsorbent for heavy metal ions. In 2010, Wang et al. [67] has prepared amino-functionalized silica-coated Fe$_3$O$_4$ nanoparticles by chemical co-precipitation method. The produced nanoparticles were in cubic spinel shape; the size of the particles was 18.4 nm. The prepared nanoparticles were tested for removal of Cu, Pb, and Cd using batch system. The initial concentrations of the three ions were 0.79, 0.48 and 0.44 mmol/L for Cu, Pb, and Cd, respectively. The adsorbent dosage was 0.3g/L at pH 6.2. The adsorption capacities of the amino-functionalized silica-coated Fe$_3$O$_4$ nanoparticles were 30, 76.6 and 22.5 mg/g for Cu, Pb, and Cd, respectively. Chen et al. [68] have prepared two types of nanoparticles namely; Hematite (α Fe$_2$O$_3$) and nano-goethite (α-FeOOH) by chemical co-precipitation method. The nanoparticles produced had a particle size of 75 nm with BET surface area of 24.82 m^2/g for Hematite (α Fe$_2$O$_3$) and Nanowires with a width in the range 10-15 nm and 500 nm in length and BET surface area of 71.49 m^2/g for nano-goethite (α -FeOOH). Both types produced were tested for adsorption of Cu in a batch system. The initial concentration of Cu was 47.43 ppm, pH 5.2 and adsorbent dosage of 0.3 g/l. The results matched with Langmuir model and the adsorption capacity of the Hematite (α Fe$_2$O$_3$) nanoparticles for Cu was 84.46 mg/g while for nano-goethite (α -FeOOH) was found to be 149.25 mg/g. Chowdhury et al. [69] have synthesized mixed magnetite-maghemite nanoparticles by chemical co-precipitation method. The produced nanoparticles were tested in the removal of Cr(VI) in a batch system. The experiments were conducted for initial concentration 100 ppm of Cr(VI), pH 2-3 and adsorbent dosage of 4.0 g/l. The maximum adsorption capacity for that adsorbent is 78.13 mg/g. Tuutijarvi et al. [70] have studied the use of γ-Fe$_2$O$_3$ prepared by chemical co-precipitation method, for the elimination of Zn(II), Cu(II) and Cr(VI). The produced nanoparticles were in the spherical shape of 10 nm diameter. The operating conditions were Co =

1000 ppm, pH 2.5 and adsorbent amount 1.0 g for each liter. The highest adsorption capacities were 15.9, 15 and 55 mg/g for Zn, Cu, and Cr(VI) respectively. In 2011, Khodabakhshi et al. [71] have prepared magnetic nanoparticles by sol-gel method. The produced nanoparticles were in the size range of 40-300 nm and used for the removal of As(III) from synthetic industrial waste water in a batch operating system. The removal carried out for As(III) concentration of 10 mg/L, an adsorbent dosage of 1g/L with shaking speed of 250 rpm was 82% of As(III). The adsorption capacity of the magnetic Fe_3O_4 nanoparticles for As(III) at pH=7 was found to be 23.8 mg/g.

In 2012, Roy et al. [72] have developed maghemite nanotubes using a template free microwave irradiation. The produced nanotubes have a 10 -15 nm diameter and 150 -250 nm length with BET surface area 321.638 m^2/g. The produced nanotubes were evaluated to remove Cd(II), Ni(II), and Co(II) in a batch reactor. The operating conditions were initial concentrations of 100 ppm for the Cd(II), Ni(II), and Co(II), pH 6 with an adsorbent dosage of 0.5g/l. The isotherm data were explained by Langmuir model. The maximum adsorption capacities were estimated as 94.33, 86.206, and 60.60 mg/g for Cd(II), Ni(II) and Co(II) respectively. Al-Saad et al. [73] have prepared a polymer coated magnetic iron oxide (Fe_3O_4) by co-precipitation method. The produced particles were in the size of 10 nm. The nanoparticles tested for adsorption of Cr(VI) from simulated wastewater in a batch reactor. The operating conditions were; Co = 25 ppm, pH 5 and an adsorbent dosage 2 g/l. The results showed 62.75% removal of Cr(VI). Parham et al. [74] have developed modified magnetic iron oxide nanoparticles (M-MIONPs) by co-precipitation method. The particles produced were in the size range of 40 -50 nm. The nanoparticles used for removal of Hg(II) using batch reactor. The operating conditions were; Co = 0. 2 ppm, pH 9 and an adsorbent dosage of 2 g/l. The results showed 96.2% removal of Hg(II) with maximum capacity 0.6mg/g. In 2013, Roy et al. [75] have synthesized maghemite nanotubes using a template free microwave irradiation. The produced nanotubes have a 10 -15 nm diameter and 150 -250 nm length with BET surface area 321.638 m^2/g. The produced nanotubes were used to remove Cu(II), Zn(II) and Pb(II). The operating conditions were as follows; initial concentrations of 100 ppm for the Cu(II), Zn(II), and Pb(II), pH 6 with an adsorbent dosage of 0.5g/l. The experimental data were described by Langmuir isotherm. The highest adsorption capacities were 111.11, 84.95 and 71.42 mg/g for Cu(II), Zn(II) and Pb(II) respectively. Shipley et al. [76] examined the adsorption of metal ions (Pb(II), Cd(II), Cu(II), and Zn(II)) to nanohematite. The adsorption was tested using batch reactor equipped with 0.5 g/L nanoparticles. The results showed that nanohematite could remove Pb, Cd, Cu, and Zn ions from solution. The percentage removals were found to be 100 % Pb, 94 % Cd, 89 % Cu and 100 % Zn. Yong et al. [77] studied the removal of Cr(VI) using γ-Fe_2O_3 nanoparticles prepared by co-precipitation method. The isotherm data were fitted to Langmuir isotherm. The experimentally obtained maximum loading capacity was estimated as 22 mg/g. In 2014, Lei et al. [78] have developed graphene oxide foam/Fe_3O_4 nanocomposite (GOF/Fe_3O_4) and studied the usage of it for Cr(VI) removal. The results showed maximum adsorption loading of 258.6 mg/g for Cr(VI) removal. Tan et al. [79] have developed silica-coated magnetite ($Fe_3O_4@SiO_2$) nanoparticles functionalized with amino, imino and sulfonic groups by a facile chemical oxidative polymerization and used them for selective removal of Pb(II) and Cr(VI) from aqueous solutions. The maximum adsorption capacities were 83.23 mg/g and 119.06 mg/g for Pb(II) and Cr(VI) respectively on $Fe_3O_4@SiO_2$ nanocomposites. Qi et al. [80] developed spherical (13 nm in diameter) water soluble Fe_3O_4 supermagnetic nanocomposite by thermal decomposition method. The nanoparticles were used to remove Hg(II) with initial concentration 50 µg/L at pH 7 with 0.4 g/l adsorbent dose. The isotherm data was best fitted by Langmuir with maximum adsorption capacity 16.9 mg/g. In 2015, Madrakian et al. [81] have prepared a maghemite nanoparticles

modified with homopolymers. The diameter of the nanoparticles found to be 15-25 nm with BET surface area 92.41 m^2/g. The results revealed that the maximum adsorption capacities were 130.12, 237.46, 218.42, and 91.46 mg/g for Pb(II), Hg(II), Ag(I) and Cd(II) respectively. In 2016, Wanna et al. [82] have used Superparamagnetic iron oxide nanoparticles (SPIONs) and the one that were coated with poly (methylmethacrylate) (PMMA) by emulsion polymerization process. the efficiencies of the heavy metal ion removal for Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) were 80.0 %, 57.7 %, 54.3 %, 40.0 %, 34.8 %, 32.5 % and 30.2 %, respectively. All iron oxide nanoadsorbents discussed in this section are summarized in Table 3.

The regeneration of nanoadsorbents is an important step, which affects the process costs and pollutant recovery. The previous literature discussing the removal of heavy metals by adsorption reported that the process is pH dependent. Therefore, the regeneration step is carried out by controlling the pH of the eluent [83]. The use of NaOH as regenerating agent for Iron oxide nanoparticles and determination of the successive adsorption-desorption cycles have been reported in the literature.

Hao et al. [83] studied the reusability of Fe$_3$O$_4$-NH$_2$ nanoparticles that were aimed at the elimination of Cu(II). The results indicated that the adsorbent could be regenerated by 0.1 mol/L HCl and the adsorption capacity of the adsorbent was changed after 15 cycles of operation. Since the use of strong acids for regeneration of adsorbent could cause possible damage to the materials of the adsorbents, ethylenediamine tetra acetic acid (EDTA), could be used as the eluent for metal cations desorption [85]. Yuwei et al. [85] have studied the use of EDTA (0.1 mol/L) for regeneration of Fe$_3$O$_4$@Chitosan nanoparticles that used for removal of Cu(II). No changes in the adsorption capacity for the regenerated Fe$_3$O$_4$@Chitosan nanoparticles have been noticed before 4 cycles of operations. Solutions that showed similar or improved desorption performance in comparison with strong acids, are HCl or HNO$_3$ for iron oxides nanoparticles regeneration, as reported in Table 4.

2.1.2 Aluminum Oxide Nanoparticles

There are different phases of Aluminum oxide namely, Alumina (Al$_2$O$_3$) which is one of the most abundantly produced chemical in nanosized particles. The γ-Al$_2$O$_3$ phase is the nanostructured one that commonly obtained by most synthetic methods. Aluminum oxide nanoparticles are characterized by low cost, high surface area, surface reactivity and a strong adsorption capacity [86]. Aluminum nanoparticles are hydrophilic. So, it is important to modify the surface of γ-Al$_2$O$_3$ nanoparticles with certain functional groups such as oxygen, nitrogen, sulfur, and phosphorus by chemical or physical methods [89]. Researchers have reported the use of alumina and modified aluminum oxide nanoparticles for the removal of heavy metals from aqueous solution. In 2010, Rahmani et al. [90] studied the use of nano structured γ-Al$_2$O$_3$ as an adsorbent for Pb(II), Ni(II) and Zn(II) in a batch system. The results fitted well by Langmuir and Freundlich models and the kinetics of the process described by pseudo-second-order. The adsorption capacities were 125, 83.33 and 58.82 mg/g for Pb(II), Ni(II) and Zn(II) respectively. Afkhami et.al [91] have used nano-alumina modified with 2,4-dinitrophenylhydrazine for discard of Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Mn(II). The adsorption capacities of the adsorbent were 100, 83.33, 100, 41.66, 18.18 and 6.289 for Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Mn(II) respectively. During 2012, Saha et al. [92] have developed a nano-alumina dispersed in chitosan-grafted polyacrylamide by microemulsions method and studied the use of produced adsorbent for the adsorption of As(V). The adsorption capacity of the adsorbent for As (V) was 6.56 mg/g. In 2014, Stietiya et al. [93]

Table 3: Iron oxide nanoadsoebents for heavy metal removal

Adsorbent	Method of synthesis	Shape and Size (nm)	surface area, m²/g	Metal removed	Operating Conditions	Sorption capacity, mg/g	Adsorption Kinetics	Adsorption isotherm	Ref.
Amino-functionalized silica-coated Fe_3O_4 nanoparticles	Chemical Co-precipitation method	Cubic spinel 18.4	216.2	Cu(II), Pb(II), Cd(II)	Co = 0.79 mmol/L for for Cu(II), 0.48 mmol/L for Pb(II), and 0.44 mmol/L for Cd(II) pH 6.2 ± 0.1; Adsorbent dosage 0.3 g/l	30 76.6 22.5	-------	Langmuir	[67]
Hematite (α Fe_2O_3)	Chemical Co-precipitation	granular shape, 75	24.82	Cu(II)	Co = 47.43 ppm, pH 5.2 ± 0.1; Adsorbent dosage 0.3 g/l	84.46	pseudo-second-order	Langmuir	[68]
Nano-goethite (α -FeOOH)	Chemical Co-precipitation	Nanowires 10-15 nm in width and 500 nm in length	71.49	Cu(II)	Co = 47.43 ppm, pH 5.2 ± 0.1; Adsorbent dosage 0.3 g/l	149.25	pseudo-second-order	Langmuir	[68]
Mixed magnetite-maghemite nanoparticles	Chemical Co-precipitation method	------	-----	Cr(VI)	Co = 100 ppm, pH 2-3; Adsorbent dosage 4.0 g/l	78.13	-----	Langmuir	[69]
γ-Fe_2O_3	Chemical Co-precipitation	Spherical particles 10	------	Zn, Cu, Cr(VI)	Co = 1000 ppm, pH 2.5; Adsorbent dosage 1.0 g/l	15.9 15 55	-------	------	[70]

Magnetic (Fe$_3$O$_4$)	Sol gel	40-300	----	As(III)	Co = 10 ppm, pH 7; Adsorbent dosage 1.0 g/l	23.8 Removal 82%	-----	Freundlich	[71]
γ-Fe$_2$O$_3$	Microwave irradiation method	Nanotubes 10-15 diameter And 150-250 nm length	321.638	Cd(II), Ni(II), Co(II)	Co = 100 ppm, pH 6; Adsorbent dosage 0.5g/l	94.33, 86.206, 60.60	pseudo-second order	Langmuir	[72]
Polymer-coated magnetic iron oxide (Fe3O4)	co-precipitation method	10	----	Cr(VI)	Co = 25 ppm, pH 5.0; Adsorbent dosage 2.0 g/l	Removal 62.75%	-----	------	[73]
Modified magnetic iron oxide nanoparticles (M-MIONPs)	co-precipitation method	40-50	------	Hg(II)	Co = 0. 2 ppm, pH 9.0; Adsorbent dosage 2.0 g/l	0.6 and Removal 96.2%	-------	Langmuir	[74]
(γ-Fe$_2$O$_3$)	Microwave irradiation method	Nanotubes 10-15 diameter And 150-250 nm length	321.638	Cu(II), Zn(II) Pb(II)	Co = 100 ppm, pH 6; Adsorbent dosage 0.5g/l	111.11, 84.95 71.42	pseudo-second order	Langmuir	[75]
Hematite nanoparticles	Commercially prepared Hematite nano particles	20.5-269.6	31.7	Pb(II), Cd(II), Cu(II), Zn(II)	0.48 μmol/L Pb(II), 0.89 μmol/L Cd(II), 0.1.6 μmol/L Cu(II), 1.5 μmol/L Zn(II), pH 8; Adsorbent dosage 0.5g/l	Removal 100 % Pb, 94 % Cd, 89 % Cu 100 % Zn	------	Freundlich	[76]

γ-Fe$_2$O$_3$	Chemical Co-precipitation	10.8	--------	Cr(VI)	Co = 50 ppm, pH 2.5; Adsorbent dosage 5.0 g/l	22.0	pseudo-second-order	Langmuir	[77]
Graphene oxide foam/Fe$_3$O$_4$ nanocomposite (GOF/Fe$_3$O$_4$)	------	-------	574.2	Cr(VI)	-----	258.6	-----	-----	[78]
Silica coated magnetite (Fe$_3$O$_4$@SiO$_2$) Functionalized by amino-imino-sulfonic group	Chemical Oxidative polymerization	-----	--------	Pb (II) Cr(VI)	-------	83.23 119.06	pseudo-second-order	Freundlich	[79]
Water soluble Fe$_3$O$_4$ supermagnetic nanocomposite	Thermal decomposition	Sphere 13	-----	Hg(II)	Co = 50 µg/l, pH 7; Adsorbent dosage 0.4 g/l	16.9	-----	Langmuir	[80]
Maghemite modified with homopolymer	-----	15-25	92.41	Pb(II), Hg(II), Ag(I), Cd (II)	------	130.12, 237.46, 218.42, 91.46	pseudo-second-order	Langmuir	[81]
Superparamagnetic iron oxide nanoparticles (SPIONs) coated with poly (methylmethacrylate) (PMMA)	Emulsion polymerization process.	------	-----	Cu (II), Mn (II), Zn (II), Cd (II), Pb (II), Co (II), Ni (II)	------	80.0 %, 57.7 %, 54.3 %, 40.0 %, 34.8 %, 32.5 % 30.2 %	--------	------	[82]

Table 4: Regeneration and reusability of Iron oxide nanoparticles for heavy metals removal

Adsorbent used	Metal removed	Reagents for regenerations	Concentration	No. of cycles	Reference
Amino-functionalized silica-coated Fe_3O_4 nanoparticles	Cu(II), Pb(II), Cd(II)	HCl aqueous solution	1 mol /L	4	[68]
Fe_3O_4-NH_2	Cu(II)	HCl aqueous solution	0.1 mol /L	15	[83]
γ-Fe_2O_3@ Polyrhodanine	Hg(II)	HCl aqueous solution	0.1 mol /L	5	[84]
Fe_3O_4@Chitosan	Cu(II)	EDTA aqueous solution	0.1 mol /L	4	[85]
nZVI@Chitosan	As(III), As(V)	NaOH aqueous solution	0.1 mol /L	5	[86]
Fe_2O_3@Orange peel	Cd(II)	HNO_3 aqueous solution	0.1 mol /L	5	[87]
Fe_3O_4@SiO_2-NH_2	Pb(II)	HNO_3 aqueous solution	0.1 mol /L	---	[88]
Water soluble Fe_3O_4 supermagnetic nanocomposite	Hg(II)	Complexing agent 2-mercaptoethanol	---	3	[80]

utilized γ-Al_2O_3 for the removal of Cd(II) and Zn(II). In 2015, Poursani et al [94] have prepared γ-Al_2O_3 by sol-gel method. The produced nano alumina has been used for the removal of Cr(VI), Ni(II), Cd(II) and Pb(II). The experimental results showed that the adsorption capacities were 13.3, 6, 1.1 and 0.33 mg/g for Cr(VI), Ni(II), Cd(II) and Pb(II) respectively.

Details about the alumina and alumina modified nanoparticles, particle size, surface area, operating conditions for the adsorption process and the adsorption capacities of Al_2O_3 nanoadsorbents are presented in Table 5. For study the reusability of the alumina or modified aluminum oxide nanoparticles, researches about desorption of metal ions from adsorbent and regeneration of the adsorbent have been reported in the literature. Details about the regenerations for aluminum oxide nanoparticles are represented in Table 6.

2.1.3 Zinc Oxide nanoparticles

Nanostructured ZnO powder is a versatile, nontoxic and very stable material that can be used as additives into numerous materials and products including plastics, glass, cement, rubber, ceramics, paints, lubricants, adhesives, foods (source of zinc nutrients), batteries, and space craft protective coatings, fire retardants, as a catalyst, photocatalyst, semiconductor devices, and many other applications [99].

Various methods are reported in the literature for the production of ZnO including; controlled precipitation [100], microemulsion [101], solvothermal [102] and sol-gel method [103]. ZnO could be produced in many different structures such as nanorods, needles, wires, tubes, nanoplate/nanosheet, and flower like [104].

In 2010, Wang et al. [105] prepared the plate-like nanostructured ZnO nanoparticles by solvothermal method. The prepared nanoparticles had a particle size in the range of 5-20 nm and surface area 147 m^2/g. The nanoparticles of ZnO tested for the removal of Cu(II) and the results showed high adsorption capacity which equal to 1600 mg/g. Ma et al. [106] prepared zinc oxide nanosheets with square sides of about 1μm and thickness in nano scale by hydrothermal method.

Table 5: Alumina and modified aluminum oxide nanoparticles for the removal of heavy metals

Adsorbent	Method of synthesis	Size (nm)	surface area m^2/g	Metal removed	Operating Conditions	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Ref.
Nano structured γ-Al$_2$O$_3$	purchased	7.21	206	Pb(II), Ni(II) Zn(II)	Co = 150 Ppm, pH 4, adsorbent dose: 4 g/L,	125 mg/g 83.33 58.82	pseudo-second-order	Langmuir and Freundlich	[90]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	-------	68-87	30.38	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	Co = 50 ppm ppm, pH 5; Adsorbent dosage 1 g/l	100 mg/g 83.33 100 41.66 18.18 6.289	-------	Freundlich Freundlich Freundlich Langmuir Langmuir Freundlich	[91]
Nano-alumina dispersed in chitosan-grafted polyacrylamide	microemulsions	----	-----	AS(V)	-----	6.56 mg/g	------	Freundlich	[92]
γ-Al$_2$O$_3$	Purchased as it is (not prepared)	< 50	185	Cd(II) Zn(II)	Co = 1 mmol/l, pH 6; Adsorbent dosage 1 g/l	73.4 mmol/kg 298.2 4 mmol/kg	-------	Freundlich	[93]
γ-Al$_2$O$_3$	Sol Gel	11.5	125.4	Cr(VI), Ni(II) Cd(II) Pb(II)	Co = 20 ppm ppm, pH 3-6.5; Adsorbent dosage 3 g/l	13.3 mg/g 6, 1.1 0.33	Both pseudo-first-and pseudo-second-order models	Langmuir and Freundlich	[94]

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γ alumina (γ-Al$_2$O$_3$)	Purchased	------	160	Cr(VI)	Co = 5 mg/dm^3 pH 5; Adsorbent dosage 1 g/dm^3	30.3 mg/g	pseudo-second order	Freundlich isotherm	[95]
Modified Nano structured γ-Al$_2$O$_3$ with natural and chemical modifiers	Sonication	61	----	Cd(II), Cu(II), Ni(II)	Co = 50 Ppm, pH 7, adsorbent dose: 1 g/L,	92.0 mg/g 97.0, 63.8	pseudo-second-order	Langmuir	[96]
Aluminum oxide nanopowder (Nano-Al$_2$O$_3$)	Purchased	20	138	Fe(II)	Co = 25 ppm, pH 4; Adsorbent dosage 1.0 g/l	14.28 mg/g	pseudo-second-order	Langmuir	[97]
Aluminum oxide/polyaniline nanocomposite	Electro-oxidation	30-50	------	Cu(II) ,Pb(II)	-------	11 mg/g 9.3	pseudo-second order	Langmuir	[98]

Table 6: Regeneration and reusability of Al$_2$O$_3$ oxide nanoparticles for heavy metals removal

Adsorbent used	Metal removed	Reagents for regenerations	Concentration	% Recovery	Ref.
Nano structured γ-Al$_2$O$_3$	Pb(II), Ni(II) Zn(II)	HNO3 aqueous solution	1 mol/ L	99.37 83.5 89.1	[90]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	HCl aqueous solution	1mol /L	84 ±1 81 ±1 79 ±2 67 ±3 84 ±1 75 ± 1	[91]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	HNO$_3$ aqueous solution	1mol /L	92 ±2 93 ±1 94 ±1 89 ±1 92 ±1 90 ± 1	[91]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	EDTA	0.1M	12 ±3 8±2 11 ±2 18 ±1 21 ±2 24 ± 2	[91]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	Mixture of HNO$_3$ and methanol	4.5mL of 1mol L−1 HNO3 + 1.5mL of methanol	99 ±1 98 ±1 99 ±1 97 ±1 98 ±2 99 ± 1	[91]
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb(II), Cd(II), Cr(III), Co(II), Ni(II) Mn(II)	Mixture of HNO$_3$ and methanol	6mL of 1molL−1 HNO3 + 1.5mL of methanol	99 ±1 96 ±1 97 ±1 96 ±1 95 ±2 97 ± 2	[91]
Nano-alumina dispersed in chitosan-grafted polyacrylamide	AS(V)	H$_2$SO$_4$ aqueous solution	0.02 M 0.05 M 0.08 M 0.1 M	20 36 Bead distorted Bead distorted	[92]
Nano-alumina dispersed in chitosan-grafted polyacrylamide	AS(V)	NaOH aqueous solution	0.02 M 0.05 M 0.08 M 0.1 M	56 99 95 Bead distorted	[92]
Nano-γ -Al2O3	Cr(VI), Ni(II) Cd(II) Pb(II)	HNO$_3$ aqueous solution	1 M	95 % 94 % 94 % 92 %	[94]

The ZnO nanoparticles were evaluated for the removal of Pb(II) and the results showed adsorption capacity equal to 6.7 mg/g.

In 2012, Sheela et al. [107] investigated the utilization of zinc oxide nanoparticles (ZnO) with particle size 26 nm, prepared by precipitation method for the removal of Zn(II), Cd(II) and Hg(II). The adsorption experiments carried out in a batch system with 100 ppm initial concentration of all ions, pH in the range from 4-8 with an adsorbent dosage of 0.5 g/l. The adsorption capacities were 357, 387 and 714 for Zn (II), Cd (II) and Hg (II) respectively. During 2013, Kumar et al. [108] succeeded in preparing hierarchical ZnO nanorods in a hexagonal shape with 24.5 nm dimension by hydrothermal method and used it in the removal of Pb(II) and Cd(II). In 2015, Angelin et al. [109] examined the usage of zinc oxide nanoparticles impregnated polymer hybrids as an adsorbent for the removal of Pb(II), Hg(II) and Cd(II) ions from aqueous solution. The experimental data found to obey Langmuir isotherm model and pseudo-second order kinetics model. Maximum recovery of Pb(II), Hg(II) and Cd(II) at 100%, were attended with 2M and 3M HCl eluent solutions, respectively. Pandey et al. [110] prepared nanosized zinc oxide encapsulated in urea-formaldehyde (UF) resin during acid catalyzed polymerization process. The experimental results showed that the prepared nanocomposite was utilized to eliminate 80% Cu(II) content from aqueous solution in 15 minutes. In 2016, Mosayebi et al. [111] studied the adsorption of copper ion from aqueous solution with zinc oxides and zinc hydroxide loaded on activated carbon cloth; details are presented in Table 7.

2.1.4 Copper Oxide Nanoparticles

Cupric oxide (CuO), having a variety of chemo-physical properties and a narrow band gap of 1.2 e.V, is recently attractive in many fields such as catalyst, energy conversion, and optoelectronic devices. CuO nanostructures have unique magnetic and super-hydrophobic properties [112]. Compared with other oxides of the transition metal such as Fe_2O_3, TiO_2, and ZnO, CuO has not got great attentions of researchers at the right level until recent years. Only a few studies that described the preparation methods that adopted for CuO nanostructures along with the introduction of their related applications have been reported in literature [113-116]. A little number of papers reported the use of CuO nanoparticles as adsorbent is presented in Table 8. In 2012, Goswami et al. [117] studied the arsenic removal using copper (II) oxide nanoparticles prepared by the thermal refluxing method. The prepared adsorbent had a surface area of 52.11 m^2/g. The adsorption experimental results showed that the highest adsorption capacity was 1086.2 μg/g. In 2013, Farghali et al. [118] have synthesized various morphologies of CuO nanostructures (oval, cluster, leaves, small rod, porous nanosheets) using microwave radiation. The produced CuO nanostructures were as follows; the oval shaped CuO nanoparticles where small spherical nanoparticles with 20 nm in size, the cluster-shaped CuO nanoparticles had a crystal size about 13 nm, the leaves structure morphology had a width range from 100 to 200 nm and length range from 250 to 450 nm, the nano rod shape with a diameter range from 6 to 12 nm and a length range from 50 to 70 nm while porous nanosheets structures with a length range from 145 to 230 nm and a width range from 70 to 100 nm with a thickness of 1 nm and pores diameter ranging from 0.8 to 2 nm. The operating conditions for the removal of Pb(II) were pH 6.5, the concentrations of the metal ions ranging from 100 to 300 mg/l. The maximum capacity of oval, cluster, leaves, small rod, and porous nanosheets CuO nanostructures for Pb(II) were 125, 116,117, 120 and 115 mg/g. In 2014, Kumar et al. [119] reported the synthesis of nanoscale copper(II) oxide. The produced nano CuO had an average diameter of 5 nm and a length extending up to 50 nm. The surface area of the nanorods was 52.57 m^2/g. The maximum adsorption capacity of Pb(II) is 3.31 mg/g. The adsorbent can be up to 84.1% regenerated using dilute acid. Vyawahare et al. [120] have prepared

Table 7: Zinc oxide nanoparticles for the removal of heavy metals

Adsorbent	Method of synthesis	Shape and Size (nm)	surface area m²/g	Metal removed	Operating Conditions	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Ref.
ZnO nanoplates	Solvothermal method	5-20	147	Cu(II)	Co = 200 Ppm, pH 4-6, adsorbent dose: 0.5g/L,	1600 mg/g	---------	Freundlich equation	[105]
ZnO nanosheets	Hydrothermal	Nanosheets with square sides of about 1 μm and thickness in nano-scale	----	Pb(II)	-----	6.7 mg/g	-----	-----	[106]
Zinc oxide nanoparticles (ZnO)	Precipitation method	Spheres 26	46	Zn(II), Cd(II) Hg(II)	Co = 100 Ppm, pH 6, adsorbent dose: 0.5g/L	357 mg/g 387 714	pseudo-second-order	Langmuir	[107]
Hierarchical ZnO nanorods	Hydrothermal method	hexagonal wurtzite 24.5	15.75	Pb(II) Cd(II)	Co = 200 Ppm, pH 6, adsorbent dose: 1g/L,	160.7 mg/g 147.25	pseudo-second-order	Langmuir and Freundlich	[108]
Zinc oxide nanoparticles impregnated polymer hybrids	-------	--------	26.4111	Pb(II), Hg(II), Cd(II)	Co = 50 ppm, pH 5, adsorbent dose: 1 g/L	0.2875 mg/g 0.1030 0.1952	pseudo-second-order	Langmuir	[109]
Zinc oxide-urea formaldehyde nanocomposite ZnO-UF	Acid catalysed polymerization process	95	-----	Cu(II)	Co = 200 ppm, pH 6.5, adsorbent dose: 1sq cm/ 100 ml solution	80% removal	------	Langmuir	[110]
Microstructured nanostructured zinc oxides and zinc hydroxide loaded on activated carbon cloth(ACC)	Hydrothermal method	flower-like	-----	Cu(II)	Co = 50 ppm, pH 5, adsorbent dose: 1 g/L	1300 mg/g	------	------	[111]

Table 8: Copper oxide nanoparticles for the removal of heavy metals

Adsorbent	Method of synthesis	Shape and Size (nm)	surface area m²/g	Metal removed	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Ref.
CuO nanoparticles	thermal refluxing technique	-----	52.11	As(III)	1086.2 µg/g	pseudo-second-order	Langmuir	[117]
CuO nanostructures	microwave radiation	the oval cluster spherical nanoparticles with 20 nm in size, the cluster shaped crystal size about 13 nm, the leaves structure had a width range from 100 to 200 nm and length range from 250 to 450 nm, the nano rod shape with a diameter range from 6 to 12 nm and a length range from 50 to 70 nm, porous nanosheets structures with a length range from 145 to 230 nm and a width range from 70 to 100 nm with a thickness of 1 nm and pores diameter ranging from 0.8 to 2 nm.	----	Pb(II)	125 mg/g 116, 117, 120 115	pseudo-second-order	Langmuir and Freundlich	[118]
Nano CuO	Soft chemical method	rod like morphology of rhombohedral CuO average diameter of 5 nm and a length extending up to 50 nm.	52.57	Pb(II)	3.31	------	--------	[119]
Nano CuO	precipitation method	crystallite size in the range of 10-30 nm and the shape was found to be spherical	-----	Zn(II)	------	------	------	[120]
Nano CuO	microwave radiation	33-160 nm	220	Fe(III) Cd(II)	126.32 84.75	pseudo second order	Langmuir Freundlich	[121]
Nano CuO	microwave radiation	33-160 nm	220	Pb(II) Zn(II)	14·859 44·248	pseudo second order	Langmuir	[122]

copper (II) oxide nanoparticles by precipitation method and produced nano oxide particles were found to have crystallite size (10-30 nm) and the shape was found to be spherical. During 2015, Taman et al. [121] have prepared copper oxide nano-particles by microwave irradiation method. The prepared oxide nanoparticles were found to have 33-160 nm particle size. In addition, the surface area was 220 m^2/g. The adsorption of Fe(III) and Cd(II) was tested in a batch reactor. The kinetics of Fe(III) and Cd(II) adsorption onto copper oxide nano particles were fitted by the pseudo-second order model. Ossman et al. [122] prepared copper oxide nanopowder by microwave irradiation method. The produced metal oxide was found to be 33-160 nm and the surface area is 220 m^2/g. The CuO nanoparticles produced were used for elimination of Pb(II) and Zn(II). The adsorption of Pb(II) and Zn(II) onto copper oxide followed Langmuir isotherm.

2.1.5 Nickel Oxide nanoparticles

Nickel oxide nanoparticles possess particular catalytic, electronic and magnetic properties [123]. NiO nanoparticles are considered as good adsorbent due to their chemical and magnetic properties. Recently, several methods have been reported to prepare nickel oxide nanopowder, such as Sol-Gel method [124], thermal decomposition [125] and sonochemical method [126]. The adsorption behavior of Nickel oxide nanopowder has been studied by many authors. In 2012, Sheela and Nayaka [127] studied the removal of Cd(II) and Pb(II) ions onto NiO nanoparticles prepared by precipitation method. The experimental data were best described by pseudo-second order model and Langmuir isotherm.

During 2014, Srivastava et al. [128] synthesized NiO nanoparticles by the sol-gel method. The Nanoparticle formed was used to study the removal of Cr(VI). The experimental data were fitted by Langmuir isotherm. Behnajady et al. [129] have synthesized mesoporous NiO nanoparticles by chemical precipitation method. The average obtained nanoparticle size was about 11 nm with surface area of these nanoparticles was 71.09 m^2/g. The mesoporous NiO was found to be good adsorbent for the removal of Cr (VI) from aqueous solutions. The results showed that adsorption isotherm and kinetics of the process follow sips isotherm and pseudo second-order kinetic, respectively with maximum adsorption capacity of 4.54 mg/g. Abdelfatah et al. [130] have prepared NiO nanopowder by precipitation method. The produced NiO nanoparticles were tested for the removal of Pb and Zn from aqueous solution. The adsorption of Pb(II) onto NiO found to be following the Langmuir isotherm, while the adsorption of Zn(II) onto NiO follows the Freundlish isotherm.

In 2015, Mahmoud et al. [131] prepared NiO nanoparticles by two different methods; precipitation method (surface area 72.505 m^2/g and average particle size 10.05 nm) and an organic solvent method (surface area 128.330 m^2/g and average particle size 6.71 nm) and tested the nanoparticles for removal of Pb(II). The results showed that NiO prepared by organic solvent method is more active than that prepared by the precipitation method for removal of Pb(II) ions from aqueous solutions details about the adsorption process can be found in Table 9. Srivastava et al. [132] studied the removal of Co(II) by NiO nanoparticles synthesized by hydrothermal at 500 °C calcination temperature. Redlich-Peterson isotherm was found to be the most suitable isotherm for Co(II) adsorption. Langmuir adsorption capacity of nanoparticles was found to be 149.51 mg/g. In 2016, Ashan et al. [133] have prepared NiO nanoparticles by sol-gel method; the average nanoparticles size was smaller than 10 nm. The results indicated that NiO nanoparticles are efficient adsorbent for the removal of Cr(VI) from aqueous solutions. The equilibrium data could be well described by Sips model. The results of adsorption kinetics study indicated that kinetics obeyed pseudo-second order kinetic model. Very few literatures have reported the regeneration of

Table 9: NiO, manganese dioxide and Titanium oxide nanoparticles for the removal of heavy metals

Adsorbent	Method of synthesis	Shape and Size (nm)	surface area m²/g	Metal removed	Operating Conditions	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Ref.
NiO nanoparticles	Precipitation	cubic structures 28	------	Cd(II), Pb(II)	Co = 100 ppm, pH 6, adsorbent dose: 5 g/L	625 909	pseudo-second-order model	Langmuir	[127]
NiO nanoparticles	Sol gel	cubic structures 4.1790 A°	------	Cr(VI)	--------	200	------	Langmuir	[128]
Mesoporous NiO nanoparticles	Chemical precipitation	11	71.09	Cr(VI)	Co = 20 ppm, pH 4.7, adsorbent dose: 6 g/L	4.54	pseudo-second-order model	Sips	[129]
NiO nanopowder	Chemical precipitation	38 -130	191	Pb(II), Zn(II)	Co = 100 ppm, pH 5, adsorbent dose: 2 g/L	50.505 63.694	pseudo 2nd order pseudo 1st order	Langmuir Freundlish	[130]
NiO nanoparticles	precipitation method	10.05	72.505	Pb(II)	Co = 100 ppm, pH 5, adsorbent dose: 1 g/L	21.54	pseudo first-order reaction	Langmuir	[131]
NiO nanoparticles	organic solvent method	6.71	128.330	Pb(II)	Co = 100 ppm, pH 5, adsorbent dose: 1 g/L	56.24	pseudo first-order reaction	Langmuir	[131]
NiO nanoparticles	hydrothermal	30-42	25.19	Co(II)	Co = 500 ppm, pH 5, adsorbent dose: 2 g/L	397.13	Pseudo second order	Redlich-Peterson	[132]
NiO nanoparticles	Sol gel	10	109.36	Cr(VI)	Co = 20 ppm, pH 4.7, adsorbent dose: 6 g/L	7.63	pseudo-second order	Langmuir	[133]
Amorphous hydrous manganese dioxide (HMO)	precipitation	----	100.5	Pb(II), Cd(II), Zn(II)	------	1.578 mmol/g 1.249 0.833	---------	Freundlich	[135]
Hydrous manganese dioxide (HMO)	Redox reaction	3.38	79.31	Pb(II)	Co = 50 ppm, pH 6, adsorbent dose:0.1 g/L	352.55	pseudo second-order	Langmuir	[136]

Hydrous manganese dioxide-poly(N-hydroxymethyl acrylamide/2-hydroxyethyl acrylate) (HMO-P(HMAm/HEA))	precipitation	--------	-------	Pb(II), Cu(II), Cd(II), Ni(II)	-------	0.972 mmol/ g 0.859 0.844 0.747	pseudo-second-order	Langmuir	[137]
Hierarchical MnO_2-coated magnetic Nanocomposite (Fe_3O_4/MnO_2)	hydrothermal process	Flower like particles with a mean diameter of 60 nm.	118	Cd(II), Cu(II), Pb(II), Zn(II)	Co = 10 ppm, pH 6, adsorbent dose: 1 g/L	53.2 for Cd(II) only	-------	Langmuir for Cd(II) only	[138]
Manganese oxide nanofibers MONFs	precipitation	10-16	94.1	Cr(VI)	pH = 2	14.6 mg/g	pseudo-second-order	Langmuir	[139]
δ-MnO_2	hydrothermal method	nanorods with diameters of 8-18 nm and length of~0.3 μm	38.02	Cu(II)	Co = 150 ppm, pH 5.3, adsorbent dose: 1 g/L	92.74	Pseudo-second order	Langmuir	[140]
Silico-manganese nanohybrid (SMNA)	hydrothermal	nanorod/nanowires with diameters in the rangeof 4-10 nm with different length	83.19	Cu(II)	Co = 150 ppm, pH 5.3, adsorbent dose: 1 g/L	88	Pseudo-second order	Langmuir	[140]
TiO_2	hydrolysis	-------	196	As(III)	Co = **3310** ppm, pH 7, adsorbent dose: 30 g/L	-----	pseudo second-order	------	[143]
TiO_2	Purchased	8.3	185.5	Pb(II), Cd(II), Ni(II)	--------	401.14 135.14 114.94	-------	Langmuir	[144]
Layered protonated titanate nanosheets (LPTNs)	urea-modulated method	5.36	535	Pb(II)	--------	366	pseudo second-order	Langmuir	[145]

Titanate nanoflowers (TNF)	hydrothermal treatment	----	290	Pb(II)	-------	1.47e−3 mol/g	pseudo second-order	Langmuir	[146]
Titanate nanotubes (TNT)	hydrothermal treatment	7-10	230	Pb(II)	--------	7.12e−4 mol/g	pseudo second-order	Langmuir	[146]
Titanate nanowires (TNW)	hydrothermal treatment	40-250	30	Pb(II)	-------	5.13e−4 mol/g	pseudo second-order	Langmuir	[146]
Acrylamide-titanium nanocomposite	Sol gel	----	----	Cd(II)	-------	322.58 mg/g	Pseudo second order	Langmuir	[147]
Humic acid coated titanium dioxide (HA-TiO$_2$)	purchased	------	49 ± 15	Cd(II)	Co = **40μg/l**, pH 7, adsorbent dose: 10 g/L	-----	pseudo-second-order	Freundlich	[148]
TiO$_2$-fly ash (TiO$_2$-FA)	hydrothermal	-------	44.948	Cu(II)	------	83.333	------	-----	[149]
➢ Titanium humic acid (Ti-H) ➢ Titanium with extractant of Walnut shell (Ti-W) ➢ Titanium diphenyl-Carbazon (Ti-C)	-------	➢ 63.7 ➢ 44.0 ➢ 86.6	-------	Cd(II) Cu(II)	Co = **50 ppm**,	9.9 mg/g for Cd 25.7 mg/g for Cd 31.7 mg/g for Cd 5.3 mg/g for Cu 15.2 mg/g 20.5 mg/g	pseudo-second-order	Langmuir	[150]

NiO nanoparticles refer to Table 10.

Table 10: Regeneration and reusability of NiO, manganese dioxide and Titanium oxide nanoparticles for heavy metals removal

Adsorbent used	Metal removed	Reagents for regenerations	Concentration	No. of cycles	Ref.
NiO nanoparticles	Co(II)	HCl aqueous solution	0. 1 M	3	[132]
Amorphous hydrous manganese dioxide (HMO)	Pb(II), Cd(II), Zn(II)	HCl aqueous solution	0.5M	-----	[135]
Hierarchical MnO_2-coated magnetic nanocomposite (Fe_3O_4/MnO_2)	Cd (II), Cu (II), Pb (II), Zn(II)	HCl aqueous solution	0.01M	5	[138]
δ-MnO2	Cu(II)	HCl aqueous solution	0.5M	5	[140]
Silico-manganese nanohybrid (SMNA)	Cu(II)	HCl aqueous solution	0.5M	5	[140]
TiO_2	As(III)	NaOH aqueous solution	5 M	21	[143]
Acrylamide-titanium nanocomposite	Cd(II)	H_2SO_4 aqueous solution	0.05 M	5	[147]

2.1.6 Manganese Oxide nanoparticles

The widely used nanosized manganese oxides for waste water treatment include two different forms namely, hydrous manganese oxide (HMO) (MnO_2 $0.5H_2O$) and nanoparticle manganese oxides (MnO_2) [134]. The adsorption of heavy metal by hydrous manganese oxides have been reported in some research articles. Su et al. [135] evaluated the removal of Pb(II), Cd(II), and Zn(II), from aqueous solution by amorphous hydrous manganese dioxide (HMO). The used HMO particles can be regenerated by HCl solution (refer to Table 10). Xu et al. [136] synthesized hydrous manganese dioxide (HMO) by redox reaction and used it for Pb(II) removal. The specific surface area and the diameter of the HMO were 79.31 m^2/g and 3.38 nm, respectively. The adsorption equilibrium could be well described by Langmuir isotherm model with maximum adsorption capacity of 352.55 mg/g. Zhu et al. [137] have fabricated a new hybrid adsorbent and use the produced adsorbent to effectively remove Pb(II), Cu(II), Cd(II) and Ni(II) from water. The results showed that adsorption process followed Langmuir model and a pseudo-second-order rate equation. Hierarchical MnO_2-coated magnetic nanocomposite (Fe_3O_4/MnO_2) was reported to be used as an adsorbent for (Cd(II), Cu(II), Pb(II), and Zn(II) [138].

Qusti prepared manganese oxide nanofibers and he revealed that the crystalline α-MnO_2 (manganese oxide nanofibers) is highly efficient for removing the toxic Cr(VI) ions [139]. If the manganese oxide adsorbents form a composite by doping with some antacid substance, the adsorption performance of manganese oxide would be improved. Recently, a novel silico-manganese nano hybrid composite adsorbent was synthesized by hydrothermal method. The elimination of Cu(II) ions from aqueous solution using silico-manganese nanohybrid was investigated [140]. Details about the use of manganese oxide nanoparticles are described in Table 9.

2.1.7 Titanium dioxide nanoparticles

Titanium dioxide (TiO_2) has been used in many applications such as photocatalysis, H_2 sensing, lithium batteries and as an adsorbent for the removal of contaminants from aqueous solutions. Layered titanates can be formed in different shapes including sheets, hierarchical shapes such as flowers, and composites [141]. These shapes can increase the surface area and ion exchange capabilities [142]. The ability of TiO_2 nanoparticles to treat heavy metals in wastewater has

reported in the literature. Luo et al. [143] discussed a novel approach for the first time by using TiO$_2$ as adsorptive removal of As(III) from wastewater and studied the adsorbent regeneration and As(III) recovery using NaOH. Luo et al. reported 21 successive treatment cycles using the regenerated TiO$_2$. Engates and Shipley [144] studied the adsorption of Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II) to commercial TiO$_2$ nanoparticles and TiO$_2$. Exhaustion experiments were also performed and showed that TiO$_2$ nanoparticles could be exhausted after 8 cycles. The experimental data found to be best correlated to Langmuir isotherm model (refer to Table 9). Lin et al. [145] reported the synthesis of layered protonated titanate nanosheets (LPTNs) by the urea-modulated method. The resulting LPTNs had excellent adsorption capacity for Pb(II) owing to their high specific surface area (535 m^2/g) and excellent ion-exchange capability. Huang et al. [146] compared between titanate nanoflowers (TNF) and titanate nanotubes (TNT)/ nanowires (TNW) obtained by the hydrothermal method, for the adsorption of Pb(II). The results showed that titanate nanoflowers possess larger adsorption capacity and more rapid kinetics than titanate nanotubes/ nanowires. It was found that the equilibrium data fitted well with the Langmuir model, while the adsorption kinetics followed the pseudo-second-order model refer to the details in Table 9. TiO$_2$ and titanate can be prepared as a composite to enhance their properties. Sharma et al. [147] prepared acrylamide-titanium nanocomposite by sol-gel reaction and used it as an adsorbent for cadmium removal from aqueous solution. The adsorption behavior of the nanocomposite was examined by kinetic and equilibrium studies in batch conditions. The maximum cadmium adsorption capacity of TiO$_2$-AM was 322.58 mg/g. Cadmium sorption showed pseudo-second-order kinetics. The nanocomposite can be used for five cycles and can be regenerated with 0.05 M acidic solutions. Chen et al. [148] developed humic acid coated titanium dioxide (HA-TiO$_2$) NPs and investigated the adsorption of Cd(II). The experimental results demonstrated that the adsorption isotherms of Cd(II) to both TiO$_2$ and HA-TiO$_2$ complied well with Freundlich model. Visa and Duta [149] developed a low-temperature TiO$_2$-fly ash (TiO$_2$-FA) composite using hydrothermal methods. These composites were applied in visible photocatalysis/adsorption simultaneous advanced wastewater processes. Combining fly ash with titanium dioxide allowed the titanium oxide crystallites to grow on the support (active fly ash). The adsorption tests were made on the removal of Cu(II). Mahdavi [150] studied the usefulness of using modified nanoparticles (MNPs) as sorbents in removing Cd(II), Cu(II), and Ni(II) from aqueous solutions by TiO$_2$ NPs modified with humic acid (Ti-H), extractant of Walnut shell (Ti-W), and 1, 5 diphenyl-Carbazon (Ti-C). The MNPs were spherical in shape. The mean diameter of MNPs was 64.7 nm. The sorption of Cd(II) and Cu(II) on MNPs fitted better in Langmuir. While Ni(II) sorption better fitted in Freundlich model. Kinetics of adsorption follows pseudo-second order kinetic model for all ions.

2.2 Carbon nanomaterials

Near the end of the nineteenth century, carbon nanotubes were discovered by Sumio Iijima [151]. Since that day; they have been studied by many researchers. Carbon nanotubes are structured as a sheet of carbon atoms rolled up into a cylindrical tube. There are two different forms of carbon nano tubes namely; Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [152].

The use of carbon nanotubes as adsorbent have been studied by many research groups because of their surface area, porosity, surface functional groups, purity and type of carbon nanotubes [153]. Surface modifications have found to be attractive techniques to improve the adsorption capacity of carbon nanotubes for heavy metals. In recent years, utilization of carbon nanotubes and the modified carbon nanotubes as adsorbents for the removal of a number of heavy metals from waste water is widely reported in the literature.

In 2011, Li et al. [154] studied the use of oxidized multiwall carbon nanotubes (OMWCNTs)

to evaluate the adsorption of Pb(II). The adsorption of Pb(II) can be described well by Langmuir model. In another research paper, Tofighy et al. [155] investigated the removal of some divalent heavy metal ions (Cu(II), Zn(II), Pb(II), Cd(II) and Co(II)) from aqueous solutions using carbon nanotube (CNT) sheets synthesized by chemical vapor deposition. Langmuir model was used to describe the adsorption of heavy metal ions by oxidized CNT sheets. Moradi et al. [156] studied the removal of Pb(II), Cd(II) and Cu(II) by SWCNTs and SWCNTs-COOH from aqueous solution. The results showed that the experimental data are obeyed the Langmuir isotherm model. The maximum adsorption capacities for Pb(II), Cu(II) and Cd(II) ions on SWCNTs-COOH were 96.02, 77.00 and 55.89 mg/g, respectively and by SWCNTs, were 33.55, 24.29 and 24.07 mg/g, respectively. Carbon nanotubes (CNTs) have been chemically functionalized with a various oxygen-containing surface groups by Jun et al. [157]. Results indicated that the functionalized CNTs have a superior adsorption capacity toward anionic chromate compared with the unmodified ones. Sheikh et al. [158] reported the use of oxidized and non-oxidized multi-walled carbon nanotubes (MWCNTs) with different shapes of Hg(II) adsorption in water samples. The sorbents showed variable sorption capacities for mercury (0.70-3.83 mg/g). In 2012, Velickovic et al. [159] reported the use of ethylenediamine functionalized multiwalled carbon nanotubes (e-MWCNT) loaded with iron(III) oxide prepared by precipitation method. The adsorbents were used for the As(V) and As(III) removal from drinking water in a batch system. The operating conditions were; pH range 3-10 and initial arsenic concentration 0.05-4 mg/L. The maximum adsorption capacities obtained from Langmuir model for As(V) on e-MWCNT/Fe2+ and e-MWCNT/Fe3+ were 23.47 and 13.74 mg /g at 25 $^{\circ}$C, respectively. Wang et al. [160] successfully fabricated magnetic-functionalized multi-walled carbon nanotubes (MWCNTs) with encapsulated Fe nanoparticles by a one-step decomposition approach. The produced adsorbents had particle sizes (2.0 nm, 6.42 nm, and 11.4 nm) and large surface area (295.4 m^2/g). The removal efficiency can be up to 97% at a Cu(II) concentration of 100 ppm using these magnetic functionalized MWCNTs as adsorbents. Zhang et al. [161] has synthesized a MWCNTs /magnetite nanocomposites (CNTs/Fe$_3$O$_4$) functionalized with Thiol group. The MPTS-CNTs/Fe$_3$O$_4$ nanocomposites had a high specific surface area (97.163 m^2/g) than that of CNTs/Fe$_3$O$_4$ (88.367 m^2/g). The adsorption behaviors of Hg(II) and Pb(II) have been studied and the results indicated that pseudo-first-order kinetic could describe the kinetics of the adsorption on both CNTs/Fe$_3$O$_4$ nanocomposite and MPTS-CNTs/Fe$_3$O$_4$ nanocomposite. The adsorbents had maximum adsorption capacities of 65.52 and 65.40 mg/g for Hg(II) and Pb(II), respectively. Ji et al. [162] have prepared MWCNTs/Fe$_3$O$_4$ by thermal decomposition method. The MWCNTs/Fe$_3$O$_4$ nanocomposites were modified with 3-aminopropyltriethoxysilane (MWCNTs/Fe$_3$O$_4$-NH$_2$). The two prepared magnetic nanocomposites were used as adsorbents to remove Pb(II) from wastewater. Both adsorbents could be separated and regenerated in 0.1 M NaOH solution (refer to Table 11). Shawky et al. [163] prepared a chitosan (CS) with different carbon nanotubes (CNTs) by the incorporation of single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and carboxylic multi-walled carbon nanotubes (MWCNT-COOHs). The adsorption performance of the prepared composites was investigated for the removal of Hg(II). The maximum Hg(II) removal values were 148.7, 183.2, 167.5, and 172.7 mg/g for CS, MWCNTCOOH-impregnated CS beads, MWCNT-impregnated CS beads, and SWCNT-impregnated CS composite beads, respectively refer to Table 12. The reusability of the beads was investigated and the results showed that the adsorption-desorption cycles were repeated 10 times with the same beads.

In 2013, multi-walled carbon nanotube-hydroxyapatite (MWCNT-HAP) composites were synthesized and used as an adsorbent for Co(II) removal from aqueous solutions by Liu et al. [164]. The repeated availability of MWCNT-HAP through many cycles of desorption/sorption was investigated to evaluate the application potential of MWCNT-HAP in the removal of

Table 11: Regeneration and reusability of CNTs for heavy metals removal

Adsorbent	Metal removed	Reagents for regenerations	Concentration	No. of cycles	Ref.
SWCNTs and SWCNTs-COOH	Pb(II)	Dilute HNO_3 solution	-----	-----	[156]
SWCNTs and SWCNTs-COOH	Cu(II) and Cd(II) ions	HCl solution dissolved	-----	-----	[156]
MWCNTs/Fe_3O_4	Pb(II)	NaOH	0.1M	5	[162]
MWCNTs/Fe_3O_4-NH_2	Pb(II)	NaOH	0.1M	5	[162]
CS/SWCNTs	Hg(II)	-----	-----	10	[163]
CS/MWCNTs	Hg(II)	------	------	10	[163]
CS/MWCNT-COOHs	Hg(II)	------	------	10	[163]
MWCNT-HAP	Co(II)	NaCl	0.01 M	5	[164]
S-MWCNTs	Hg(II)	HCl	-----	6	[165]
SWCNT-SH	Hg(II)	HCl	2 M	5	[166]
MWCNTs-SH	Hg(II)	HCl	0.5 M	5	[167]

Co(II) from wastewater. The sorption capacity of MWCNT-HAP to Co(II) found to be decreased slightly from 5.64 mg/g to 5.45 mg/g after five cycles. Pillay et al. [165] have prepared sulfur containing multi-walled carbon nanotubes (S-MWCNTs) and the product was employed as adsorbents for the removal of mercury. The results revealed that (S-MWCNTs) could adsorb mercury at the parts per billion (ppb) levels. The maximum uptake capacity for Hg(II) as 72.8 μg/g. The S-MWCNTs may be regenerated with thiourea and reusable for 6 cycles. Bandaru et al. [166] succeeded in preparing thiol-derivatized single-walled carbon nanotube (SWCNT-SH) powders. The maximum adsorption capacity of the SWCNT-SH powders was estimated using equilibrium isotherms, such as Freundlich and Langmuir, and the maximum adsorption capacity of the SWCNT-SH powder was found to be 131 mg/g. Desorption studies revealed that SWCNT-SH powders could be regenerated and reused for 5 cycles. In 2014, Hadavifar et al. [167] have developed functionalization of multi-walled carbon nanotubes (MWCNTs) by introducing amine and thiol functional groups onto the nanotube sidewalls. The synthesized amino and thiolated MWCNTs used to study the removal of Hg(II). The regeneration of MWCNTs-SH was evaluated by HCl, H_2SO_4, and HNO_3 acid treatment. The 0.5 M HCl was more effective than other concentrations as well as other acid types. The adsorbent could be reused for five adsorption/desorption cycles. Xiao et al. [168] have synthesized carboxylated multi-wall carbon nanotube (c-MWCNT)-Fe_3O_4 magnetic hybrids (c-MWCNTMCs). The c-MWCNTMCs showed a high adsorption capacity for Cu(II). The c-MWCNTMCs could be regenerated at pH < 2.0 and reusable for 5 adsorption/desorption cycles. During 2015, MnO_2-coated carbon nanotubes (MnO_2/CNT) were prepared by Moghaddam et al. [169]. The synthesized MnO_2/CNT sorbent possessed a specific area of 110.38 (m^2 /g) and particle size (2.70 nm). Hg adsorption on MnO_2/CNT was a fast process and the kinetics followed a pseudo-second-order rate equation. Liang et al. [170] prepared an adsorbent of alumina decorating onto the surface of multi-wall carbon nanotubes (MWCNTs) and use this adsorbent for study the removal of Cd(II) ion from groundwater. The adsorption kinetics of Cd(II) ion followed the pseudo-second-order kinetic model. Equilibrium data of Cd(II) ion were best fitted by Langmuir model. The maximum adsorption capacities of Al_2O_3/MWCNTs for Cd(II) ion was 27.21 mg/g, which were higher than that of Al_2O_3, MWCNTs, and the functionalized MWCNTs.

Table 12: CNT for the removal of heavy metals

Adsorbent	Size (nm)	surface area, m²/g	Metal removed	Operating Conditions	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Ref.
Oxidized MWCNTs	10-30	197	Pb (II)	pH 4.1 ± 0.1, Co=0.0483 mmol/L,, adsorbent dosage = 0.75 g/L	0.0211 mmol/g	-------	Langmuir	[154]
CNT sheets	inner tube diameter of about 10nm and outer tube diameter of about 30-40 nm	--------	Cu(II), Zn(II), Pb(II), Cd(II) Co(II)	pH 7, initial concentration = 1200 mg/L, adsorbent dosage = 2 g/L	64.935 mg/g 74.6268 117. 647 92.592, 85.7400	pseudo-second-order	Langmuir	[155]
SWCNTs	Diameter 1-2 nm; length, 5-30 nm	400	Pb(II), Cd(II) Cu(II)	pH 5, initial concentration = 20 mg/L, adsorbent dosage = 50 mg/L	33.55 mg/g 24.29 24.07	--------	Langmuir	[156]
SWCNTs-COOH	Diameter 1-2 nm; length, 5-30 nm	400	Pb(II), Cd(II) Cu(II)	pH 5, initial concentration = 20 mg/L, adsorbent dosage = 50 mg/L	96.02 mg/g 77.00 55.89		Langmuir	[156]
CNTs	-----	293	CrO_4^{-2}	------	16 µmol / g	-------	Langmuir	[157]
Functionalized CNT(CNT-O)	----	301	CrO_4^{-2}	------	249 µmol / g	---------	Langmuir	[157]
Ox-MWCNTs	diameter 40-60 nm and length 5-15 µm	-----	Hg(II)	Co = 1-10 ppm, pH 7, adsorbent dose: 0.5 g/L	3.83 mg/g	------	Langmuir	[158]
e-MWCNT/Fe3+	------	------	As(V) and As(III)	pH range 3-10 and initial arsenic concentration 0.05-4 mg L−1.	23.47 mg/g	pseudo-second-order	Freundlich	[159]
e-MWCNT/Fe2+	-------	-------	As(V) and As(III)	pH range 3-10 and initial arsenic concentration 0.05-4 mg L−1.	13.74 mg/g	pseudo-second-order	Freundlich	[159]
magnetic-functionalized MWCNTs	3 kinds of pores (2.0 nm, 6.42 nm and 11.4 nm)	295.4	Cu(II), Pb(II) Cd(II)	Co = 100 ppm, pH 6	-----	----	------	[160]

CNTs/Fe$_3$O$_4$	--------	88.367	Hg(II) Pb(II)	initial metal ions concentration from 5-90 mg/L, magnetic adsorbent dose 1 g/L, pH = 6.5	37.57 31.92	pseudo-first-order kinetic	Langmuir	[161]
CNTs/Fe$_3$O$_4$ functionalized with Thiol group	---------	97.163	Hg(II) Pb(II)	initial metal ions concentration from 5-90 mg/L, magnetic adsorbentdose 1 g/L, pH = 6.5	65.52 65.40	pseudo-first-order kinetic	Langmuir	[161]
MWCNTs/Fe$_3$O$_4$	13.7	108.37	Pb(II)	initial metal ions concentration from 30 mg/L, adsorbent dose 0.5 g/L, pH = 2.5-3.5	41.77	Pseudo-second-order	Langmuir	[162]
MWCNTs/Fe$_3$O$_4$-NH$_2$	22.9	90.68	Pb(II)	initial metal ions concentration from 30 mg/L, adsorbent dose 0.5 g/L, pH = 2.5-3.5	75.02	Pseudo-second-order	Langmuir	[162]
CS/SWCNTs	-------	------	Hg(II)	initial metal ions concentration from 1000 mg/L, adsorbent dose 0.4 g/L, pH = 4	167.5	-----------	Langmuir	[163]
CS/MWCNTs	---------	-------	Hg(II).	initial metal ions concentration from 1000 mg/L, adsorbent dose 0.4 g/L, pH = 4	172.7	--------	Langmuir	[163]
CS/MWCNT-COOHs	----------	--------	Hg(II).	initial metal ions concentration from 1000 mg/L, adsorbent dose 0.4 g/L, pH = 4	183.2	-------	Langmuir	[163]
MWCNT-HAP	------	-------	Co(II)	pH = 5.5, Adsorbent dosage 0.6 g/L, C[Co(II)]initial=1.69×10−4 mol/L,	5.64 mg/g	pseudo-second order	Langmuir	[164]
S-MWCNTs	------	------	Hg (II)	--------	44.7 µg/g	-------	Freundlich	[165]
SWCNT-SH	---------	-------	Hg(II)	pH = 5.0, initial metal ions concentration 30 mg/L. adsorbent dose = 0.25 mg/mL	131mg/g	Pseudo-first order kinetic	Freundlich	[166]
MWCNTs-SH	--------	-------	Hg(II)	initial metal ions concentration 100 mg/l, adsorbent dose of 400 mg/l and pH 6.0	84.66 mg/g	Pseudo-second-order	Langmuir	[167]

c-MWCNTMCs	-----	109	Cu(II)	initial metal ions concentration 20 mg/l, adsorbent dose of 100 mg/l and pH 6.0	60.60mg/g	pseudo-second-order	Freundlich	[168]
MnO$_2$/CNTs nanocomposite	2.70	110.38	Hg(II)	initial metal ions concentration 50 mg/l, adsorbent dose of 1 g/l and pH 7.0	58.8	pseudo-second-order	Freundlich	[169]
Al$_2$O$_3$/MWCNTs	10.979	109.82	Cd(II)	---------	27.21	pseudo-second-order	Langmuir	[170]

Table 13: Polymer-base adsorbents for the removal of heavy metals

Adsorbent	Size (nm)	surface area m²/g	Metal removed	Operating Conditions	Sorption capacity	Adsorption Kinetics	Adsorption isotherm	Reagents for regenerations	No. of cycles	Ref.
• PS-(HFO)-39a • PS-(HFO)-78a • PS-(HFO)-350	29.9 11.6 4.2	45 88 388	As(III) As(V)	initial As(III)=10 mg/L, initial As(V)=10 mg/L, adsorbent dosage=0.050 g/L, I=0.01 mol/L pH 7.0 for As(III) adsorption and pH 4.0 for As(V) adsorption)	• 178.7 mg/g for As(III) and 233.9 for As(V) • 197.7 mg/g for As(III) and 268 for As(V) • 220.5 mg/g for As(III) and 326.4 for As(V)	-------	------	------	------	[173]
Carboxymethyl-β-cyclodextrin conjugated magnetic CMCD-MNPs	-------	110.9	Cu(II)	pH 6, initial concentration = 200 mg/L	47.20	pseudo-second-order	Langmuir	0.1 M citric acid, 0.1 M Na₂EDTA 0.1 M acetic acid	3	[174]
carboxymethyl-β-cyclodextrin (CM-β-CD) polymer modified Fe_3O_4 nanoparticles	8 to 15	-----	Pb(II), Cd(II) Ni(II)	pH 5.5, initial concentration = 300 mg/L	64.50 mg/g 27.70 13.20	pseudo-second-order	Langmuir	0.01 m HNO_3 0.1 M Na₂EDTA 0.02 M Phosphoric acid	4	[175]
carboxymethyl-β-cyclodextrin (CM-β-CD) polymer modified Fe3O4 magnetic nanoparticles (CMPCDMNPs)	--------	------	Pb(II),	pH 5.5, initial concentration = 200 mg/L	-----	pseudo-second-order	Langmuir	-------	-----	[176]
Chitosan/TiO_2 composite nanofibrous	-----	------	Cu(II) Pb(II)	Adsorption dosage 0.5g/l Initial concentration 1000 ppm, pH 6	710.3 579.1	pseudo-first-order	Langmuir	1 M HNO3	5	[177]

2.3 Polymer-based nanomaterials

Although nanosized materials have high surface areas, they are unstable so they tend to agglomerate. Once they agglomerated they lose their high adsorption capacities. Also, since they are very tiny they cannot be used in a plug-flow-type configuration including fixed-bed columns because they led to very high-pressure drops and mass transport problems [171]. To overcome these limitations, polymeric materials could be used in two different ways: 1) coat the particles with polymers; 2) Use the polymer as support to synthesize and grow nanoparticles on it [172].

The use of polymer-based adsorbents has been reported for heavy metal removal in some studies which are summarized in Table 13.

3 Comparative evaluation of different adsorbents previously used for Copper and lead removal

Table 14: Adsorption capacities (mg/g) of different adsorbents for Copper and lead removal

Metal	Adsorbent	Sorption capacity (mg/g)	Ref.
Cu(II)	Amino-functionalized silica-coated Fe_3O_4 nanoparticles	30	[67]
	Hematite (α Fe_2O_3)	84.46	[68]
	Nano-goethite (α -FeOOH)	149.25	[68]
	γ-Fe_2O_3	15	[70]
	(γ-Fe_2O_3)	111.11	[75]
	Modified Nano structured γ-Al_2O_3 with natural and chemical modifiers	97	[96]
	Aluminum oxide/polyaniline nanocomposite	11	[98]
	ZnO	1600	[105]
	Microstructured nanostructured zinc oxides and zinc hydroxide loaded on activated carbon cloth(ACC)	1300	[111]
	δ-MnO_2	92.74	[140
	Silico-manganese nanohybrid (SMNA)	88	[140]
	TiO_2-fly ash (TiO_2-FA)	83.333	[149]
	CNT sheets	64.935	[155]
	SWCNTs	24.07	[156]
	SWCNTs-COOH	55.89	[156]
	c-MWCNTMCs	60.60	[168]
	Chitosan/TiO_2 composite nanofibrous	710.3	[177]
	Amino-functionalized silica-coated Fe_3O_4 nanoparticles	76.6	[67]
	(γ-Fe_2O_3)	71.42	[75]
	Silica coated magnetite (Fe_3O_4@SiO_2) Functionalized by amino-imino-sulfonic group	83.23	[79]
	Maghemite modified with homopolymer	130.12	[81]
	Nano structured γ-Al_2O_3	125	[90]
	Nano-alumina modified with 2,4-dinitrophenylhydrazine	100	[91]
	Aluminum oxide/polyaniline nanocomposite	9.3	[98]
	ZnO nanosheets	6.7	[106]
	Hierarchical ZnO nanorods	160.7	[108]
	CuO nanostructures (different structures)	125, 116, 117,120 115	[118]
	Nano CuO	14·859	[122]
	NiO nanoparticles	909	[127]
	NiO nanopowder	50.505	[130]
	NiO nanoparticles	21.54	[131]

Pb(II)	NiO nanoparticles	56.24	[131]
	Hydrous manganese dioxide (HMO)	352.55	[136]
	TiO$_2$	401.14	[144]
	Layered protonated titanate nanosheets (LPTNs)	366	[145]
	CNT sheets	117. 647	[155]
	SWCNTs	33.55	[156]
	SWCNTs-COOH	96.02	[156]
	CNTs/Fe$_3$O$_4$	31.92	[161]
	CNTs/Fe$_3$O$_4$ functionalized with Thiol group	65.40	[161]
	MWCNTs/Fe$_3$O$_4$	41.77	[162]
	MWCNTs/Fe$_3$O$_4$-NH$_2$	75.02	[162]
	Chitosan/TiO$_2$ composite nanofibrous	579.1	[177]

4. Conclusions and Future Perspectives

1. Metal oxides, CNTs, and polymer based nanoparticles have got great attention and extensively used for removal of heavy metals from aqueous solutions.
2. The CNTs found to have great potential for removal of many heavy metals.
3. The studies dealt with regeneration and reusability of CNTs was limited.
4. The studies dealt with regeneration and reusability of ZnO or polymeric-based nanoparticles were limited also.
5. Surface modification of CNTs improved the adsorption capacity of the CNTs.
6. Nanomaterials as adsorbent are studied only on lab scale and mostly in a batch system.
7. ZnO nanoparticles showed high adsorption capacity for copper ion removal from aqueous solutions while NiO nanoparticles showed high adsorption capacity for Pb(II) removal from aqueous solutions.

Concerning future research deals with these materials,

1. Regeneration studies for the nanoadsorbents need to be addressed in detail to recover adsorbent and reuse it. This will improve the economic studies of the treatment process.
2. Although Surface modification for carbon nanotubes materials improves the removal efficiency of them but uses large amounts of chemicals which lead to environmental pollution. Therefore, researchers should search for novel environmental friendly methods that can be used to modify the surface of CNTs.
3. Researchers should work for developing an economical process for the mass production of CNTs since the price of carbon nanotubes does not suggest the applications of CNTs on a large scale.
4. The possibility of using nanoadsorbents in large scale treatment needs to be studied.

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