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REVIEW ARTICLE

Removal of Lead and Mercury from Water Using Nanoparticles: A Concise Review on Adsorption

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ABSTRACT: Water is the most essential natural resources in the ecosystem and vital for the existence of all living beings as well as humans growth. Due to the rapid industrialization, water pollution is now the most vital matter of concern. A common ecological issue is water pollution with heavy metals, such as lead (Pb) and mercury (Hg), which has become a major environmental problem due to the detrimental consequences on human health and ecosystems. Additionally, research into new and more effective water treatment methods is being driven by the persistence, toxicity, and accumulation of Pb and Hg in the human body. This is done to reduce the amount of Pb and Hg in water. To remove or lower the amount of Pb and Hg in water, several researchers make substantial use of the adsorption. Adsorption continues to be a practical method with flexible design and execution. In the past few years, nanotechnology has come to be a promising approach for the remediation of water polluted with these hazardous metals by adsorption. It will become more and more difficult to deploy technologically sophisticated alternative water treatments to meet the growing demand for lower levels of Pb and Hg in drinking water using current methods. Compared it to alternative approaches, nanotechnology has a lot of benefits. Nanoparticles, owing to their unique physicochemical properties, have garnered attention as competent adsorbents for Pb and Hg removal from water. This review gives an in-depth account of several nanoparticle preparation methods. The review also highlights the recent advancements in the application of different nanoparticles for the remediation of Pb and Hg from aquatic environments.

INTRODUCTION

Fresh water is one of the most vital assets in the earth and that is crucial for the survival of all living beings and the advancement of human civilization. However, water resources around the globe are in danger due to the pollution caused by the discharge of elevated industries and the expanded urban side. Industrial activities including mining, battery, textile, tannery, metallurgical, chemical, nuclear, pharmaceuticals, fertilizers, shipping and shipbreaking, agriculture, etc. are mainly responsible for massive attacks on the water body [1]. Most of the sources release numerous pollutants that can be categorized as pathogenic pollutants, organic pollutants, inorganic pollutants, radioactive pollutants even thermal pollutants. Among the various types of contaminants, heavy metals (inorganic) are the most threatening pollutants because of their stability, solubility, and non-

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degradable nature and these are capable of circulating in the environment retaining the same toxicity levels for a long time [2]. Nowadays, it is a very impractical idea to eliminate or shut down these polluting industries due to the market demand. On the other hand, the rate of water consumption is rising rapidly along with speedy industrialization and urbanization, and the issue of freshwater scarcity has emerged as a significant barrier in everyday life and economic growth. The invisible and health-threatening heavy metals in water have become a major headache on a worldwide scale to be mitigated by environmentalists and hydrological scientists [3, 4]. Since the complete prevention of heavy metal pollution is impossible, scientists are focusing their attention on treating the contaminated water as necessary. Advanced heavy metals treatment technologies are now available such as ion exchange, electrocoagulation, magnetic field embodiment, adsorption using natural and modified adsorbents, membrane filtrations, advanced oxidation processes, photochemical isolation, chemical precipitation, reverse osmosis, solvent extraction, etc. [5]. Each technique offers some advantages along with certain limitations mostly related to economic factors. For example, membrane filtration is expensive and needs high energy to operate whereas all the chemical treatment generates a huge sludge discharge. Moreover, the tedious operational setup, unavailability of technical support and the potential secondary pollution caused by the discharge of treatment facilities limited these techniques in practical implementation. However, a technique is desired that will provide several outstanding features as simple, efficient, cheap, reusable as well as ecofriendly. Till now, the absorption process based on different adsorbents offers most of the intended features mentioned above [6]. The utilization of materials of their nano-size form showed significant performance the adsorption of heavy metals from contaminated water [7]. Though certain things such as clay, zeolite, activated charcoal, sand and biomaterials of plant origin were used traditionally in water purification, these are now gradually being replaced by more popular nano-candidates like metal oxides, graphene-based nanocomposites, nano carbons (tubes, roads, sheets, etc.), metal-organic and inorganic frameworks, biopolymeric composites, etc. [8, 9]. Metal and metal oxide nanoparticles possess exclusive physiochemical properties namely specific surface activity, high surface area, tunable morphology, shape, and size which make them potential players for various environmental applications including water purification [4, 10]. For example, chitosan has both hydroxyl and amino groups which are very active in binding heavy metals. Nano-cellulose composite has also a huge active site to make effective bonding with heavy metal ions. About 104,109 papers have been published on heavy metals removal by adsorption of nanomaterials in the past ten years until March 2023 [11, 12].

This concise review aims to summarize a succinct outline of the latest advancements in the field of nanoparticles for the adsorptive removal of heavy metals especially Pb and Hg from its water matrix. The subsequent sections of this mini-review will delve into heavy metals (especially Pb and Hg) and nanoparticles. The discussion will encompass different classifications, various synthesis procedures and removal methods of heavy metals with nanomaterials in wastewater treatment scenarios. Ultimately, a comprehensive understanding of the capabilities and limitations of nanoparticles for the effective removal of Pb and Hg from the contaminated water will provide valuable insights to researchers, policymakers, and environmental engineers working towards the development of effective strategies for addressing Pb and Hg contamination in aquatic systems. As society strives to safeguard water quality and protect the environment as well as human health, harnessing the potentiality of nanoparticles holds the promise of advancing sustainable solutions to mitigate to adverse impacts of Pb and Hg pollution.

Heavy metals

Heavy metal is a diverse term that indicates the individual chemical identity of metals and their actions on biological function [13]. A trace amount of any metals and metalloids of Al, Ni, Cr, Co, Ag, Mn, Fe, Cd, Hg, Zn, Cu, As, Sn, Pb, etc. having atomic density of 4 ± 1 g cm^{-3} or greater are generally treated as heavy metals [14]. The density of heavy metals is larger than 5 gcm^{-3} and their atomic mass ranges from 63.545 to 200.5 amu [15]. These heavy metals have high physiological and biochemical activities motivated by their atomic structure having high reactivity and complexing power, especially with biomolecules [16]. These metals get enriched into the plant body along with the nutrient consumption causing malfunction in the metabolic vital activities. From the heavy metal enriched species these heavy metals are transferred into the human body through the food chain and adversely affect when reached at a certain threshold limit of concentration [17-19].

Table 1 shows the tolerable limit of Pb and Hg for human beings concerning their weights.

Different metals have different threshold limits of contamination [TLC] in drinking water and exert significant disease Symptoms on human health, some of them identified by the US Environmental Protection Agency (USEPA) listed below in Table 2.

Table 1. Tolerable daily intake (mg 50-60 kg^{-1} body weight).

Heavy metals	WHO/FAO	JECFA
Pb	0.214	2.0
Hg	0.005	1.0

Table 2. TLC standards and disease symptoms of some heavy metals [20].

Heavy metals	Diseases symptoms	TLC, mg L^{-1}
Zn	Increased thirst, Neurological symptoms, Drowsiness, Depression	0.80
Pb	Cerebral disorder, Renal, Circulatory and Nervous disorder	6.0×10^{-3}
Ni	Cancer-causing, Long-lasting Asthma, Skin irritation	0.20
Hg	Arthritis of the joints, Cardiovascular and Neurological maladies	3.0×10^{-5}
Cu	Sleeplessness, Wilson’s syndrome, Liver impairment	0.25
Cr	Diarrhea, Headache, Nausea, Carcinogenic	0.05
Cd	Oncogenic, Renal dysfunction and deterioration	0.01
As	Intestinal carcinoma, Dermal and arterial disorder	0.05

Due to their biological accumulation potential in the food chain, heavy metals including Pb, Zn, Cu, Hg, and others might represent a serious hazard to human health [3]. Based on their significance for human health, heavy metals are designated into four major classes- Essential: Mn, Cr, Co, Zn, Cu, and Fe; these metals are identified as micronutrients, are harmful if consumed more than what is necessary, (2) Non- Essential: Li, Al, Ba, etc. (3) Less toxic: Sb and Sn; and (4) Highly toxic: Cd, Pb, and Hg [21].

Lead

Pb is a group 4A element in the periodic table that appears as a silvery white or grayish colored and physically soft metal. It is highly toxic, very flexible, pliable, bio-accumulative, nondegradable, and poor conductor [22]. Pb, with an atomic number of 82 and atomic mass of 207.19 amu, has a melting point of 327.5°C and boiling point of 1744°C. It is a dense metal with a density of 11.29 gcm^{-3} and exhibits oxidation states of +2 and +4 in its chemical compounds [23]. The extensive usage of lead nowadays has an impact on the environment and is a source of pollution. Industrial operations, food and smoking, drinking water, and residential sources are all important sources of Pb [24]. Formerly lead was extensively released into the environment from gasoline combustion as tetraethyl lead is an anti-knocking agent. Also, home paints, Pb build plumbing pipes, Pb bullets, toy pewter pitches, lead acid batteries, and nozzles are responsible for Pb release to the environment. It comes into contact with humans through meals or drinking water [25]. Different types of human-related activities including smelting, leaded gasoline, lead paint, smoking, contaminated food, and industries, are major contributors to Pb poisoning [26]. The human body can easily absorb Pb in different forms especially an organic form which can adversely affect all the metabolic functions and organs such as the skeleton and the normal function of bones, liver, kidneys, reproductive system, endocrine, central nervous system, enzymatic, blood circulatory and cardiovascular system, essential biomolecule synthesis and damage the ultimate immune system. As a result, it is regarded as a major threat to the mankind [22, 27].

Mercury

Hg, popularly known as quicksilver, is a liquid metal of group 2B of the periodic table. Hg is an extremely poisonous and volatile element found in the environment. It has a strong capability to bond with almost all metals forming amalgams and alloys [28]. Hg, with an atomic number of 80 and atomic mass 200.592 amu, melting point of -38.83 °C and boiling point of 356.62 °C. It is a dense metal with a density of 13.546 gcm^{-3} and exhibits oxidation states of +1 and +2 in its chemical compounds [29]. Hg enters the atmosphere via a variety of natural and manmade sources. Forest fires, Hg-rich soil and volcano eruptions are examples of natural sources. Mobilization of Hg from fossil fuels, incinerators, chlor-alkali industries, gold mining, processing, and mercury ores refinery sites are also a few of the main anthropogenic sources [28]. It can undergo extensive physical and chemical alterations if discharged into the environment. Rain and water stream converts and releases Hg vapors into a soluble form, which is then deposited in the soil and water. Inorganic Hg is transformed into methyl mercury by microbial activity and enters the food chain. Low-dose Hg exposure can affect various organs and normal metabolic systems. Alzheimer's disease, dementia, decreased fertility, atypical birth, autism, memory loss, and so on [30]. Figure 1 shows the metabolism of Pb and Hg in the human body.

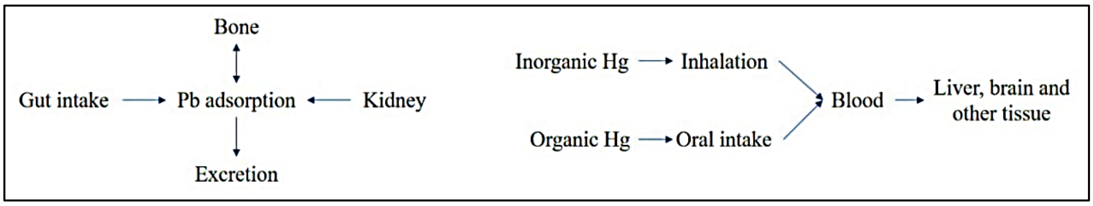


Figure 1. Metabolism of Pb (left) and Hg (right) in the human body [25, 31].

Nanomaterials

Nanomaterials have evolved into an intriguing group of substances that are highly sought after for a variety of real-world applications. To demonstrate how tiny the nanometer is, imaging five silicone atoms or ten hydrogen atoms lined up, each measuring one nanometer. Materials are considered to be nanomaterials if one or more of their dimensions fall between 1 and 100 nm in size [32]. Different types of nanomaterials we can find according to the dimensions are shown in Table 3.

Table 3. Categories of nanomaterials depending on the dimensions of the nanoscale (<100 nm) [33].

Dimensions	Definition	Examples
0-D	All three dimensions of the materials in this area inside the nanoscale range	Nanoparticles
1-D	Only one of the materials' three dimensions is in the nanoscale range	Nanorod, nanowire, nanotube etc.
2-D	Here any two dimensions among the three are in the nanoscale	Nanolayers, nanofilms, nanocoating, nanosheets, etc.
Bulk or 3-D	These nanoparticles are not in nanoscale in any dimension	Core-shell, nanocomposite, multi monolayer, a bundle of nanowires, etc.

A few examples of the distinctive characteristics that nanomaterials typically exhibit at the nanoscale are the effect of surface, tiny size, quantum, and micro quantum tunnel [34]. Figure 2 shows some properties of nanomaterials. Since the introduction of nanomaterials in the 1970s, researchers have increasingly focused on utilizing them to remove contaminants from polluted surface waters, groundwater, sediments, and soil, including heavy metals, organic pollutants, and pathogens [35- 37]. Currently, nanomaterials are employed in electronics, sensors, supercapacitors, sports equipment, scratch-resistant paints, cosmetics, energy storage, environmental remediation and surface coatings [32].

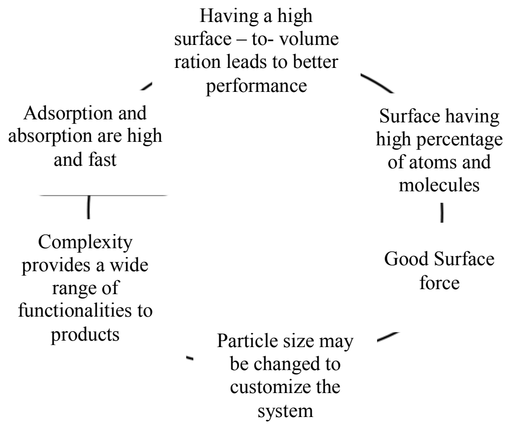


Figure 2. Properties of nanomaterials [38].

Synthesis of nanomaterials

The preparation of nanomaterials primarily employs top-down and bottom-up strategies, top-down techniques break bulky substances to create nanostructured materials. Bottom-up strategies, on the other hand, turn molecular/atomic-level species into nanostructured materials. Table 4 shows different synthesis methods of nanoparticles with their advantages and applications.

Table 4. Different types of approaches for the synthesis of nanoparticles along with advantages and uses.

Methods	Principle	Advantages	Uses	Ref.
		Top-down approaches		
Mechanical milling	Ball milling method	Effective technique for creating mixtures of various phases is also useful for making nanocomposites	To generate aluminum oxide and carbide alloys, Cu/Al/Mg/Ni-based nanoalloys, durable spray coatings, and many other nanocomposite materials	[39, 40]
Electrospinning	Two coaxial capillaries make up the spinneret in coaxial electrospinning. Core-shell nano architectures are built in an electric field by these capillaries using viscous and non-viscous liquid	The most simple, effective, and simplest top-down technique for mass-producing core-shell ultrathin fibers.	To manufacture nanofibers from versatile materials, especially polymers, and to construct core-shell and hollow polymers as well as inorganic, organic, and hybrid materials.	[41, 42]
Lithography	Constructing nano architectures with a laser or an electron beam	Developed nano architectures	-	[43]
Sputtering	Bombarding solid surfaces with high-energy particles such as plasma or gas	Efficient for nano-films generation. Fewer impurities and cost-effective	To fabricate WSe_2-layered nanofilms on substrates made of SiO_2 and carbon paper	[32, 44]
Arc-discharge method	Carbon rod vaporization is caused by an arc discharge between the ends of the graphite rods. Two graphite rods are kept carefully in a helium gas-adjusted chamber	-	To create pyrolytic graphite, nano-graphite, fullerenes, carbon nanohorns, carbon nanotubes, graphene having few layers, polyhedral graphite particles with high-purity, and amorphous spherical carbon nanoparticles	[32, 45-48]
Laser ablation	Nanoparticle production is done using a powerful laser beam which vaporizes	The average size and distribution may be manipulated by altering the fluence, wavelength and addition of salt	To produce metal nanoparticles, oxide composites, carbon nanomaterials, and ceramics	[49-54]
		Bottom-up approaches		
Methods	**Principle**	**Advantages**	**Uses**	Ref.
Chemical vapor deposition (CVD)	Vapor-phase precursors form a thin film by chemical reaction on the substrate surface	Low cost, high purity, sufficient volatility, non-hazardous, good stability during evaporation, and a long shelf-life	Carbon-based nanomaterials	[55]
Hydrothermal	High pressure and temperature are employed on reactants in their solution phases	Preparation of good-quality crystals while controlling the composition	Useful for producing various nano-geometries such as nanorods, nanowires, nanospheres, and nanosheets	[32, 56]
Sol-gel	Wet chemical technique	Polycondensation persists during the aging process, resulting in changes to the structure, characteristics,	Useful for the preparation of hybrids of organic and inorganic nanomaterials, metal and non-metal oxides and, composites.	[32, 56]

		and porosity		
Co-precipitation	This can be done by surface adsorption, mixed-crystal formation, occlusion, and mechanical entrapment	Homogeneous	Versatile nanoparticles from soluble precursors	[56]
Sonochemical	Ultrasound energy is employed in the medium that chemically excites the matter generating bubbles of high temperature and pressure	Safe, rapid, and selective nanoparticle synthesis	Selenides like ZnSe, CdSe, and alloys, oxides, CoS_2	[56]

Remediation of heavy metals by nanomaterials

Heavy metals must be removed from water to make it safe for usage. The removal process is crucial because even a minor overload of heavy metals above its permitted limit can be hazardous to human health. To ensure that a specific metal ion is completely removed from the aqueous system, a correct removal approach must be used. Care must also be given to choosing a removal method that is safe to use environmentally responsible, and cost-effective. Nanomaterials are exciting catalysts and adsorbents for environmental cleanup because of their high chemical reactivity, broad adsorption surface, mild temperature alteration, and proactive atomicity. [57, 58]. Due to the nanoparticles' small size, charge stabilization is made possible by the surface atoms' easier ability to adsorb and interact with other atoms [59]. Adsorbent adsorption capabilities can be considerably improved by having a large specific surface area [60, 61]. Furthermore, because of their small size, nanomaterials have highly reactive surfaces [62]. They have special redox qualities that are advantageous for the breakdown of redox-sensitive contaminants in addition to their exceptional ability to effectively adsorb pollutants [63, 64]. The number of articles published each year (Figure 3) demonstrates the growing importance and research interest in studies on heavy metal removal using nanomaterials. However, certain regularly utilized nanomaterials have disadvantages, such as high costs, possible poisoning, recycling problems, and easy association with other media [65]. Even though nanomaterials have been extensively researched in the area of heavy metal remediation, a profound and more systematic assessment of the implementation of nanomaterials for heavy metal ion removal is somewhat missing [66].

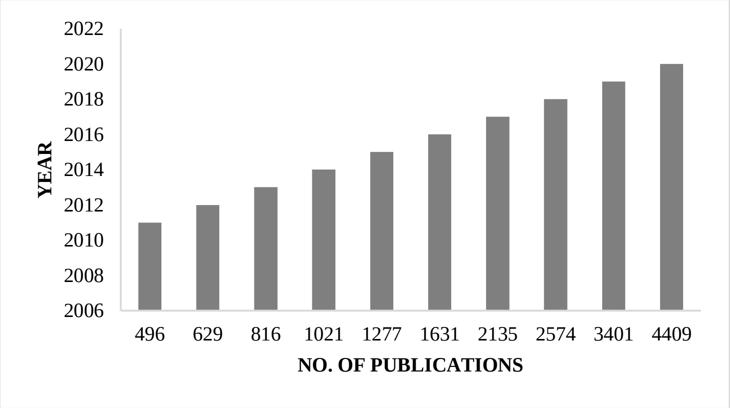


Figure 3. Number of publications over the world according to year.

Nanomaterials frequently display several unique features at the nanoscale, which contribute to their exceptional adsorption capacity and reactivity, both of which are advantageous for heavy metal ion removal. So far, extensive study on nanomaterials has been conducted to examine their uses in heavy metal water treatment, and they have shown significant promise as a possible alternative to heavy metal adsorption from wastewater [67]. Heavy metal ions have been eliminated from water using a variety of techniques (Figure 4), the most noteworthy of them include chemical precipitation, adsorption, ion exchange, etc., which are frequently used to remove metal ions from the aqueous systems [68].

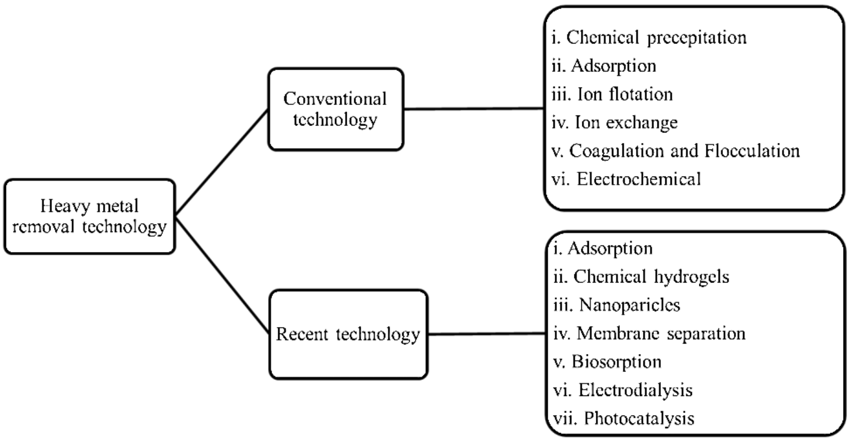


Figure 4. Different technology for heavy metal removal.

Conventional technology

Chemical precipitation is a method of removing ionic elements in wastewater by adding precipitating agents, which causes a chemical process that changes the soluble substance into an insoluble form. The majority of metals are precipitated in the form of their hydroxides, however, alternative processes including the precipitation of carbonate and sulfide are also frequently used [69]. The precipitation mechanism for metal ions is - $M^{2+} + 2(OH)^{-} = M(OH)_2 \downarrow$; where, M^{2+}, OH^-, and $M(OH)_2$ are the metal ions, precipitating ion, and insoluble metal hydroxide produced, accordingly. Magnesia (MgO) is more successful than lime in removing Cd (II), Ni (II), Pd (II), Cu (II), Cr (III), and Fe (III), with a removal efficiency of more than 97% at the recommended MgO does [70]. For the removal of heavy metals from the leachate of acidic soil saline, chemical precipitation and electrocoagulation were explored. Chemical precipitation using $Ca(OH)_2$ shown to be successful in decreasing the cntent of Ni, Zn, Cr, and Cu but not Cd and Pb [71].

Ion flotation is one of the most commonly used processes for extracting metal from industrial wastewater. At the lab and industrials scales, metal removal from water and wastewater has been demonstrated with various degrees of effectiveness [72]. Other ions were also removed between 99.1 and 99.7% effectively using either pure nitrogen to air, with re-crystallized octanoyl-cysteine (octanoyl-cys) surfactant utilizing pure nitrogen gas achieving a mercury ion removal efficiency of 99.9% [73]. Using a substance capable of exchanging cations for anions, heavy metals are removed from industrial effluent using ion exchangers [74]. In one study, 99.99% of the Hg, Cu, and Cd were removed from sewage sludge by applying a commercially available magnetic ion exchange resin with a capacity of 4.5 $meqg^{-1}$ and particle size of 100-300 m [75].

For the proper disposal of wastewater and, eventually, the creation of high-quality drinking water, coagulation, and flocculation are essential treatment procedures. Following the application of a coagulant or chemical, coagulation occurs when a chemical reaction takes take place in wastewater. In an aqueous solution, colloidal components mix to form flocs or small aggregates. These microscopic aggregates, sometimes known as flocs, draw in suspended materials like metals. The sluggish mixing of water may contribute to the production of small flocs that enlarge and settle inside the solution. The technique in question is referred to as flocculation [76]. An electron transfer process, such as electroreduction or electrooxidation, is involved in the electrochemical treatment of wastewater [77]. This method uses an aqueous solution of metal ions to conduct a direct current between the cathode and anode. Metal ions having positive charge stick to a cathode having negatively charge [78]. It is a cathodic deposition, as indicated by-

$$M^{n+}(aq) + ne^{-} = M(s) \;;$$

where, M^{n+} = metal ion and M= neutral of metal deposited. Electrochemical methods provide the advantages metal selectivity, no need for additional chemicals, quick, well-managed set-up with excellent removal efficiency, and less sludge created [79].

Modern technology

Modern technology includes hydrogels, membrane separation, biosorption, electrodialysis, *etc*. Using Hydrogels, where hydrogel being a three dimensional network of hydrophilic polymers that keeps its structure via chemical and physical bonding between certain chains. The hydrogel's capacity to absorb a lot of water and hold it while maintaining its structure is its most important property [80]. In the membrane separation process, feed water is forced at high pressure across a semipermeable membrane to extract certain substances from the solution. Based on pore size, the process is divided into four categories: microfiltration, nanofiltration, ultrafiltration, and reverse osmosis [81]. The maximum super adsorbent capacities for Pb^{2+}, Cu^{2+}, and Cd^{2+} ions were found to be 1017, 413, and 396 mgg^{-1}, respectively. Additionally, following treatment with 0.2 M HNO_3, recovery for Pb^{2+}, Cu^{2+}, and Cd^{2+} was 96%, 99%, and 99%, respectively [82].

Physiochemical metal ion binding to a biosorbent's surface takes place during biosorption. In recent years, biosorption has emerged as the preferred technique for removing heavy metals from wastewater effluent discharged by various manufacturing sites that is both efficient and ecologically benign. Potential sources of metal biosorbents include fungi, algae, yeasts, bacteria, agricultural and industrial waste, and biopolymers [83, 84]. For the metal, the percentage of biosorption (RE), known as biosorption effectiveness, can be calculated as: $RE = \frac{C_i - C_e}{C_i} \times 100\ \%$; where C_i is the initial (in mgL^{-1}) and C_e is the equilibrium concentrations (in mgL^{-1}) of metal ions in the solution. Electrodialysis, which employs electrically powered ion-exchange membranes to extract ions from aqueous solution, is one of the most economically advantageous emerging technologies [85]. One of the most inventive methods for swiftly and completely removing environmental toxins is photocatalysis. In this technique, a semiconductor-electrolyte interface is irradiated with light energy above the semiconductor bandgap, which results forming electron-hole (e-/h+) pairs in the conduction and valance bands of the semiconductor [76]. These moving charge carriers in solution can oxidize or reduce species with an appropriate redox potential. Some of the often-studied semiconductors include SnO_2, TiO_2, CeO_2, ZnO, CdS, and ZnS [86].

Adsorption of Pb and Hg by nanomaterials

Heavy metals have been removed from water using a variety of techniques. The economics and the concentration of heavy metals are the primary factors influencing the choice of a certain treatment approach [87]. Adsorption is a surface -occurring phenomenon that is defined as the addition of a certain material to a solid surface through physical or chemical bonding [88]. An adsorbate is a substance (species) that binds to a solid surface, whereas an adsorbent is the solid surface itself. Transporting heavy metals from the bulk to the adsorbent surface, adsorption on the particle surface, and ultimately transit inside the adsorbent particles are the three sequential phases in the adsorption of heavy metals [89]. Adsorption has been successful in lowering metal content, and is another physiochemical technique for removing heavy metals. There are three crucial steps in the adsorption onto adsorbent: (i) penetration from the bulk to the adsorbent surface, (ii) adsorption of the metals on the adsorbent surface, and (iii) penetration in the adsorbent structure [90]. Adsorption is a cost-efficient technique for removing contaminants from water. Several adsorbents have already been employed but they are suffering from low adsorption capacities [90]. A vast number of research have been conducted to create highly effective nano-adorbents capable of removing heavy metals from wastewater at a cheap cost and with great performance. The most prevalent and commercially explored adsorbents have included zeolite, carbon nanotube, activated carbon, and graphene [91-95]. As a result, researchers are looking at new, potential adsorbents such as carbon-based nanomaterials, inorganic nanoparticles, metal-organic framework (MOF), imprinted polymers, etc.

Carbon-based nanoparticles

The nanoparticles and their derivatives were separated into different groups to examine the Pb and Hg ion adsorption on carbon-based nanoparticles such as carbon nanotube (CNT), graphene (G), graphene oxide (GO) reduced graphene oxide (rGO), etc. Figure 5 shows the structures of graphene, graphite, SWCNT, MWCNT, CNT, GO, and rGO. In recent years, have seen a lot of interest in novel nanocomposites based on modifying the adsorbent with a naturally occurring chemical as a green sorbent due to its suitable properties including biodegradability, biocompatibility, low toxicity, and so forth. Maximum removal was 100% for Hg(II), Pb(II), and Cd(II), 73% for Cu(II), and 92% for Ni(II) by coir pith carbon was shown to rely on pH, with pH of 4.0 for Pb(II), 3.5 for Ni(II), and Hg(II), 5.0 for Cu(II), and 4.0 for Cd(II) [73].

Carbon nanotube

As a noble adsorbent, CNTs have been widely employed to remove a number of heavy metals from water along with Pb and Hg. It has been widely employed for the removal of various impurities from aqueous solutions due to its vast surface area, low mass density, high porosity, hollow structure, and strong interaction between pollutant molecules and CNTs [87]. CNTs are cylindrical carbon nanostructures, rolled graphite sheets with sp^2 hybridization on each carbon atom. It has an extremely hydrophobic surface and a conjugative structure with hexagonal arrays of carbon atoms [96]. Because of their hydrophobicity, carbon nanotubes (CNTs) are used as a specialized adsorbent for the removal of nonpolar contaminants. Due to the high porosity structure of CNTs, polar and ionic substances may also be absorbed into the pores of CNTs dependent on their molecular size. CNTs are classified into two types: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs are produced by rolling a single graphite sheet into a cylinder with a diameter of 1-2 nm, whereas MWCNTs are formed by stacking several separated and nested graphite cylinders with a diameter of 2-2.5 nm [97]. The application of CNTs and their derivatives for the removal of Pb and Hg are represented in Table 5.

Graphene

Graphene is a unique two-dimensional allotrope of carbon. The high application of graphene is due to the honeycomb lattice structure with one-atom thickness and high π- conjugated systems [120]. It has been recognized as a suitable adsorbent because to its excellent stability, surface area (2630 $m^2\ g^{-1}$), and outstanding mechanical strength [121]. Graphene's implications for the elimination of Pb are lower than those of other carbon-based nanomaterials because it lacks an appropriate functional group to interact with, is chemically inert, and difficult to functionalize [122]. Deposition of metals and metal oxides into graphene structure can boost the adsorption capacity in addition to functionalizing it [121]. The application of graphene and its derivatives for the removal of Pb ions are represented in Table 6.

Reduced graphene oxide

Reduced graphene oxide (rGO) is typically generated by reducing GO utilizing chemical reducing agents (such as ascorbic acid, sodium borohydride, hydroquinone, and hydrazine), heat treatment, and electrochemical reduction to remove multiple functional groups, including oxygen, from graphene (GO) [120]. Figure 6 shows the conversion of different CNTs from graphene and graphite. To remove heavy metal ions, rGO has not been used alone as an adsorbent. Heavy metals removal has frequently employed its functionalized compounds or composites with metal or metal oxides. Due to the presence of various functional groups like hydroxyl, carboxyl,, and ether on its surface, rGO can be functionalized more easily than graphene. It is obvious that given the right circumstances, the chemical process can activate the functional groups and replace them with others. The structure of functionalized rGO composites and their capacity to remove heavy metals can be considerably influenced by the technique, reactants, and reaction conditions used. Table 7 provides examples of functionalized rGO composites for Pb and Hg removal [120].

Graphene oxide

Due to the catalytic capabilities, ease of separation after adsorbing heavy metals, and capacity to oxidize or decrease heavy meals by nanoparticles, the deposition of metal and metal oxide nanoparticles in GO can help. [130]. Additionally, these composites are reusable, cheap, high efficiency adsorbents for the removal of heavy metals [131]. Table 8 shows some GO and its composites for the removal of Pb and Hg.

Table 5. Application of CNTs and their derivatives for the removal of Pb and Hg from aqueous solution.

Metals	**Adsorbent**	**Adsorption capacity (mg g^{-1})**	**Ref.**
Pb (II)	CNTs	37.594	[98]
	N-doped magnetic CNTs	6.74 mmol g^{-1}	[99]
	Oxidized CNTs	82.6	[100]
	HNO_3-CNTs	82	[101]
	L-CNTs	199	[102]
	MWCNTs/PAAM	37.44	[103]
	O- MWCNTs	35.08	[104]
	MWCNTs/TAA	71	[105]
	MCNTs/DE	60.80	[106]
	MHC/OMWCNTs	101.10	[107]
	MWCNTs/SiO_2	13.23	[108]
	Acidified MWCNTs	11.2	[109]
	TiO_2/MWCNTs	4.63	[110]
	MWCNTs/Fe_3O_4-NH_2	101.05	[111]
	3-MPTS grafted MWCNTs/Fe_3O_4	42.12	[112]
	SWCNTs/WSh	294.10	[113]
Hg (II)	MWCNTs	0.493	[114]
	N-doped magnetic CNTs	2.59 mmol g^{-1}	[99]
	Phenolic hydroxyl functional group P-MWCNT	28.22	[115]
	OH-MWCNTs	89.42	[115]
	Carboxylic functional group COOH-MWCNT	81.57	[115]
	MPTS grafted MWCNTs/Fe_3O_4	63.65	[112]
	Ox-MWCNTs impregnated Chitosan beads	181.8	[116]
	Amino and thiolated functionalized MWCNTs	83.33	[117]
	MnO_2-coated carbon nanotubes	14.28	[118]
	MWCNT-OX	27.77	[119]
	Iodide incorporated MWCNT (CNT-I)	100	[119]
	Functionalized sulfur incorporated MWCNT (CNT-S)	100	[119]

(L-CNTs) lignin-grafted carbon nanotubes, **(MWCNTs/PAAM)** multiwalled carbon nanotubes/polyacrylamide, **(MWCNTs/PAAM)** multiwalled carbon nanotubes with tris(2-aminoethyl) amine, **(MCNTs/DE)** magnetic carbon nanotubes/diatomite earth composite, **(MHC/OMWCNTs)** magnetic hydroxypropyl chitosan/oxidized multiwalled carbon nanotubes, **(3-MPTS grafted MWCNTs/Fe_3O_4)** 3-mercaptopropyltriethoxysilane grafted MWCNTs/Fe_3O_4

Table 6. Removal of Pb from aqueous solutions using graphene and its derivatives

Metals	**Adsorbent**	**Adsorption capacity (mg g^{-1})**	**Ref.**
Pb	G-C8P and G-PF6	74.18-405.9	[122]
	G/MnO_2	781 µmol g^{-1}	[121]
	G-nZVI	181.04	[123]
	3D-PG/L/SA	226.24	[124]

(G-nZVI) of nano zerovalent iron nanoparticles-graphene composite, , **(3D-PG/L/SA)** 3D porous graphene/lignin/sodium alginate composite

Table 7. Some functionalized rGO composites for Pb and Hg removal

Metals	Adsorbent	Adsorption capacity (mg g^{-1})	Ref.
Pb	PoPD/rGO	228	[125]
	nZVI/rGO	904	[120]
	TCAS-rGO	230.41	[126]
	SMGI	1666.6	[120]
	MoS_2/rGO	384.16	[127]
	PrGO-Fe_3O_4	777.28	[128]
	rGO-PDTC/ Fe_3O_4	147.06	[129]
Hg	rGO-PDTC/Fe_3O_4	181	[129]

(PoPD/rGO) poly(o-phenylenediamine)/reduced graohene oxide, **(TCAS-rGOf)** thiacalix arenetetrasulfonate-functionalized reduced graohene oxide, **(PrGO-Fe_3O_4)** partially reduced graohene oxide -Fe_3O_4, **(rGO-PDTC/ Fe_3O_4)** dithiocarbamate(DTC)-modified magnetic reduced graohene oxide, **(SMGI)** Sodium modified reduced graohene oxide - magnetic iron oxide

Table 8. Some GO composite for the removal of Pb and Hg.

Metals	Adsorbent	Adsorption capacity (mg g^{-1})	Ref.
Pb (II)	GO	2.27 mmol g^{-1}	[132]
	GO	125	[133]
	MGO	58.43	[134]
	EDTA-GO	479 ± 46	[135]
	EDTA-mGO	508.4	[136]
	TEPA-GO/$MnFe_2O_3$	263.2	[130]
	MGL	173	[137]
	GO-$MnFe_2O_3$	673	[138]
	HMO@GO	553.6	[139]
	GO-SBA-15	255.1	[140]
	PS-GO	256	[141]
	LS-GO-PANI	216.4	[142]
	PVK-GO	887.98	[143]]
	HPA-GO	819.7	[144]
	GO-PANI	1416	[145]
	MCGO	76.94	[146]
	MCGO	112.35	[147]
	GO/Ch/FeOOH	111.11	[148]
	Pb-MCGO	79.8	[149]
	CHI-APSGO	566.2	[150]
	β-CD-GO	149.53	[131]
	β-CD-mGO	279.21	[151]
	mp-CA/GO	368.2	[152]
	PVA/GO-SA	279.4	[153]
	SAGO	267.4	[154]
	Few-layered GO	842	[155]
	NH_2/GO	96	[156]
	L-Trp-/GO	222	[157]
	PAS/GO	312.5	[158]
	PAMAMs/GO	568.18	[159]

	HPEI/GO	438.6	[160]
	Ag/GO	312.57	[160]
	Graphene nanosheet	476.19	[160]
	Chitosan/GO	461.3	[161]
	Chitosan/SH/GO	447	[162]
	CSGO	216.9	[163]
	GO-OMS	39.97	[164]
	MMSO-GO	333	[165]
Hg (II)	GO/CS	381	[166]
	GO-OMS	48.21	[164]
	Magnetic PPy-GO	400	[167]
	Fe_3O_4-xGO	118.5	[136]
	MGO	71	[168]

(MGO) Magnetic GO, **(EDTA-GO)** Ethylenediamine tri acetic acid-GO, **(EDTA-mGO)** Ethylenediamine tri acetic acid-functionalized magnetic GO, **(TEPA-GO/$MnFe_2O_3$)** Tetraethylenepentamine modified GO/$MnFe_2O_3$ nanohybrids, **(MGL)** Magnetic–GO-layered double hydroxide composites, **(GO-$MnFe_2O_3$)** GO-hydrated manganese oxide nanocomposites, **(HMO@GO)** Mesoporous silica (SBA-15)-grafted GO, **(PS-GO)** Sponge-like polysiloxane-graphene oxide gel, **(LS)** Lignosulfonate, **(PVK-GO)** Poly (N-vinyl carbazole)-GO, **(HPA-GO)** Hyperbranched polyamine functionalized GO, **(GO-PANI)** GO-Polyaniline, **(MCGO)** Magnetic chitosan/graphene oxide composites, **(GO/Ch/FeOOH)** GO/chitosan/FeOOH nanocomposites, **(CHI-APSGO)** Cross-linked chitosan-functionalized GO, **(β-CD-GO)** β-cyclodextrin modified graphene oxide nanosheets, **(β-CD-mGO)** β-cyclodextrin modified graphene magnetic oxide nanohybrids.

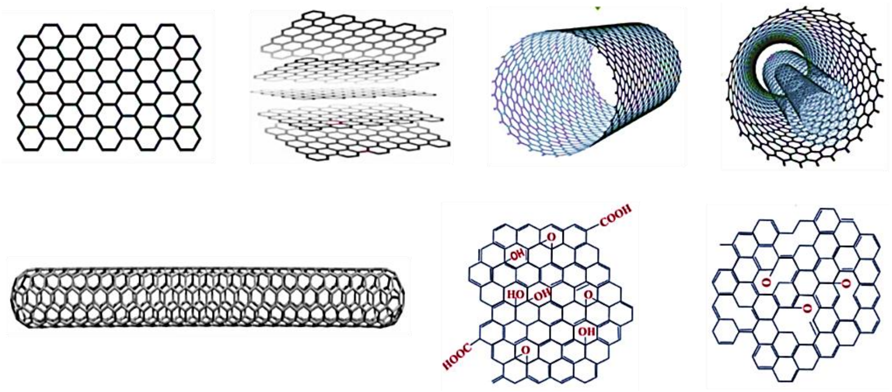


Figure 5. From the top left, graphene, graphite, SWCNT, MWCNT, CNT, the chemical structure of GO and rGO [169-171].

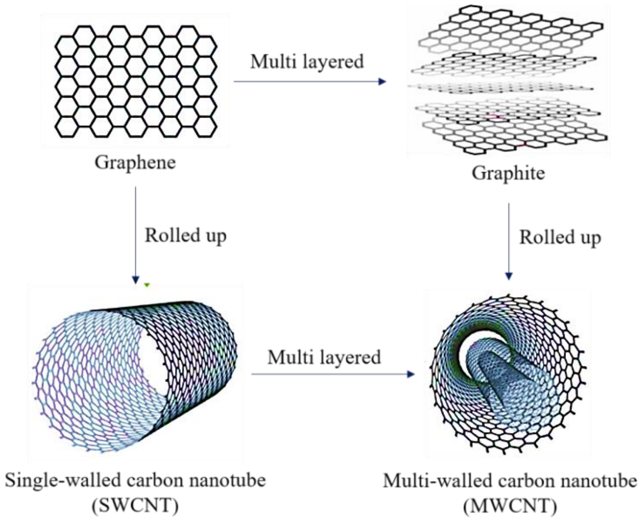


Figure 6. Conversion of different carbon nanotubes from graphene and graphite [169].

Inorganic nanoparticles

Recovery of magnetic inorganic nanoparticles using adsorption is simpler and more efficient when compared to another popular adsorbent [172, 173]. Cerium oxide (CeO_2), titanium oxide (TiO_2), and zinc oxide (ZnO) are the main metal oxides utilized as nano adsorbents due to their high surface areas and the possibility to use different functionalized groups to boost their affinity [174]. To eliminate Pb and Cr from wastewater, magnetic iron oxide nanoparticles (Fe_3O_4 NPs) were used. A solution containing 10 ppm Pb (II) ion was treated with Fe_3O_4 for two minutes, and 90% of the Pb (II) ion was eliminated [175]. Table 9 shows a list of inorganic nanoparticles for the removal of Pb and Hg from water.

Table 9. A summary of inorganic nanoparticles for the removal Pb and Hg.

Metal ion	Inorganic nanoparticles	Adsorption capacity (mg g^{-1})	Ref.
Pb (II)	Ferric oxide nanoparticles	< 0.05 mg L^{-1}	[176]
	Zinc oxide nanoparticles	5.57	[177]
	Fe_3O_4	36	[178]
	Mixed magnetite hematite	617.3	[179]
	Nickel oxide nanopowder	-	[180]
	Nickel oxide nanocatalyst	-	[181]
	Chromium-doped nickel oxide	-	[182]
	Zinc oxide-green synthesis	-	[183]
	Iron-oxide nanoparticles (Fe_3O_4)	68.07	[184]
	ε-MnO_2 nanoflowers	239.7	[185]
	Fe_3O_4@MnO_2 core–shell	666.67	[186]
	MnO_2/PDA/Fe_3O_4 fibers	196.67	[187]
	γ-Fe_2O_3 nanoparticles	48.90	[188]
	NZVI	807.23	[189]
	Manganese dioxide/gelatin	318.7	[190]
Hg (II)	Fe_3O_4/SiO_2/APTES	-	[191]
	Fe_3O_4/HA	-	[192]
	Iron oxide	-	[193]
	Ag NPs	95%	[194]
	Alumina sol	99%	[195]
	Au NP-Al_2O_3	97%	[196]
	Fe_3O_4 @PTMT	603.16	[197]
	ZnO NPs	714	[198]

Metal-organic frameworks

Metal-organic frameworks (MOFs) are a type of porous materials with wide variety of applications due to their tunable structures, large surface areas, and unique properties. MOFs are created via the combination of metal-containing groups with organic linkers, resulting in highly porous crystalline frameworks with good stability, tunability, and organic functionality [199, 200]. They can be thought of as having a multidimensional lattice structure made up of coordination bonds connecting organic linkers and inorganic metal nodes in the structure as shown in Figure 7 [201]. As it is well established, when two or more entities work together cooperatively, they sometimes can achieve outcomes that are more efficient, effective, or beneficial than what each entity could accomplish on its own. This effect is called the synergetic effect and the unique properties of MOFs are influenced by this effect having both metal ions and organic components [202]. Moreover, the structures of MOFs can be tuned easily via different nano-engineering approaches to achieve the surface of the desired area, porosity, and functionality targeting the selective applications [199].

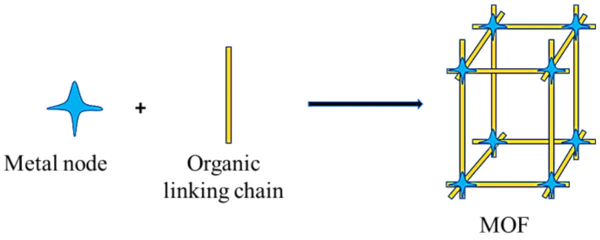


Figure 7. A conventional metal-organic framework is made up of metal nodes and organic linkers [203].

A well-known attempt called the self-assembly of organic ligands and inorganic metal ions or nano-clusters can make the organic-inorganic hybrid MOFs with structural diversity and easy modifications of all the expected parameters [204, 205]. Due to the several utilization advantages, MOFs have become a more prominent candidate than traditional materials in order to remediate heavy metal-contaminated water. That's why researchers think that MOFs will dominate the wastewater treatment field shortly. Modification of MOF-808 by -SH organic group has shown an excellent adsorptive removal selectively Hg(II) (977.5 mg g^{-1}) with enhanced repeatability [206]. A novel Zr-MOF was synthesized adopting a facile single step hydrothermal methodusing mercaptosuccinic acid and zirconium chloride salt. The produced composite had good electrostatic and chelation capability and hence could adsorb 1080 mgg^{-1} of Hg (II) and 510 mgg^{-1} of Pb (II) under optimum conditions [207]. Also, bimetallic MOF can be made by doping one metal in another MOF composite. For example, Fe was doped in HKUST-1 known as MOF-199 and the resultant bimetallic MOF consumed a maximum of 565 mgg^{-1} of Pb (II) [208]. It is worth mentioning that the pristine MOFs have also a huge specific surface area and porosity initially revealed exceptional performance in gas adsorption. As a result, the remediation of contaminants in aqueous solutions has since been thoroughly explored [209]. Despite the high specific surface area (1222 m^2g^{-1}) and porosity, pristine MOFs have certain limitations. That's why it showed very weak adsorption performances. For example, 47 mg g^{-1} [210], 75 mg g^{-1} [211] of Hg(II), and 40.5 mg g^{-1} [212], 48.7 and 55.8 mg g^{-1} [213] of Pb(II) adsorption were reported.

Outstanding performance can be achieved using functionalized MOFs. They have received a lot of attention in the study of eliminating heavy metals from the water because they may combine the properties of various materials at the same time [209]. Ji *et al.* showed that the –SH functional group was outstanding in removing Hg(II). He fabricated MOF-808-SH by grafting thioglycollic acid on MOF-808 representing a high adsorption capacity 977.5 mgg^{-1} for Hg (II) [206]. Zr-based MOF (UiO-66-NH_2) has a maximum capture amount of Hg(II) is 480 mgg^{-1}, which was modified by glutaraldehyde and 4,6-Diamino-2-mercaptopyrimidine (DMP) to obtain UIO-66-DMP in two steps, and the capture of Hg(II) was at amount up to 822 mgg^{-1} [216]. Wang *et al.* synthesized MOF-MA directly by a one-step reaction using $ZrCl_4$ and mercaptosuccinic acid (MA). This method is cheap, facile, and eco-friendly. The maximum adsorption capacity of MOF-MA was 1080 mg g^{-1} and 510 mg g^{-1} for Hg(II) and Pb(II) respectively. Furthermore, the adsorbent's actual use in wastewater demonstrated that it could preferentially adsorb Hg(II) and Pb(II) from the mixed ion solution [207]. Matériaux de l'Institut Lavoisier (MIL)-101(Fe) was modified by 1,2,4,5-benzenete-tra carboxylic to form MIL-101-$(COOH)_2$. Compared with the pristine MIL-101, its adsorption capacity is 12 times greater than MIL-101-$(COOH)_2$ because of its porous surface having more active sites relative to MIL-101 and showed the maximum adsorption capacity of Pb(II) was 468 mgg^{-1} [212]. Zhong *et al.* synthesized copper-based (Cu-BTC) MOFs, Cu-BTC-Th, by introducing organic ligand 4-thioureidobenzoicacid (Th) within Cu-BTC using a one-step method. The performance of the adsorbent was greatly increased by inserting active sites such as -NH_2 and -S, and the capture quantity of Pb(II) was 732.86 mgg^{-1}, which was much higher than that of Cu-BTC aqueous solution [218]. Li *et al.* presented a green and simple method for synthesizing defective MOFs (SS-NH_2-UIO-66-5) by reacting UIO-66-NH_2 with various dosages of seignette salt, and the findings revealed that the defective MOFs had the highest adsorption performance when 5 mol of seignette salt was added. The adsorbent's adsorption quantity was approximately 34 times that of the native UIO-66-NH_2, which is 186.14 mgg-1 for Pb(II). The absence of a linker or cluster was responsible for the creation of hierarchical porous adsorbents with many vacancies and defect sites, resulting in high Pb(II) adsorption [217].

MOFs composites also have tremendous contributions to the adsorption of Pb (II) and Hg (II) in water. Huang *et al.* fixed Fe_3O_4@SiO_2 into UIO-66, and then replaced terephthalic acid in UIO-66 with thioglycolic acid by solvent-assisted ligand exchange to successfully prepare magnetic material MFC-S which had large adsorption capacity (282 mg^{-1}) for Hg^{2+}. Due to the presence of a large amount of –SH, the adsorbent showed fast kinetic and excellent selectivity and reproducibility for Hg^{2+} [219]. Abdollahi *et al.* proposed Fe_3O_4@TMU-32 as a magnetic material, by applying pore functionalization and surface-charge modulation strategies, showed adsorption capacities were 905 and 1600 mg^{-1} for Hg (II) and Pb (II) respectively [220]. Mahmoud *et al.* prepared MOF nanocomposite by microwave green chemical process. There, the –NH_2 functional group via 3-aminopropyltrimethoxysilane (APTMS) was selected to anchor onto the pore surface of the prepared MOF nanocomposite, which showed was introduced into a large number of active sites (Fe-O, Si-O, –NH_2), showed an adsorption capacity of 536.22 mg g^{-1} for Pb (II). Similarly, some other magnetic core–shell nanocomposites have been reported previously, such as Bi-I-Fe_3O_4@SiO_2@HKUS-1 (Hg^{2+}, 264 mg g^{-1}) [221] and Fe_3O_4@$Cu_3(btc)_2$ (Hg^{2+}, 348.4 mg g^{-1}; Pb^{2+}, 215mg g^{-1}) [222]. Liang *et al.* adopted a mild and facile method to prepare ultrasmall In_2S_3 nanoparticles (about 2.5 nm) in the cavities of an MOF for the first time. Due to the strong interaction between S and Hg^{2+}, it showed excellent removal efficiency (99.95 %) and an adsorption capacity of 518.2 mg g^{-1} for Hg(II) [211]. For Pb(II) removal, PHCS-15@ZIF-8 was synthesized by Chen et al., which was a core–shell nanosphere composed of porous hollow carbon spheres (PHCS) with controllable particle size and ZIF-8 nano particles. The adsorption capacity is 462.9mg g^{-1} [223]. ZIF-8@GO is a novel zeolitic imidazole framework complex grown from ZIF-8 nanoparticles on GO, which enables ZIF-8 to be effectively dispersed on the surface of GO, which is conducive to sufficient contact with metal ions. The results show that the adsorption amount reached 356mg g^{-1} for Pb (II) [224]. UiO-66-NH_2 MOF, synthesized by microwave heating method, was incorporated into the PAN/chitosan nanofibers, which had an adsorption amount of 441.2 mgg^{-1} for Pb^{2+} [214]. There are so many other MOFs that have adsorption characteristics towards Hg (II) and Pb (II) listed in Table 10 below.

Table 10. Some MOF adsorbent for the removal of Pb and Hg.

Metal ion	MOF adsorbent	Adsorption capacity (mgg^{-1})	Ref.
Pb (II)	MOF-MA	510	[207]
	Fe dopped HKUST-1 MOF	565	[208]
	MIL-101(Fe)	40.5	[212]
	UIO-66	48.7	[213]
	UIO-67	55.8	[213]
	MOF-5	658.5	[215]
	MIL-101-$(COOH)_2$	468	[212]
	SS-NH_2-UIO-66–5	186.14	[217]
	Cu-BTC-Th	732.86	[218]
	Fe_3O_4@TMU-32	1600	[220]
	Fe_3O_4@$Cu_3(btc)_2$	215	[222]
	PHCS-15@ZIF-8	462.9	[223]
	ZIF-8@GO	356	[224]
	NH_2-MIL-53/WC	223.4	[225]
	PAN/chitosan/UiO-66-NH_2	441.2	[226]
Hg(II)	MOF-808-SH	977.5	[206]
	MOF-MA	1080	[207]

UIO-66	36.45	[214]
ZIF-90	47	[210]
MIL-101(Cr)	75	[211]
ZIF-90-THP	596	[210]
ZIF-90-THF	403	[210]
UIO-66-NH_2	480	[214]
UIO-66-DMP	822	[216]
MFC-S	282	[219]
Fe_3O_4@TMU-32	905	[220]
Bi-I-Fe_3O_4@SiO_2@HKUS-1	264	[221]
Fe_3O_4@$Cu_3(btc)_2$	348.4	[222]
In_2S_3@MIL-101	518.2	[211]

Imprinted polymers

Molecularly imprinted polymers (MIPs) synthesized through a series of polymerization reactions in which a complex is formed between a template and a monomer with functional groups that are specifically interactive with the template via covalent or noncovalent interactions, followed by a polymerization reaction between the complex and a cross-linking agent. Generally, a highly polar solvent (porogen) is used for removing the template resulting in MIPs having specific binding sites or pores [227]. Figure 8 shows the schematic diagram of an MIP synthesis and the structure of commonly used monomers and cross-linkers for MIPs are shown in Figures 9 and 10, respectively. For heavy metal removal, among many physical and chemical applied processes, MIPs are of cheap, stable, and satisfactorily selective way compared to other traditional techniques [230].

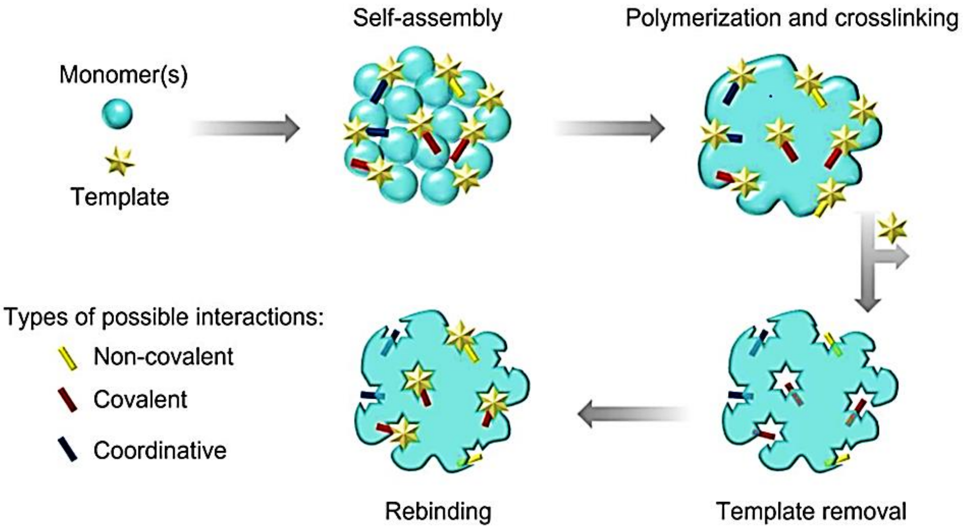
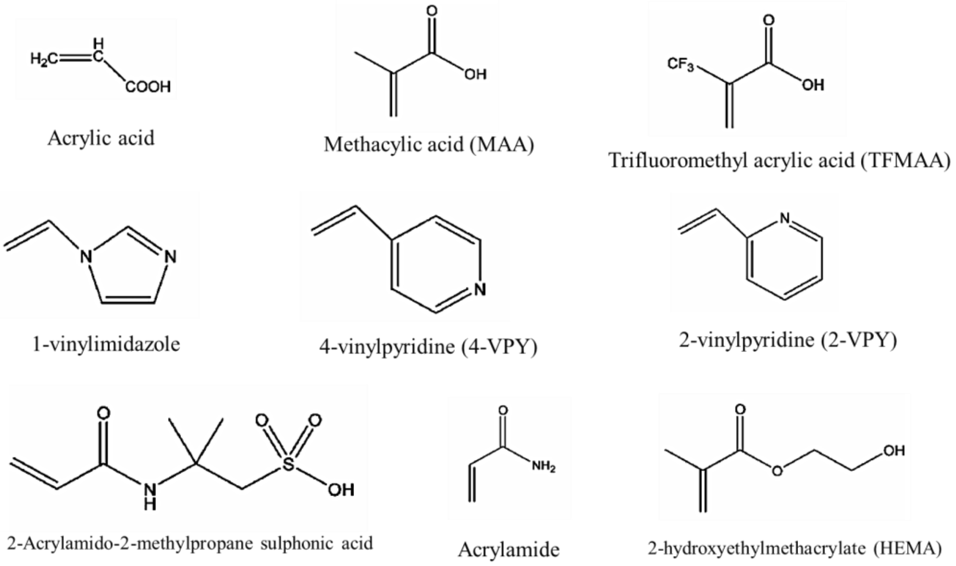


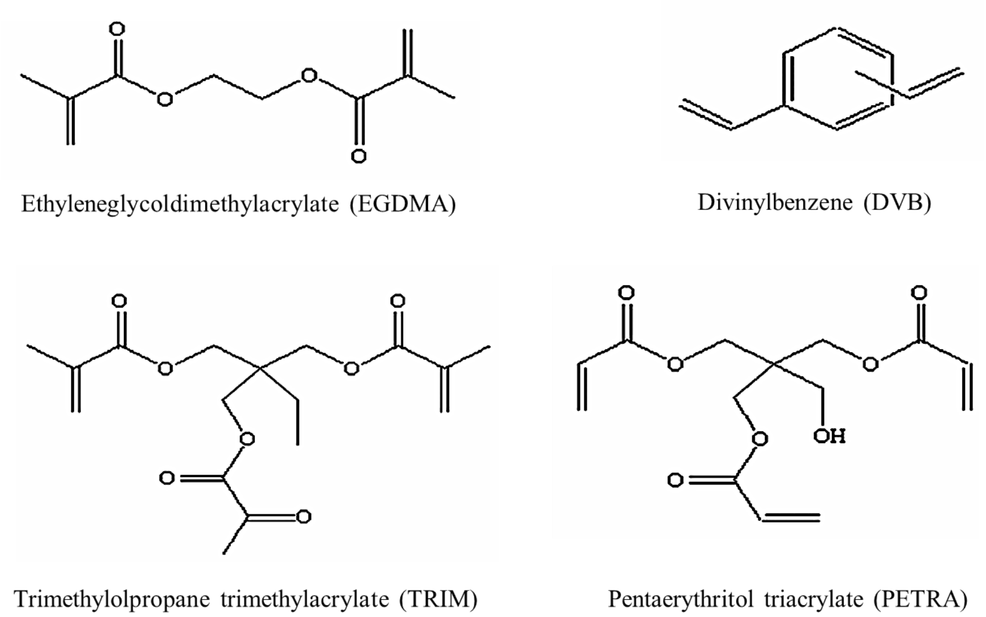
Figure 8. Schematic diagram of the MIPs synthesis [228].


Acrylic acid Methacylic acid (MAA) Trifluoromethyl acrylic acid (TFMAA)

1-vinylimidazole 4-vinylpyridine (4-VPY) 2-vinylpyridine (2-VPY)

2-Acrylamido-2-methylpropane sulphonic acid Acrylamide 2-hydroxyethylmethacrylate (HEMA)

Figure 9. Structure of some commonly used monomers for molecular imprinting [229].


Ethyleneglycoldimethylacrylate (EGDMA) Divinylbenzene (DVB)

Trimethylolpropane trimethylacrylate (TRIM) Pentaerythritol triacrylate (PETRA)

Figure 10. Structure of some commonly used cross-linkers for molecular imprinting [229].

Ion imprinted polymers (IIPs) are also simple for synthesis and have several advantages, such as high stability, selectivity towards target ions, etc. [231]. According to Fu *et al.* IIPs being good adsorbents, are useful for identifying, monitoring, and removing metal ions in aqueous and biological environments [232]. Figure 11 depicts the schematic synthesis and site recognition of IIPs in determination applications and adsorption materials against metal ion targets.

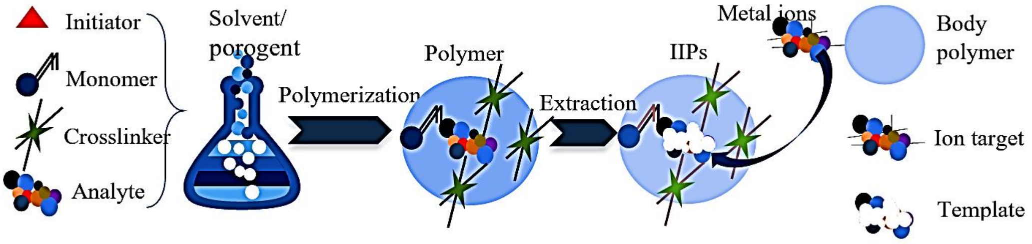


Figure 11. Schematic synthesis and site recognition of IIPs in determination applications and adsorption materials against metal ion targets [231].

Jiang, *et al.* synthesized Me-Hg IIMN from the complex ion of 1-pyrrolidinecarbodithioic acid and MeHg (PDC-CH_3Hg^+) as a template, methacrylic acid (MAA) as functional monomer and trimethylolpropane trimethacrylate (TMPTM) as cross-linker, which showed adsorption capacity of 25mg g^{-1} for Hg(II) ion [233]. Zhang, *et al.* prepared a novel magnetic ion-imprinted polymer (MIIP) with incorporated Fe_3O_4@SiO_2 nanoparticles via surface imprinting technique using allylthiourea (ATU) as a functional monomer, which showed an adsorption capacity 78.3 mg^{-1} for Hg(II) ion [234]. Soleimani, et al. made an IIP via SPE using 2-vinylpyridine, ethyleneglycol dimethacrylate and 2,2′-azobisisobutyronitrile as Hg^{2+} complexing reagent monomer, cross-linker and initiator, respectively, which had an adsorption capacity of 24.6 mg^{-1} for Hg(II) ion [235]. To remove Hg, radical polymerization was adopted by Djabal et al. He used complexes of Hg(II) ions with 3-mercaptopropyltrimethoxysilane ligands as a template, vinyl trimethoxysilane as a monomer, and ethylene glycol dimethacrylate as a crosslinker to prepare the Hg-IIPs which exhibited an adsorption capacity of 62.27 mg g^{-1} for Hg(II) ion [236]. Lim et al. fabricated MIPs by free radical polymerization method using Hg (II) nitrate dehydrate as a template and vinylcarbazole as the functional monomer, which had a maximum adsorption capacity of Hg (II) was 10.13mg g^{-1} [237]. Liu *et al.* synthesized Hg-IIps using Diazoaminobenzene (DAAB) and vinylpyridine (VP) as a monomer, 2,2′-azobisisobutryonitrile as initiator, and ethyleneglycoldimethacrylate (EGDMA) as cross linker, which has a maximum adsorption capacity 41mg g^{-1} for Hg(II) ion [238].

Zhu, *et al.* synthesized a two-dimensional montmorillonite-based surface ion-imprinted polymer (IIP-MMT) via activators generated by electron transfer for atom transfer radical polymerization (AGET-ATRP), which had high adsorption capacity of 201.84mg g^{-1} towards Pb (II) [239]. Zhang, *et al.* successfully constructed MIPs onto HMS, exhibiting a fast adsorption having 40.52 mg g^{-1} adsorption capacity with approximately 100% recovery of Pb (II) ions [240]. Ebrahimzadeh, *et al.* used 2-vinyl pyridine as the functional monomer, ethylene glycol dimethacrylate as the cross-linker and, 2,2-azobisisobutyronitrile as the initiator to synthesize Pb(II)-IIP by copolymerization technique then that was imprinted with Pb(II) as the template ion, 2-amino pyridine as the ligand. Subsequently, the imprinted Pb(II) was completely removed by leaching the dried and powdered imprinted polymer with HCl (2mol L^{-1}). The MIP synthesize by this process shows an adsorption capacity of 85.6 mg g^{-1} for Pb (II) ions [241]. Behbahani, *et al.* prepared Pb^{2+} ion-imprinted polymer (Pb^{2+}-IIP) nanoparticles, which were followed by precipitation polymerization of 4-vinylpyridine (the functional monomer), ethylene glycol dimethacrylate (the cross-linker), 2,2′-azobisisobutyronitrile (the initiator), 4-(2-pyridylazo) resorcinol (the lead-binding ligand), and Pb ions (the template ion) in acetonitrile solution. That (Pb^{2+}-IIP) nanoparticles showed an adsorption capacity of 9.8 mg g^{-1} for Pb (II) ions [242]. Huang, *et al.* used a solid phase extraction method to prepare Pb-ion IPs. He used 8-hydroxyquinoline grafted gelatin and chitosan as monomers, and genipin as cross linker. That Pb-IPs showed a high adsorption capacity of 235.7 mg g^{-1} towards Pb [243]. Mostafa et al. synthesized Pb-ion imprinted polymers (Pb(II)-IIP) using 4-vinylpyridine (VP), ethyleneglycoldimethacrylate (EDMA) and 2, 2-azobisisobutyronitrile (AIBN) as functional monomer, cross-linking agent and initiator, respectively by copolymerization of Pb(II)–morin complex. That Pb-IIP had an adsorption capacity of 39.0 mg g^{-1} towards Pb [244]. There are some other IPs had been synthesized for the removal of Pb (II) and Hg (II) are listed in Table 11.

Table 11. Application of some IPs for the removal of Pb and Hg

Metal ion	IPs	Constituents (Monomer/ Initiator/Template/ Modifier/ Ligand/ Crosslinker)	Adsorption capacity (mg g^{-1})	Ref.
Pb (II)	IIP-MMT	CMSHA/ IIP-MMT/	201.84	239
	MIP	MAA + 4-VP/ H-MIPs	40.52	240
	Pb^{2+}-IIPs	2-VP/ 2-2′-ABBN/ Pb^{2+}/ 2-AP/ EGDMA	85.6	241
	Pb^{2+}-IIP	4-VP/ 2-2′-ABBN/ Pb^{2+}/ EGDMA	9.8	242
	Pb^{2+}-IIP	8-HQL@ GL+CS/ GP	235.7	243
	Pb^{2+}-IIP	4-VP/ 2-2′-ABBN/ EGDMA	39.0	244
	Pb^{2+}-IPs	CS	22.7	245
	Pb^{2+}-IPs	DDDPA + 4-VP	116.9	246
	IIPs	4-VP/ 2-2′-ABBN/ PAN/ EGDMA	39.0	247
	$Fe_3O_4@SiO_2@$IIP	AAPTS/ Pb^{2+}/ TEOS	19.61	248
	PHEMAC-Pb^{2+}	MAC	2.01	249
	Pb^{2+}-IIP	4VB-18-C	27.95	250
	IIHC (PVICTMSPMA)	1-VI/ TEOS	7.6	251
Hg (II)	Me-Hg IIMN@ $Fe_3O_4@SiO_2$	MAA/ PDC-CH_3Hg^+/ TMPTM	25	233
	MIIP@$Fe_3O_4@SiO_2$ NPs	ATU	78.3	234
	IIP/Hg^{2+}	2-VP/ 2-2′-ABBN/ EGDMA	24.6	235
	Hg^{2+}-IIPs	VTMS/3-MPTOS/ EGDMA	62.27	236
	MIPs	VC/ MND	10.13	237
	Hg^{2+}-IIPs	DAAB+VP/ 2-2′-ABBN/ EGDMA	41	238
	Hg^{2+}-IIPs	TAR/ 2-2′-ABBN/ MAA/ EGDMA	25	252
	Hg^{2+}-IIPs	MAA/ 2-2′-ABBN / 2-MEA / EGDMA	28	253
	IIPs	MAA/ 2-2′-ABBN/ TAAN/ TMPTM	6.4	254
	Hg^{2+}- ITFSG	3-MPTOS	92	255

(**MAA**) methacrylic acid; **(PDC-CH_3Hg^+)** 1-pyrrolidinecarbodithioic acid and MeHg; (**TMPTM**) trimethylolpropane trimethacrylate; (**MIIP**) magnetic ion-imprinted polymer; (**ATU**) allylthiourea; (**2-VP**) 2-vinylpyridine; (**2-2′-ABBN**) 2,2′-azobisisobutyronitrile; (**EGDMA**) ethyleneglycol dimethacrylate; (**3-MPTOS**) 3-mercaptopropyl trimethoxysilane; (**VTMS**) vinyl trimethoxysilane; (**MND**) mercury(II) nitrate dehydrate; (**DAAB**) Diazoaminobenzene; (**VP**) vinylpyridine; (**TAR**) 4-(2-thiazolylazo) resorcinol; (**TEOS**) tetraethoxysilane; (**2-MEA**) 2-mercaptoethylamine; (**TAAN**) 1-(2-Thiazolylazo)-2-naphthol; (**PAN**) 1-(2-pyridylazo)-2-naphthol; (**2-AP**) 2-amino pyridine; (**2-VP**) 2-vinyl pyridine; (**8-HQL**) 8-hydroxyquinoline; (**GL**) gelatin; (**CS**) chitosan; (**GP**) genipin; (**DDDPA**) 1,12-dodecanediol-O,O'-diphenyl-phosphonic acid; (**AAPTS**) AAPTS 3-(2-aminoethylamino) propyltrimethoxysilane; (**MAC**) N-methacryloyl-(L)-cysteine; (**4VB-18-C**) 4-vinylbenzo-18-crown-6; (**1-VI**) 1-Vinylimidazole; (**ITFSG**) imprinted thiol-functionalized silica gel; (**IIHC**) ion-imprinted hybrid copolymer; (**PVICTMSPMA**) poly(1-vinylimidazole)-co-(3-(trimethoxysilyl)propyl methacrylate, **(VC)** vinylcarbazole.

CONCLUSIONS

Water is a basic human need. It is a must for our survival. Industrialization makes the water polluted by throwing excessive effluents into it thereby polluting the other elements of the ecology. Being a common environmental issue, heavy metals draw the most attention of the researchers to remove them from the ecosystem. Among the heavy metals Pb and Hg have become a major environmental problem due to their persistence and accumulation in the food chain. To lower the level of Pb and Hg levels in drinking water, several methods were adopted by the researchers for water treatment. Among the methods nanoparticles cover the most attention for their unique characteristics for the removal of Pb and Hg from water through the adsorption process. This review provides various synthesis methods for nanoparticles synthesis with their application and advantages. This review also highlights the adsorption performance of different nanoparticles such as carbon based nanoparticles, inorganic nanoparticles, MOF, and imprinted polymers.

It is evident from the discussed research that the interaction between adsorbent nanoparticles and the ions of Pb and Hg is complicated and can involve chemisorption, electrostatic interaction, surface complexation, *etc*. The effectiveness of Pb and Hg removal is greatly influenced by these interactions. As the field progresses, challenges persist in realizing the full-scale application of different nanoparticles for water purification. Factors such as nanoparticle aggregation, potential toxicity, and cheap and easy synthesis routes need to be addressed to ensure the practical feasibility of this technology. For the removal of Pb and Hg from water, modern technologies are more effective than conventional technologies due to their large-scale production, application and, ease of handling. Among the modern technologies adsorption is the best for their effortlessness in application. As adsorbents- carbon-based nanoparticles, inorganic nanoparticles, MOF, and IPs were discussed for the removal of Pb and Hg from water. The potential of adsorbent nanoparticles as versatile and effective tools for the removal of Pb and Hg from water is undeniably promising. Their tunable properties and high adsorption capacities make them attractive candidates for mitigating water contamination, safeguarding both human health and ecosystems. Continued interdisciplinary research, collaboration between scientists, engineers, and environmental experts, and innovative technological developments are crucial to overcoming the existing challenges and understanding the transformative potential of nanoparticles in the field of wastewater remediation.

Future aspect

In the future, expect significant advancements in the implication of nanomaterials for Pb and Hg adsorptive removal from contaminated water, driven by innovations in nanomaterial design, surface modification, and green synthesis methods. Researchers will focus on scalability, real-world applications, safety, and regulatory frameworks. Integration with IoT and sensor technologies will enable efficient monitoring while addressing global water quality challenges will be a top priority.

CONFLICT OF INTERESTS

The authors declare that there are no conflicts of interest.

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