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Adsorption of heavy metal ions from wastewater: a critical review

Yared Daniel Reta[a,*], Temesgen Debelo Desissa[a,*], Yiene Molla Desalegn[b]

[a]*Department of Materials Science and Engineering, School of Mechanical, Chemical and Materials Engineering, Adama Science and Technology University, Ethiopia, P.O. Box: 1888, Adama, Ethiopia, Tel.: +251942187431; emails: yared.daniel@astu.edu.et (Y.D. Reta), temesgen.debelo@astu.edu.et (T.D. Desissa)*
[b]*Department of Mechanical Engineering, Woldia Institute of Technology, Woldia University, email: yiene21ayl@gmail.com (Y.M. Desalegn)*

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ABSTRACT

Processing and manufacturing industries produce wastes, such as heavy and toxic metals to the environment and water bodies. Removing of these species from different sources has never been easy and becoming a primary concern for environmental and societal health. Several techniques can be employed to eliminate or minimize the level of these heavy metals, including adsorption on adsorbent materials. The adsorption method is considered a highly efficient technique due to its cheap materials, operation cost, and easy and flexible design. This paper reviewed the adsorption process and related parameters affecting the process as well as different adsorbent materials such as carbon-based materials, clays, metal oxides, and clay-based nanocomposites for the potential removal of heavy and toxic metals from wastewater.

Keywords: Adsorbent material; Adsorption process; Heavy metals; Wastewater

1. Introduction

Water is the essential substance for human beings' survival, although its pollution by different pollutants or contaminants threatens the environment's and societies' health [1]. Processing industries are the primary sources of these pollutants [2], among which are toxic heavy metal ions, organic dyes, particulate matter, and so on. Heavy metal ions such as cadmium (Cd), lead (Pb), mercury (Hg), tin (Sn), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), chromium (Cr), cobalt (Co), arsenic (As), and nickel (Ni) can be released from different processing industries such as mineral mining, metallurgical plating, batteries, and fertilizer plants [3,4]. Among these different heavy and toxic metal ions Pb, Cd, Hg, and As are highly carcinogenic [5].

Heavy metal concentrations in sediments and suspended particles in water have increased dramatically as a result of their discharge into the environment, causing serious water pollution problems [6]. The presence of heavy metals in the aquatic environment has been linked to a variety of health issues in humans and animals [7]. Many heavy metals, especially when present in high amounts, are harmful to even the most resistant bacteria, algae, and fungi [8]. As a result, biological treatment would be impractical in many cases of severely contaminated industrial wastewater. Trace metal concentrations in groundwater near contaminated sources might also be high.

As shown in Fig. 1, several techniques eliminate or minimize the level of these heavy metals, such as ion exchange, chemical precipitation, electrolysis, membrane separation, solvent extraction, and adsorption. However, these methods are ineffective for removing low metal concentrations, which harm both the environment and human health [9]. Among these methods, adsorption is considered the most effective due to its easy operation, low cost, available adsorption materials, and high efficiency [10].

For the adsorption process, different adsorbent materials can be utilized. The adsorption materials include:

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* Corresponding authors.

carbon nanotubes (CNTs) [12–15], activated carbon [16–19], clay minerals with good adsorbing and ion exchangeability [3], porous nanomaterials [20,21] inorganic nanoparticles [22–24], metal oxides [25–28], and clay-based nanocomposites [29–31].

Clay materials have a low cost and are most abundant, so they are among the best adsorbent options. For the adsorption of heavy metals most commonly used clay minerals are montmorillonite, bentonite, and kaolinite [32]. In addition to clay minerals, metal oxides are one of the promising adsorbent materials to remove heavy metal ions. It is possible to use metal oxides separately or in composite form for adsorption. For example, zinc oxide (ZnO) is used to remove cadmium and chromium due to its stability [33,34]. Titanium dioxide (TiO_2) is an available, low cost, non-toxic material, so it is also preferable to adsorbent material. TiO_2 is used for adsorption to remove Cu, Cd, and As(III). The composite form of metal oxides like aluminum and magnesium-based composite is also effective for adsorption [34].

Recently nanomaterials are greatly recommended for heavy metal removal due to their outstanding properties [3,26]. Nanomaterials possess a high specific surface area resulting in enhanced reaction with many chemical species; therefore, nanomaterials exhibit excellent adsorption properties. Putting nanomaterials like nanostructured metal oxide into clay minerals to form nanocomposite for adsorbing purposes is currently of significant interest [35]. This enthusiasm is due to those nanocomposite materials having broad applicability and better properties than the other materials. This paper reviewed the effect, adsorptive potential, compositions, and outcomes of various adsorbents (carbon-based materials, biosorbents, clays, metal oxides, and clay-based nanocomposites) for removing heavy metals from water and wastewater, with a focus on recent papers. The primary purpose of this review is to offer detailed information about the natural or modified forms of these adsorbents and their superior adsorption capabilities for various hazardous heavy metals from aqueous solution and wastewater.

2. Adsorption process

Heavy metal pollution challenges demand appropriate approaches for heavy metal removal. Adsorption is an environmentally friendly solution to this problem. It has a lot of potential in wastewater treatment due to its ease of operation and availability, cost-effectiveness and easy handling [3]. However, the majority of these complex procedures may provide certain obstacles, such as high costs, inefficiency in low-concentration pollutants, massive time consumption, reagents, and energy usage, and the creation of chemical sewage sludge [36,37]. Adsorption is the deposition and adhesion of ions or molecule species onto a surface [38]. It is based on two fundamental parameters: the adsorbent and the adsorbate as exhibited in Fig. 2.

The reverse process is called desorption, in which the adsorbed species are separated from the adsorbent surface to the liquid phase [3]. The pH value, temperature, and concentration differences are very important in this process. In addition, the adsorbent uptake capacity depends on the adsorption properties, such as porosity, specific surface area, pore volume, cation exchange capacity, interaction time, and adsorbent dose [39].

If the solid and liquid are in contact for an extended period an equilibrium distribution is obtained, which can be expressed quantitatively. An isotherm is a type of equilibrium model that describes equilibrium behaviour by describing the amount of adsorbate adsorbed as a function of gases or liquids at a constant temperature [40]. adsorption isotherm models are fundamental for studying the adsorption process [41]. Adsorption isotherms serve as the foundation for defining substance adsorption. Currently, various equilibrium models, such as the Langmuir, Freundlich, Temkin, Sips, Hill, Radke–Prausnitz, and Flory–Huggins isotherms, are used to explain the adsorption process (Table 1). In contrast, the most commonly used model is Langmuir and Freundlich's adsorption isotherm [42]. According to the Langmuir model, the adsorbent surface for metal ion removal is homogeneous and flat, with no interaction between adsorbed molecules or ions. The Freundlich model, on the other hand, assumes that adsorption occurs on a heterogeneous surface. Each localized adsorption site has its bond energy, and the stronger binding sites are settled first until the adsorption process is completed [43].

2.1. Parameters affecting the adsorption process

2.1.1. Contact time

Various parameters influence the adsorption process; among those parameters, contact time has a significant effect on the adsorption [49]. As the contact time increases, the adsorption rate of clay minerals also increases; then, after reaching the equilibrium, the removal rate is constant. Physical and chemical properties can seriously affect the contact time for the adsorption of heavy metals in wastewater. Abukhadra et al. [39] studied the kaolinite nanotubes (KNTs) for adsorption of Zn(II), Cd(II), Pb(II), and Cr(VI). In their investigation, KNTs had a longer equilibrium time than other adsorbents, including kaolinite, single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs). For instance, the equilibration time of Cd(II) and Pb(II) adsorption was 360 min, suggesting that various kinds of functional groups require enough time for the adsorbed metal ions to be saturated.

Based on other parameters such as clay mineral composition, heavy metal type and pH of the system, complete removal of heavy metals could occur within 6 h [38]. These parameters are also responsible for an extended period water treatment. For instance, one research observed that heavy metal adsorption did occur in the first 21 d of the experiment, whereas after 111 d, 75% of heavy metals were removed [50]. This was caused by the inclusion of clay minerals, which resulted in a substantial decrease in the water-extractable and interchangeable types of heavy metals.

The high amount of active sites on the adsorbent and high concentration of heavy metals could improve the adsorption rate. However, as the time further increased, the adsorption rate is slowed due to the reduction of available active sites filled with heavy metal ions [3,38]. If the reaction is left to go on, the heavy metal cations begin to move from the outer to the inner sites of the clay minerals, resulting in a slower removal rate. Adsorption efficiency increases

Table 1
Equations for some common isotherm models

Isotherm model	Non-linear equation	Linear equation	Plot	References
Langmuir	$q_e = \frac{q_{\max} b C_e}{\left(1 + bC_e\right)}$	$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}}$	$\frac{C_e}{q_e}$ vs C_e	[44]
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \frac{1}{n}\ln C_e + \ln K_F$	$\ln q_e$ vs $\ln C_e$	[44]
Temkin	$q_e = \frac{RT}{b_T}\left[\ln\left(A_T C_e\right)\right]$	$q_e = \left(\frac{RT}{b_T}\right)\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e$	q_e vs $\ln C_e$	[45]
Sips	$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$	$\beta_S \ln C_e = -\ln\left(\frac{K_S}{q_e}\right) + \ln\left(a_S\right)$	$\log\left(\frac{K_S}{q_e}\right)$ vs $\ln C_e$	[46]
Hill	$q_e = \frac{q^S H C_e^n H}{K_D + C_e^n H}$	$\log\left(\frac{q_e}{q_S H - q_e}\right) = nH \log C_e - \log K_D$	$\log\left(\frac{q_e}{q_S H - q_e}\right)$ vs $\log C_e$	[47]
Radke–Prausnitz	$q_e = \frac{\left(a_R \mathrm{Pr}_e C_e^{\beta_R} R\right)}{a_{\mathrm{RP}} + r_R C_e^{\beta_R - 1}}$	–	–	[48]
Flory–Huggins	$\frac{\theta}{C_0} = K_{\mathrm{FH}} - \left(1 - \theta\right)^{n_{\mathrm{FH}}}$	$\log\left(\frac{\theta}{C_0}\right) = \log K_{\mathrm{FH}} - n_{\mathrm{FH}} \log\left(1 - \theta\right)$	$\log\left(\frac{\theta}{C_0}\right)$ vs $\log\left(1 - \theta\right)$	[46]

where q_e (mg/g) is the adsorption capacity at equilibrium time, $q_{\max}$ (mg/g) is the maximum adsorption capacity achieved by the adsorbent, b (L/mg) is the Langmuir adsorption constant, C_e (mg/L) is the equilibrium concentration, K_F is the Freundlich constant [(mg/g)(L/g)$^{1/n}$] which represents binding energy of the adsorbents, and n is the adsorption intensity.

for Cd(II) from 39.12% to 52.31%, for Cu(II) from 31.24% to 82.13%, for Ni(II) from 13.13% to 27.36% and Zn(II) is 10.26% to 40.74% as the contact time increases from 15 to 240 min [51]. The obtained result suggested that the uptake capacity is higher during the initial stage due to the availability of a many active sites on the adsorbent. At 45 min of stirring time, the maximum removal was obtained and after 180 min, no change in the adsorption efficiency due to the occupation of the active site by the metal ions.

The contact time for the adsorption process was less than that of polyaniline nanocomposite material's heavy metal adsorption process [34,52]. The rate of arsenic adsorption was quite high for the first 10 min, then slowed, and finally obtained equilibrium about 1 h of contact time. Polyaniline nanocomposite eliminated 76% of the arsenic at equilibrium. It was also observed that physical and chemical properties affect the contact time for heavy metals' adsorption present in the water.

2.1.2. pH of the solution

The pH value plays a crucial role in the adsorption process. The pH of a solution influences its surface charge, ionization potential, and metal ion distribution [53]. When the pH of a negatively charged adsorptive surface is reduced, the surface is neutralized by the H^+ ions that are present in high numbers, reducing the impediment to diffusion and enhancing the rate of adsorption [54]. Various researchers studied the effect of pH on adsorption capacity. Some of these studies are presented in this section. Previous investigations have revealed that the degree of adsorption decreases at low pH levels whereas increases at higher pH values [55]. Most metals adsorbed rise with increasing pH of a solution until specific point, and then decrease if pH is increased further [56]. The adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) in an aqueous solution on raw kaolinite clay was investigated [57]. The solution pH severely impacted the adsorption of metal ions onto kaolinite clay. As the pH of solutions increased, the adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) was also increased. For instance, 98% Pb(II) at a pH of 6.0, 98% Cu(II) at pH of 6.5 can be removed. These removal rates are explained is due to the surface of the kaolinite clay becoming more negatively charged and containing many active sites, which enhances the adsorption of the positively charged metal ions over an electrostatic force of attraction.

AjayKumar et al. [51] investigated heavy metal biosorption on activated sludge. They proposed that at low pH, metal uptake was reduced because cell walls are closely associated with H_3O^+, and metal ion access to cell walls would be restricted due to repulsive forces. Metal uptake increased with pH from 3–4, which could be attributed to ligands exposing their negative charge, increasing attraction sites to positively charged metal ions. Beyond this point, the authors did not find much more efficiency increase until pH 6. However, the formation of metal hydroxides with their respective metal ions dramatically increased the biosorption process's efficiency after pH 6. Rather than biosorption, this is due to metal precipitation as hydroxides, which is influenced by pH and ion concentration. At higher pH levels, metals were thought to accumulate inside cells or cell walls *via* a process known as combined sorption-micro precipitation [58].

Southichak et al. [59] investigated the biomass of reed consisting of leaves as a biosorbent for Cu(II), Cd(II), Ni(II), Pb(II), and Zn(II) removal from aqueous solutions. The effect of solution pH upon heavy metals removal by reed biomass treated with NaOH (RTN) and its relation to the electrical charge was studied. Initially, the pH for 12 h adsorption experiments was only 0.2. The maximum adsorption of Pb(II) was observed from pH 4, Cu(II) from pH 5, Ni(II) from pH 6, and Zn(II) and Cd(II) from pH 7. The %age of heavy metal removal by reed biosorbent at the optimum pH was over 80% for all heavy metals. At a pH higher than 8, the higher removal efficiency of heavy metal could be obtained due to the precipitation phenomenon. Nevertheless, the authors suggested that no heavy metal precipitation was observed in this study probably due to the low concentration of heavy metal used.

The conducting polymer, polypyrrole, polyaniline, coal fly ash, mixed metal oxide, titanium oxide, zinc oxide, and aluminum oxide have been utilized to remove heavy metals from wastewater in the pH range from 2 to 8 [34]. Based on the obtained result at high pH, a high adsorption rate of heavy metals was observed. The adsorption characteristic of carbon nanotubes is also affected by the concentration of metal concentrations and pH values. The polymeric materials observed the highest removal of metal ions from aqueous medium between pH 6 to 8 [60], and its value pH 4 may be for Cr(VI) at ambient temperature [61].

2.1.3. Temperature of the solution

Temperature plays a significant role in the adsorption of heavy metals. Generally, as the temperature increases, the rate of adsorbate diffusion across the external boundary layer also increases in the internal pores of the adsorbate particles due to liquid viscosity decreases [51]. In addition to that, it also affects the equilibrium capacity of the adsorbate depending on whether the process is exothermic or endothermic. Increasing temperature in the endothermic adsorption process enhances adsorption effectiveness by increasing the movement of molecules to the adsorbent's active sites [62]. Exothermic adsorption, on the other hand, exhibits a decrease in adsorption ability with rising temperature, which may be due to diminishing adsorptive interactions between adsorbed species and adsorbed sites [63].

The influence of temperature on heavy metal adsorption can be effectively studied through the use of adsorption isotherms. The equilibrium relationships between the adsorbent and the adsorbate are described by sorption isotherms, which depict the ratio between the quantity sorbed and that which remains in the solution at a fixed temperature [64]. By changing the temperature, it is possible to observe how the adsorption capacity of the adsorbent changes and how the concentration of heavy metals in the solution is affected [65]. The adsorption isotherm is very useful in providing information about adsorption mechanisms, surface properties, and the affinity of an adsorbent towards heavy metals ions. Furthermore, the analysis of the isotherm data using common isotherm models allows for a better understanding of the adsorption process [42].

The influence of temperature on the adsorption of Cd(II) by a highly stable covalent triazine-based framework was studied at 298, 303, 313, and 318 K [66]. The acquired results demonstrated that adsorption rises dramatically with increasing temperature, implying that it is endothermic. The increased mobility of metal ions through the adsorbent's external boundary layer results in easy passage of Cd(II) into the organized tiny pores of covalent organic frameworks, resulting in higher adsorption. The linear graphs of the Langmuir isotherm at varied temperatures (298–318 K) at pH 7 indicated a good fit to the adsorption data with high correlation coefficient values (R^2), confirming surface uniformity and mono-layer coverage during sorption.

Qiu et al. [67] investigated the relationship between the adsorption capacity and temperature for two different materials systems, that is, activated carbon and $CoFe_2O_4$ towards Cr(VI) removal. As a whole, it is seen that as the temperature increases the loading capacity for the same initial adsorbate concentration decreases. This result means that the desorption rate was more significant than the rate of adsorption, which implies that adsorption is an exothermic reaction. Mustapha et al. [68] studied raw and beneficiated kaolin to remove heavy metals (Cr(VI), Cd(II), and Zn(II)) from tannery wastewater was studied. They observed that, as temperature increases, the removal ability of kaolin was also increased; this showed that, the adsorptive property was also temperature-dependent. According to Karthikeyan et al. [69], the adsorption of Cr(VI) on activated carbon rises with temperature, indicating that the reaction of adsorption is endothermic character. Adsorption capacity may be increased due to chemical interactions among adsorbate molecules and adsorbent, the formation of novel adsorption sites or an increase in Cr(VI) intraparticle migration into adsorbent holes at elevated temperatures.

2.1.4. Dosage of adsorbent

Adsorbent dosage is a critical factor in controlling adsorption rates. There are no specific guidelines on the recommended dosage for efficient adsorption: however, it has been demonstrated that a small amount of adsorbent is sufficient to remove a reasonable concentration of heavy metals from contaminated media [34]. Adsorbent dosage on the biosorption of various metal ions increases removal efficiency as sludge mass increased due to an increase in binding sites [70]. After a certain point, sorption capacity remained constant or decreased with biomass concentration due to a screen effect between cells, resulting in a blockage of the active sites caused by increased biomass in the system. For example, the removal efficiency of Cd(II) increases from 37.61% to 61.11%, Cu(II) from 23.36% to 50.28%, Ni(II) from 12.04% to 27.54%, and Zn(II) from 9.2% to 36.28% as the mass increases from 0.5 to 3 g [51]. This difference in adsorption indicates that the adsorbent prefers Cd(II) over Cu(II), Ni(II), and Zn(II). The effect of adsorbent dosage was investigated by filling the column with 100, 75, and 50 mg melanin-impregnated activated carbon while keeping the other parameters constant [71]. As adsorbent loading in the column grew, so did the breakthrough point and time. As the amount of adsorbent grows, more active sites for metal ions to attach become available, and the metal ion solution can be in contact with the adsorbent for a longer period of time, enhancing the adsorption efficiency.

2.1.5. Specific surface area of the adsorbent

The adsorption rate directly depends on the surface area of the adsorbent: that is, the larger the surface area of the adsorbent, the high efficiency of adsorption [72]. A solid powder adsorbent's surface area depends on its particle size. Various nanostructured carbon-based materials such as CNTs, graphene, and carbon fibers, are well-known for their extraordinary adsorption properties [3]. Among these carbon materials, CNTs are one of the favorable materials as they have a specific surface area (SSA) of around 950 m^2/g. The effect of the SSA of biochar and the adsorption capacity against different heavy metals was investigated [73]. A direct relation was observed between surface area and adsorption capacity for chromium, zinc, and lead, whereas a positive correlation could not be observed for copper and cadmium. High adsorption capabilities observed at extremely small surface areas may reflect underlying processes that are similarly efficient in regulating adsorption. According to some studies [74–76], the adsorption capacity of biochar is determined by the exchange of ions instead of the physical features of the adsorbent.

3. Adsorbent materials

Various adsorbent materials for adsorption were studied by many researchers such as activated carbon, carbon nanotubes, biosorbents, clay minerals, metal oxides, and clay-based composites. This section reviews some of these materials and their performance in the adsorption of heavy metal ions.

3.1. Carbon-based materials

The high surface area and distinct chemical and physical properties of carbon-based materials, such as activated carbon, carbon nanotubes, and graphene oxide, are the main properties that lead those materials to be the most efficient adsorbents for the remediation of wastewater from different contaminates. Various studies have reported the applications of activated carbon, carbon nanotubes, and graphene oxide as effective adsorbents for removing organic and inorganic pollutants [51].

3.1.1. Activated carbon

Activated carbons (ACs) include various amorphous carbon-based materials with high specific surface area and porosity [77]. Activated carbon exhibits various important features such as high specific surface area, large pore volume, and various oxygen-containing functional groups on the surface, wide availability, high surface reactivity, and ability to modify its physical and chemical properties for synthesizing adsorbents with improved characteristics and so [78,79]. Due to these reasons, many researchers used this material as an efficient adsorbent material for the removing of heavy metals from wastewater.

Various researchers used raw and modified activated carbon to improve the adsorptive properties (Table 2). Karni et al. [80] studied the capacity of activated carbon and silica/activated carbon (2:3) composite to remove lead, cadmium, nickel, chromium, and zinc from water. Nickel showed the highest uptake capacity by activated carbon at all concentrations. Authors highlight that as heavy metal concentration increased, removal %age of removal decreased. Also, silica/activated carbon (2:3) composites were more efficient in removing nickel ions than the evaluated activated carbon.

The melanin-impregnated activated carbon as an adsorbent to remove heavy metals from the aqueous medium was studied by [71]. Maximum adsorption was obtained at pH 3 for Cr(VI) whereas pH 5 Hg(II), Pb(II), and Cu(II) showed high uptake capacity. The temperature was also showed a considerable effect on the removal efficiency, with the adsorption process for all metals showing maximum removal at 328 K. Adsorption rate increases with increasing temperature due to increased collision frequency of heavy metal ions with active sites. The adsorption of the four metals on melanin is an endothermic process because effective adsorption occurs at high temperatures. Melanin-impregnated activated carbon could adsorb 84.59% Hg(II), 86.6% Cr(VI), 91.1% Pb(II) and 93.8% Cu(II) from 5 mg/L heavy metal solution. Therefore, the authors recommend using activated carbon as an adsorbent after various physico-chemical treatment steps like coagulation/clarification, filtration, and dissolved air flotation [81].

Mdoe [77] modified porous activated surface by nanomodification. They used two commercial activated carbons (ACs) (AG-5 and NWC) as adsorbents. The adsorbents were modified with CNTs by chemical vapor deposition. The CNTs were synthesized by the sol–gel method. The obtained

Table 2
Applications of activated carbon for the removal of heavy metal ions

S/N	Raw materials	Activating agent	Type of metal(s) removed	Adsorption capacity (mg/g)	References
1	Tire-derived activated carbon (AC)	Potassium hydroxide	Lead(II)	322.5	[85]
2	Leather waste-derived AC	Nitrogen	Lead(II)	231.0	[86]
3	Sulfone-modified magnetic AC		Arsenic(III)	151.51	[18]
4	Lignocellulosic waste-derived AC	Potassium hydroxide	Chromium(VI)	113.63	[87]
5	Powdered activated carbon/magnetite nanoparticles	Green tea extract	Copper(II)	23.61	[88]
6	Activated carbon/$NiFe_2O_4$ magnetic composite		Zinc(II)	105.8	[89]
7	Honeydew peel-activated carbon	Nitric acid	Cr(III)	834.94	[90]

results showed that the nanomodification of ACs enhanced their equilibrium adsorption of heavy metals (Ni(II) and Co(II)) by 10%–30%.

Generally activated carbon is a high-cost adsorbent material due to its chemical and physical treatments used in its synthesis, its low yield, its production's high energy consumption, or the thermal treatments used for its regeneration and the losses generated meanwhile [82]. Consequently, low-cost and willingly available alternative lignocellulosic materials are in need, while methods of production are developed [83]. Furthermore, the AC's reusability is sometimes challenging to achieve due to the formation of strong bonding with heavy metals [84]. Hence, many researchers are still attempting to develop novel and better adsorbent materials that are feasible to use in many adsorption cycles.

3.1.2. Carbon nanotubes

CNTs are novel materials that consist of one or more graphene sheets wrapped around them to form a cylindrical shape with a length of more than 20 mm and a radius of fewer than 100 nm [12], often created in hexagonal structures. There are two types of carbon nanotube: MWCNTs, which contain more than one graphene sheet, while SWCNTs contains only one sheet.

In recent years, many researchers studied CNT and modified CNT as an efficient adsorbent to remove heavy metal ions from water with greater attention.

CNTs have outstanding chemical, physical and electrical properties. Due to that, they are utilized in various applications including medical science, environmental engineering, electrical engineering, and material science [12]. For example, in carbon nanotubes, the chemically active sites are located in defective segments like pentagons, which may give CNTs their outstanding ability to interact with other compounds. Also, functional groups are often added to these materials' surfaces to improve the efficiency of CNTs.

Ihsanullah et al. [91] studied the adsorption of Cr(VI) by raw and modified MWCNT. They modified the MWCNT surface with nitric acid [91]. The maximum removal efficiency of raw MWCNT and acid-modified MWCNT was 3.115 and 1.314 mg/g at pH 3.0, adsorbent dose 75 mg, and contact time was 240 min. This modification was seriously enhancing the active surface area of the raw MWCNT.

Ghasemi et al. used magnetized SWCNTs functionalized by polydopamine (SWCNTs/Fe_3O_4@PDA) to remove of mercury ions from an aqueous solution. The adsorption study proved that the maximum adsorbents' uptake efficiency of SWCNTs/Fe_3O_4@PDA predicted by Langmuir model was 249.07 mg/g, which was higher than the maximum adsorbent uptake efficiency of thiol-derivatized SWCNTs, which was 131 mg/g [92].

Aliyu studied the practicability of Zn(II) adsorption by CNTs from aqueous solutions [93]. CNTs were synthesized by using the chemical vapor deposition (CVD) technique. The obtained result suggested that the maximum removal efficiency was 99.50% for Zn(II) ions at adsorbent dosage 50 mg, pH 6.0, contact time 60 min and contact speed 125 rpm.

Furthermore, the results showed that CNTs are efficient adsorbent materials for Zn(II) ion removal compared to gold standards (example: commercial activated carbons). Ihsanullah et al. [94] used activated CNTs to remove Cd(II) from water. The obtained maximum adsorption capacity was 2.02 mg/g at 1 mg/L of solution. Chen et al. [95] studied the adsorption performance of MWCNTs in various functional groups. They suggested that functionalization with oxygen-containing groups enhanced the adsorption capacity of the MWCNTs to remove Hg(II). CNTs have excellent adsorption properties, but they have also exhibited some drawbacks resulting from CNTs interactive forces that arise between the carbonic nanostructures, which can lead to aggregation, that manipulated dispersion is so tricky. Besides, CNTs have a high cost, and unresolved environmental effect requires a controlled process along with sorbent restoration and recycling [96]. Some application of CNTs for the removal of heavy metal ions are summarized in Table 3.

3.1.3. Graphene oxide

Graphene oxide (GO) is a carbon family material. These are single-layer graphene nano-plastics connected by oxygen-containing functional groups. This material can be synthesized by various methods, such as chemical oxidation or graphite exfoliation [104]. GO has many excellent properties, such as high specific surface area, high electrical conductivity, and thermal conductivity [105]. It also contains functional groups such as epoxy, hydroxyl, carbonyl, and carboxyl groups, these oxygen groups on the surface of GO ensure the surface's hydrophilicity and negative charge density, which is very useful for removing contaminants [106]. In the past, functionalized graphene was used to remove heavy metal ions [29], like lead and cadmium ions [107].

Table 3
Applications of carbon nanotubes for the removal of heavy metal ions

S/N	Raw materials	Activating agent	Type of metal(s) removed	Adsorption capacity (mg/g)	References
1	Graphene/MWCNTs	Polydopamine	Lead(II)	350.87	[97]
2	MWCNTs	Polymer	Nickel(II)	230.78	[98]
3	CNT	Acid	Cadmium(II)	2.02	[94]
4	Magnetic MWCNTs	Polymer	Chromium(VI)	56.1	[99]
5	SWCNT	Thiol	Mercury(II)	131.58	[100]
6	MWCNTs	Chitosan and acrylic acid	Nickel(II)	19.86 m	[101]
7	CNT	Dithiocarbamate	Cadmium(II)	167.2	[102]
8	CNT	Oxidized	Lead(II)	342.36	[103]

The adsorption affinity of GO for many metal ions is very high and varies with the type of heavy metal ions. The authors highlight the affinity of GO with heavy metals follow the sequence Pb(II) ≥ Cu(II) ≥ Cd(II) ≥ Zn(II) [108]. It is essential to observe that this sequence agrees with the metal's electronegativity and the first stability constant of the corresponding metal hydroxide [109].

The attraction of heavy metal ions to the negatively charged GO surface is stronger. In addition, the formation of complexes between heavy metal substances and surface oxygen functional groups (such as –OH and –COOH) is also a possible adsorption mechanism, as the constant stability of GO determines the morphology of heavy metal particles. Therefore, the method mentioned above can be a suitable choice for modifying other absorbents (such as montmorillonite) [110].

Adsorption is propelled by the electrostatic attraction between positively charged heavy metal ions and negatively charged GO sheets. One mechanism for adsorption is the ion exchange reaction between heavy metal ions and protons on –COOH or –OH oxygenous functional groups. In the adsorption process, the proton on –COOH or –OH was released into the solution, resulting in a lower equilibrium solution pH than the initial value [111,112]. Surface complexation of heavy metal ions with surface oxygenous functional groups has been shown to play a dominant role in Pb(II) adsorption on GO [113]. The oxygenous functional groups primarily complexed Pb(II) at the edges of GO sheets, and Pb(II) bridged different GO sheets by simultaneously bonding the hydroxyl or carboxyl groups at the edges [114]. Because of its dispersibility, nano-sized GO is difficult to separate from water using conventional separation methods. Therefore, the authors propose incorporating magnetic nanoparticles into GO and its derivatives to easily separate solids from liquids under external magnetic fields [107,115].

3.2. Biosorbents

The use of biosorbents for the removal of heavy metals from wastewater has gained significant attention in recent years. Researchers have recognized the effectiveness of biosorbents in removing heavy metals from wastewater, making them a promising alternative to conventional methods [116]. Additionally, the use of biosorbents offers several advantages such as high efficiency, minimization of secondary waste, and low cost. Various biomasses, either dry or wet, are used to remove heavy metals from wastewater [117]. Biosorbents can be chemically modified to improve their biosorption characteristics and durability. Surface and internal modification are the two broad categories of chemical modification. The primary goal of surface modification is to remove contaminants from the cell surface and to enhance the heavy metal binding site on the biological cell's surface [118]. Internal biological cell modification includes changes in the internal structure or composition of living organisms, such as protein expression and enzyme activity.

Different researchers suggested various lignocellulosic industrial and agricultural wastes can reduce the cost of production and the environmental effects of agricultural and industrial wastewater. Hernández-Montoya et al. [119] used lignocellulosic materials through carbonization activation to prepare activated carbon. During the carbonization, thermal decomposition of raw materials and removal of non-carbon species occurred and produced a fixed carbon mass with a rudimentary pore structure. In this step, tiny and closed pores are created. In contrast, activation aims to enlarge the diameters of the tiny pores and create new pores.

The sorption properties of biochar produced from *Enteromorpha prolifera* and magnetically manipulated were investigated. The authors observed that the pH and ion strength of the background solution had a substantial effect on Cr(VI) adsorption [120]. Furthermore, the *Enteromorpha prolifera* charcoal could be retrieved magnetically and regenerated with an alkaline solution. As a result, this magnetic biochar has the potential to be effective adsorbent for water contamination reduction. Kumarathilaka et al. [121] investigated the capacity of nano zerovalent iron-graphene composite (nZVI-Gn) to eliminate Cr(VI). The results showed that the nZVI-Gn composite had a remarkable removal efficiency under acidic environments. The kinetic analysis revealed that pseudo-second-order may demonstrate the adsorption characteristics of nZVI-Gn composite, implying that the rate-limiting component could be a chemisorption process. The Langmuir isotherm model showed an improved correlation of the experimental equilibrium data, implying that sorption of Cr(II) onto nZVI-Gn composite might be a single-layer process. As a result, the prepared nZVI-Gn composites are regarded as an effective and magnetically detachable adsorbent for the removal of Cr(VI) from the environment.

Manfrin et al. [122] produced activated carbon and biochar from cigarette waste for the removal of lead(II). Tobacco biomass was used for producing two types of adsorbents namely, CT biochar (thermal activation) and CT $ZnCl_2 + CO_2$ (chemical, thermal, and physical activation). Because of their enormous surface area, high porosity, and internal structure, these materials are effective adsorbents for a wide range of pollutants, including lead ions. Pseudo-second-order and Langmuir adjustments yielded the best results. It was discovered that Pb(II) adsorption occurs in monolayers and is primarily chemical. Both chemical and physical forces impact the adsorption process, with the initial adsorption being largely chemical and the following adsorption potentially involving physical forces. The time required to reach equilibrium for lead removal varies based on the substance employed, although it can be as little as 45 min. Overall, the combination of biochar and activated carbon produced from tobacco waste represents a viable and cost-effective method for decontaminating lead-contaminated water supplies.

Schwantes et al. [123] developed environmentally friendly biosorbents from cassava solid waste to remove Cd(II), Pb(II), and Cr total from aqueous solutions. Cassava solid wastes, such as cassava root husks and cassava sludge-based activated carbon, are used as biosorbents due to their high adsorption ability for heavy metals. In low concentrations of metals, the greater adsorption capabilities were determined to be 94.9% at pH 7.0, utilizing 16 g/L of adsorbent. Metal removal reaches equilibrium within 5–10 min of contact time, with pseudo-second-order optimal modifications to the observed events. The Freundlich model best fits the metal adsorption by a cassava adsorbent. Based on the findings, the authors concluded that biosorbents are capable of effectively removing heavy metals from water, hence helping to the remediation of contaminated water sources. This environmentally friendly technology provides a cost-effective and efficient method for treating heavy metal-contaminated water.

Cassava peel was also utilized as an adsorbent material to remove metal ions from contaminated water [124]. Cassava peel is chemically treated using H_2O_2, H_2SO_4, and NaOH to remove metal ions Cd(II), Pb(II), and Cr(III) from contaminated water. The modifications changed the chemical composition and surface charge of the adsorbents, enhancing their adsorptive capacity for Cd(II), Pb(II), and Cr(III) relative to the unmodified cassava peels. The Langmuir model was found to be the best fit for the adsorption isotherms, with values such as 19.5 mg·Cd(II)/g of M. NaOH, 42.4 mg·Pb(II)/g of M NaOH, and 43.9 mg·Cr(III)/g of M H_2O_2, indicating monolayer adsorption of Cd(II), Pb(II), and Cr(III). The modified cassava peels also demonstrated high Cd(II) and Pb(II) desorption percentages, showing their potential for metal recovery. As a result, the findings revealed that using modified cassava peels as adsorbents is a realistic and low-cost option for metal removal from industrial effluent.

3.2. Clay minerals for adsorption

Clays are layers of aluminosilicates composed of mixtures of fine-grained clay minerals, crystals of other minerals, and metal oxides [9]. Clays have various physical properties such as plasticity, shrinkage under fire and air drying, fineness of grain, color after firing, hardness, and cohesion. Physical properties depend on different parameters that control the behavioral pattern of the material. Porosity, saturation, pore fluid conductivity, water content, and clay content are important for electrical conductivity. The sedimentation of clay depends on porosity, water content, and mineral contents of different specific gravity [125]. To enhance the adsorption properties like specific surface area, surface functional group, pore volume and size, and cation exchange capacity, many researchers have used modified clay minerals by treating them with various chemicals [3]. Kaolinite, montmorillonite, and bentonite are commonly used clay minerals due to their high specific area, availability, stability and structural characteristics, and nontoxicity [3,68]. This section contains commonly used clay minerals (kaolinite, montmorillonite, and bentonite) for heavy metal removals in their raw and modified forms. Here common clay minerals used in the raw and modified form for the removal of heavy metal pollutants with their results are reviewed by focusing on the most recent research.

3.2.1. Kaolinite

Kaolinite is clay mainly formed by the kaolinization process by decomposing potassium feldspars, granite, and aluminum silicates [126]. It has white or greyish-white color. The melting point of kaolinite clay is about 1,750°C. Kaolinite crystal system is triclinic which has space group P1, in addition lattice parameters are a = 0.515 nm, b = 0.895 nm, c = 0,740 nm, α = 91.68°, β = 104.87°, γ = 89.9°. Its crystal-chemical formula is $Al_4Si_4O_{10}(OH)_8$. Its molecular formula is $Al_2Si_2O_5(OH)_4$, which contains 39.8% alumina, 46.3% silica, and 13.9% water representing a two-layer crystal (silicon-oxygen tetrahedral layer joined to alumina octahedral layer exists alternately).

Several researchers have investigated the uptake capacity of various heavy metal ions from water solutions using raw and modified kaolinite. Jiang et al. [57] calculated the adsorption of Pb(II) ions onto natural kaolinite clay from water kaolinite. The adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) in an aqueous solution on raw kaolinite clay was studied using a variety of physicochemical parameters (varying metal ion concentration, clay amount, pH, and mixing time). On the other hand, the pH of the solution significantly affected the adsorption of metal ions onto kaolinite clay. Adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) increased as solution pH increased; for example, 98% of Pb(II) can be removed at pH 6.0, and 98% Cu(II) can be removed at pH 6.5. These results are due to the kaolinite clay's surface becoming more negatively charged and containing many active sites, which increases the adsorption of positively charged metal ions over the electrostatic force of attraction [127]. Kaolinite clay was used to remove metal ions from wastewater, such as Pb(II), and its composition was reduced from 160.0 to 8.0 mg/L.

Mustapha et al. [68] used raw and beneficiated kaolin to remove heavy metals (sulfate, chromium, cadmium, and zinc) from tannery wastewater. The beneficiated kaolin sample was used to remove the unwanted mineral to improve the adsorption capacity of raw kaolin. The beneficiation process was done by the wet/soaking method. The beneficiated kaolin showed a reduction of Fe % and the existence of K in the raw kaolin. These results suggested that there is a tendency for cations exchange between exchangeable cations in the kaolin samples and metal ions in solution, enhancing the adsorption and removal capacity of the metal ion by the kaolinite samples. Furthermore, as temperature increases the removal ability of kaolin was also increased; this shows that adsorptive properties were also temperature-dependent. From these results, we understand that beneficiated kaolin is an effective and low-cost adsorbent to remove contaminants from tannery wastewater.

Abukhadra et al. [39] synthesized the kaolinite nanotubes (KNTs) from the raw kaolinite by the method of ultrasonic scrolling for adsorption of Zn(II), Cd(II), Pb(II), and Cr(VI). This conversion enhanced the pore volume and surface area compared to the raw kaolinite. By using these KNTs for Cd(II), Zn(II), Cr(VI), and Pb(II), they obtained removal capacities of 116, 103, 91, and 89 mg/g, respectively. These values are higher than various kaolinite and CNTs-based adsorbents. In this study, KNTs exhibit longer equilibrium time; for instance, the equilibration time of Cd(II) and Pb(II) adsorption was 360 min, suggesting that the various types of functional groups need enough time with the adsorbed metal ions to be saturated, and also there is an existence of high adsorption sites on the surface of KNTs. Recyclability of these KNTs is also possible. It can be used about five times for the removal of heavy metal ions; however, the removal % is decreased in new absorption cycles. So, modification of kaolinite sheets into KNTs could provide outstanding adsorption properties. This paper also suggested that the adsorption ability of KNTs than that of CNTs consequently, KNTs with different modifications could provide better adsorption properties and be used practically for tap, ground, and sewage water from several contaminants.

Chen et al. [128] investigated the adsorption properties of composite by the additive of graphene oxide onto a kaolin-based geopolymer. Geopolymers are inorganic polymers that can synthesize by the chemical reaction between an alkaline solution and aluminosilicate minerals (kaolin in this case). They synthesized graphene oxide by Hummer's method. First, they modified the raw kaolin into metakaolin (MK) by heating the kaolin at 750°C for 3 h. Then, they produced the composite precursor *via* the geo-polymerization process. The impact of adding grapheme oxide (0–10 wt.%) to the geopolymer on the adsorptive properties was also investigated. From the adsorption study, adding graphene oxide enhanced the uptake capacity, that is, 65% at 10 wt.% of GO for Cr(VI) after adsorption equilibrium was achieved. These excellent results are due to the high surface area and several oxygen functional groups like hydroxyl and carboxyl groups of graphene oxide. Consequently, the GP-GO composite has the capability for wastewater remediation applications.

3.2.2. Montmorillonite

Montmorillonites (smectite) consist of an octahedral alumina sheet between two rival tetrahedral silica sheets, which have a 2:1 layer structure. Some of the oxygen exists on both tetrahedral sheets as well as an octahedral sheet. In addition, it has weak bonding between two tetrahedral sheets. Therefore, water and exchangeable ions easily enter between sheets, which is the main reason for the evolution of swelling capacity. Bentonite montmorillonite's crystalline structures and other additional crystalline structures like quartz, volcanic glass, feldspar, organic matter, and gypsum [129]. Montmorillonite is the main component of bentonite (70%–95%). In tetrahedral substitution of cations occurred. When exchangeable interlayer cations [Na(I), Ca(II), and Mg(II)] are introduced layer charge is compensated [130]. As a result, active sites will be provided on the crystal's inner and outer surface. These individualities of montmorillonite structure indicate particular properties of bentonite clays, mainly high adsorption ability towards heavy metals.

Montmorillonite clay is used for adsorption by various researchers in raw or modified form. This section tries to review some papers related to this area by focusing on the most recent findings. Adsorption of arsenate and arsenite from aqueous solutions using Ti-pillared montmorillonite (Ti-MMT) was studied [131] by varying such parameters as contact time, pH, and temperature. The removal capacities of these Ti-MMT for As(III) and As(V) were 14.72 and 12.503 mg/g, respectively. These findings suggested that Ti-pillared montmorillonite is an effective adsorbent material for the removal of these heavy metal ions.

Ghorbanzadeh et al. [132] also investigated the removal of arsenate and arsenite by adsorption on montmorillonite in streams. They obtained adsorption rates of 99.5% for arsenate and 68.2% for arsenite. Based on that they stated that this clay mineral is an efficient adsorbent for heavy metals. Furthermore, montmorillonite clay can be utilized as an efficient adsorbent to adsorb La and Yb species was investigated by Alshameri et al. [133]. Mu'azu et al. [134] studied the effect of montmorillonite with different content in a natural clay mineral on the sorption properties for the removal of Cu(II) and Ni(II) from water. To investigate this, they used various physiochemical parameters such as contact time, the mass of the adsorbent, pH, and initial metal concentration. The composition of clay was mainly kaolinite and muscovite with a small amount of quartz, whereas the bentonite contained a high amount of montmorillonite with a surface area of 20.83 and 44.27 m^2/g, respectively. As the content of montmorillonite content increased in the clay the uptake capacity for Ni(II) adsorption was increased. In contrast, the montmorillonite increase resulted in decreased for Cu(II) removal. Montmorillonite content also showed a series effect on the equilibrium time. As the montmorillonite content increased, the time required to reach equilibrium also increased, but with a higher period for natural clay than bentonite. The optimum uptake capacity for Cu(II) and Ni(II) was 16.38 and 8.66 mg/g, respectively. The results indicated that using various mineralogical components in clay adsorbents could influence the sorption of heavy metal ions from water and the composition of montmorillonite content control the removal of various metal ions from the aqueous solution.

3.2.3. Bentonite

Various researchers have already studied bentonite clay in its raw and modified form. Here some papers regarding this clay are revised in detail. Kurnosov et al. [144] produced modified bentonite clay by MWCNTs to obtain efficient adsorption material. This composite material was produced by immersing the raw clay with a catalyst solution and heat treatment. The MWCNTs were synthesized by chemical vapor deposition (CVD) under pilot production conditions. The removal capacity of the modified nano-adsorbent was studied in comparison with the raw bentonite. The nanocomposite presented reduced time to reach equilibrium than natural bentonite, that is, the nano-adsorbent is saturated within 100–300 min, while in the case of the raw adsorbent, saturated time was 400–1,200 min. This result suggested that modification of the structure of the bentonite clay with the MWCNTs could enhance the uptake capacity and reduce the required time to reach equilibrium during the adsorption of heavy metals. The uptake capacity of modified bentonite showed a 1.5–1.8-fold increase, and a 4-fold increase was exhibited in the absorption rate. The authors compared the degree of heavy metal removal for the synthesized composite, obtaining the following heavy metal ions sequence: $Cu^{2+} > Cr^{3+} > Zn^{2+}$. Thus, modification of the bentonite aluminosilicate structure by MWCNT highly enhanced the efficiency of the liquid-phase adsorption of pollutants like heavy metals, and significantly reduced the adsorbent equilibrium time.

Kakaei et al. [145] investigated bentonite clay modified with imidazole (Ben@S-Im) for the remove Co, Cu, and Pb in the wastewater. They have also studied the effect of contact time, pH, initial heavy metal ions concentration, and kinetics. Finally, the authors investigated the raw bentonite clay modified by imidazole for the uptake of heavy metals from wastewater and later, utilization of removed metal as a catalyst in the A^3 coupling reaction for the first time. For Co(II), Cu(II), and Pb(II), the removal efficiency of 20 mg Ben@S-Im was 84%, 87%, and 90%, respectively. The removal efficiency was greater than 100% when the authors used 200 mg of Ben@S-Im. The results showed that the Ben@S-Im has a high potential for use in industrial wastewater. From the kinetics study, the modified bentonite by imidazole showed higher uptake capacity and adsorption efficiency than the raw bentonite and modified bentonite by imidazolium. Furthermore, is indicated that at pH 5 the highest amount of metal was adsorbed. The results showed that the modified bentonite by imidazoline has a high potential for use in industrial wastewater.

Pawar et al. [146] studied the uptake of toxic heavy metal ions, that is, Cu^{2+} and Pb^{2+} by fabricating activated bentonite-alginate (ABn-AG) composite beads. ABn-AG was produced by the ionic gelation method. At higher acidic conditions, 58% of Cu^{2+} and 77% of Pb^{2+} were detached at pH 2. The optimum sorption capacity for Cu^{2+} and Pb^{2+} was about 17.3 and 107.52 mg/g, respectively. Due to the presence of various sites in ABn-AG composite adsorption of both Cu^{2+} and Pb^{2+} was made possible. The removal efficiency of Cu^{2+} and Pb^{2+} was decreased only by 10% during the reusability test; these suggested that reusing of ABn-AG is practicable with a negligible decrease in uptake ability. After using these composite beads for the application of adsorption, separation and recovery were also possible by varying some physicochemical parameters. Consequently, their investigation indicated that ABn-AG composite beads could be employed as an effective and economical adsorbent for the uptake of Cu^{2+} and Pb^{2+} from wastewater. Table 4 Summarized some application of clay-based materials for the removal of heavy metal ions.

3.3. *Metal oxides for adsorption*

Metal oxides are crystalline solids that contain metal cation and an oxide anion. Different types of metal oxide exist, such as binary metal oxides (MB), mixed metal oxides, and spinel structured metal oxides and spinel structured (MB_2O_4 type) oxides.

3.3.1. *Binary metal oxides*

Metal oxides that consist of at least one transition metal ion and one or more electrochemically active/inactive ions are called binary metal oxides such as zinc oxide, titanium

Table 4
Application of clay-based materials for the removal of heavy metal ions

S/N	Raw materials	Modifying agent	Type of metal(s) removed	Adsorption capacity (mg/g)	References
1	Kaolinite nanotubes (KNTs)		Zinc(II)	103	[135]
			Cadmium(II)	116	
			Lead(II)	89	
			Chromium(VI)	91	
2	Kaolinite	Hydrochloric acid	Chromium(VI)	18.15	[136]
			Iron(III)	39.80	
		Acetic acid	Chromium(VI)	10.42	
			Iron(III)	19.34	
3	Kaolinite	Zirconium oxychloride	Iron(III)	9.7	[137]
			Cobalt(II)	9.6	
			Nickel(II)	8.8	
4	Kaolinite	Raw	Cadmium(II)	14.11	[138]
		Manganese oxide	Cadmium(II)	36.47	
5	Kaolinite	Raw	Lead(II)	16.16	[139]
		Sodium tetraborate	Lead(II)	42.92	
		Raw	Cadmium(II)	10.75	
		Sodium tetraborate	Cadmium(II)	44.05	
6	Montmorillonite	Zirconium oxychloride	Iron(III)	23.8	[137]
			Cobalt(II)	22.8	
			Nickel(II)	22.0	
7	Montmorillonite	Raw	Lead(II)	89.08	[140]
		Histidine	Lead(II)	23.93	
		Raw	Copper(II)	107.73	
		Histidine	Copper(II)	30.72	
8	Montmorillonite	Tourmaline	Lead(II)	303.21	[141]
9	Bentonite	Benzylhexadecyldimethyl ammonium chloride	Copper(II)	50.76	[142]
			Zinc(II)	35.21	
10	Bentonite	Organophilic	Lead(II)	22	[143]
			Cadmium(II)	2.8	

oxide, and iron oxide. These oxides can be used as adsorbent materials due to their excellent properties. This section reviews the commonly used binary metal oxides, zinc oxide, and titanium dioxide for the adsorption of heavy metals.

3.3.1.1. Zinc oxide

Zinc oxide is highly stable and non-toxic, considered an efficient adsorbent to remove heavy metal ions from water [34]. Ghiloufi et al. [26] investigated Ga-doped ZnO nanoparticles (GZO) with different Ga contents by using a modified sol–gel process for adsorption of Cd(II) and Cr(VI) from an aqueous solution. They suggested that doping Ga in zinc oxide enhanced the uptake capacity of nano-adsorbent, and GZO with 1 wt.% of Ga has improved the adsorption properties of the rest of the Ga-doped samples to uptake the heavy metals from aqueous solution.

For example, the adsorptive capacity of Cr(VI) by ZnO was 140 mg/g and increased to 220 mg/g when ZnO was doped with 1 wt.% Ga. From the obtained result they concluded that GZO is the novel and more effective nano-adsorbent material for the removal of heavy metals from aqueous solution.

As(III) adsorption using ZnO nanoparticles was studied by Yuvaraja et al. [33] for the first time by varying some physio-chemical parameters like pH, adsorbent dose, contact time, and temperature. As a result, they obtained the optimum As(III) removal capacity of ZnO nanorods was 52.63 mg/g at pH 7, adsorbent dose 0.4 g, contact time 105 min, and temperature 323 K.

Le et al. [155] investigated the removal mechanisms of heavy metal ions by using the ZnO particles solid precipitation method was used to synthesize ZnO particles. Although they obtained high uptake efficiency (>85%) of heavy metal ions such as Cu(II), Ag(I), and Pb(II) ions by these particles, poor removal efficiency, that is, <15%, was noticed for Cr(VI), Mn(II), Cd(II) and Ni(II) ions. The removal of these heavy metal ions was in the form of metals or metal oxide *via* an adsorption mechanism. However, even though utilizing of ZnO nanoparticles (NPs) for adsorption can enhance the adsorption properties, this particle also exhibits its limitations such as low surface area, rapid agglomeration, and small particle size, which makes recyclability from the aqueous phase very difficult. In addition, releasing ZnO NPs into the environment could cause a series of health and environmental problems. Consequently, to afford this kind of problem, preserving of ZnO NPs on an appropriate matrix is mandatory to overcome these problems [156].

3.3.1.2. Titanium dioxide

Titanium dioxide naturally occurs in different crystallographic forms, that is, anatase, rutile, and brookite. It also has excellent properties like nontoxicity in nature, high resistance to corrosion, chemical stability, and high affinity to metal ions dyes, and other substances. Therefore, it is applicable for water treatment and removal of various contaminates [157]. Several authors used TiO_2-based composite materials for the adsorption of heavy metals like Ni^+, Cu^{2+}, Cd^{2+}, and Pb^{2+}.

Mahdavi et al. [158] studied the removal of Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solutions using TiO_2 nanoparticle sorbent with various experimental approaches. The maximum removal for the summation of four metals with multiple component solutions were 594.9, 114.6, and 49.4 mg/g, for MgO, Al_2O_3, and TiO_2, respectively. The main sorption mechanism for heavy metals was attributable to heavy metal sorption by TiO_2 adsorbent was due to adsorption. Therefore, this nanoparticle can be used as an effective adsorbent for heavy metal removal from aqueous solutions.

Maleki et al. [159] investigated the removal of heavy metals Pb^{2+} from industrial wastewater using TiO_2 nanoparticles modified with poly-amidoamine dendrimer. The effects of several parameters including initial metal ion concentration, temperature, pH solution, the nanohybrid dosage, and contact time were studied. After 60 min, Pb^{2+} ion adsorption on PAMAM dendrimers revealed 99.9% removal effectiveness. The results showed that the nanohybrid is an efficient absorbent for heavy metals from industrial wastes. Furthermore, nanoparticles (NPs) such as TiO_2 NPs have high adsorption capacity due to their large surface area, so using of these materials has excellent attention for many researchers in the adsorption of heavy metal ions.

The utilization of TiO_2 has shown great attention due to its essential features, such as low-cost, environmentally friendly, and sustainable treatment to remove heavy metal ions from water. However, in contrast, it also exhibits some drawbacks including low adsorption capacity for hydrophobic contaminants, uniform distribution in aqueous suspension, and recyclability of the TiO_2 particles after water treatment [160]. Therefore, doping, that is, doping of carbon-based nanoparticle, and various modification such as, surface organic modification, stabilization by support structures, and magnetic separation, are needed to improve the adsorption properties of TiO_2-based adsorbents. Some application of metal oxides for elimination of heavy metal ions are summarized in Table 5.

3.3.2. Spinel ferrites structured (MF_2O_4 type) oxide

Spinel ferrites with the MFe_2O_4 formula (M = Fe(II), Mn(II), Co(II), Zn(II), etc.) are a group of metal magnetic nanoparticles. These materials are widely used as efficient adsorbent materials to remove heavy metal ions due to their magnetic features and easy separation [1].

Many researchers focused on spinel ferrites due to their outstanding properties. Some of the research are presented in this section. The removal of zinc from an aqueous medium was investigated using $MnFe_2O_4$ and $CoFe_2O_4$ spinel ferrites nanoparticles. $MnFe_2O_4$ and $CoFe_2O_4$ spinel ferrites were synthesized by the co-precipitation method. The effects of initial pH, contact time, metal ion concentration, and temperature on Zn(II) adsorption were also studied. The maximum adsorption capacity was 454.5 and 384.6 mg/g for $MnFe_2O_4$ and $CoFe_2O_4$ at pH 6, respectively. Also, adsorbents' reusability and desorption capability were investigated [1].

The adsorption capacity of different MFe_2O_4 (M = Mn, Fe, Co, Ni) ferrite nanocrystals was compared. The nanoparticles were synthesized by the hydrothermal method. They suggested that the distribution of MFe_2O_4 cations of ferrites is essential for adsorption capacity. The ferromagnetic behavior of MFe_2O_4 nanoparticles allowed the high-efficient magnetic separation from wastewater. Based results, $CoFe_2O_4$ nanocrystals exhibit a higher saturation magnetization of 86.1 emu/g and outstanding adsorption capacity. The obtained result showed the maximum adsorption capacity of $CoFe_2O_4$ for CR is 244.5 mg/g.

Santhosh et al. synthesized magnetic cobalt and nickel ferrites ($CoFe_2O_4$ and $NiFe_2O_4$) with graphene nanocomposites ($CoFe_2O_4$-G and $NiFe_2O_4$-G) *via* a solvothermal process [107]. The composite was used as an adsorbent to remove lead and cadmium ions from an aqueous solution. The effect of various parameters like contact time, adsorbent dose, solution pH, and temperature was studied. As a result, the maximum adsorption equilibrium for the Pb(II) was about 142 and 111 mg/g at a pH of 5 for $CoFe_2O_4$-G and $NiFe_2O_4$-G, respectively. Whereas for Cd(II), it was about 105 and 74 mg/g at a pH of 7. Based on the obtained result, they suggested that this material can be used for efficient adsorption.

Vazquez-Olmos et al. [161] investigated the adsorption of Pb(II) from an aqueous solution by using MFe_2O_4 nanoparticles (M = Co, Ni, and Zn). Nanoferrite samples were prepared *via* the mechanochemical method used to prepare nanoferrites. At room temperature, $NiFe_2O_4$ and $ZnFe_2O_4$

Table 5
Application of some metal oxide materials for the removal of heavy metal ions

S/N	Raw materials	Modifying agent	Type of metal(s) removed	Adsorption capacity (mg/g)	References
1	ZnO	PAN/GO	Chromium(VI)	690	[147]
2	ZnO NPs		Chromium(III)	88.54	[148]
3	ZnO nanoflowers		Cadmium(II)	71.5	[149]
			Lead(II)	115	
4	Cu/ZnO		Lead(II)	1,111.0	[150]
5	Mesoporous TiO_2	Sodium	Zinc(II)	93	[151]
			Strontium(II)	208.4	
			Barium(II)	274.6	
6	Titanate/TiO_2	Lignin	Lead(II)	677.6	[152]
			Copper(II)	258.2	
			Cadmium(II)	308.5	
7	TiO_2	Carbon	Lead(II)	331.7	[153]
8	TiO_2	Hydroxide ethyl aniline	Lead(II)	26.05	[154]

Table 6
Application of spinel ferrite-based materials for the removal of heavy metal ions

S/N	Raw materials	Modifying agent	Type of metal(s) removed	Adsorption capacity (mg/g)	References
1	$MnFe_2O_4$		Zinc(VI)	454.5	[1]
	$CoFe_2O_4$		Zinc(VI)	384.6	
2	$CoFe_2O_4$		Lead(III)	326.79	[165]
	Fe_2O_3			140.84	
	Co_3O_4			284.90	
3	$CoFe_2O_4$	Chitosan	Cadmium(II)	71.53	[166]
			Lead(II)	151.06	
4	Bentonite/$CoFe_2O_4$	MnO_2	Cadmium(II)	115.79	[167]
5	$CoFe_2O_4$	Cetyltrimethylammonium bromide	Lead(II)	32.11	[168]
6	$MnFe_2O_4$	Chitosan	Copper(II)	22.6	[169]
			Chromium(III)	15.4	
7	TEPA-GO/$MnFe_2O_4$	Carbon	Lead(II)	263.2	[61]
8	Neem leaves/$MnFe_2O_4$	Corynebacterium glutamicum	Arsenic(III)	343.54	[170]
			Arsenic(V)	550.67	
9	$ZnFe_2O_4$	NH_2-SiO_2	Lead(II)	267.2	[171]
10	Ce^{3+}-doped $ZnFe_2O_4$		Chromium(VI)	57.24	[172]
11	Bentonite/$CoFe_2O_4$/hydroxyapatite		Lead(II)	67.1	[173]
12	$MnFe_2O_4$		Chromium(III)	39.6	[174]
			Chromium(VI)	34.84	

samples showed superparamagnetic behavior. Table 6 shows some applications of MFe_2O_4 for the adsorption of heavy metal ions.

3.3.3. Mixed metal oxides

Various metal oxide compositions represented higher adsorption capacity of heavy metals in comparison to individual metal oxides such as MgAl–, CuAl–, and CuO–ZnO [34]. Liu et al. [162] used magnesium and aluminum-based composite material for the adsorption process of binary heavy metals ions Cu^{2+} and Cr(VI). The results showed that from this composite, they obtained 0.80 and 2.90 mmol/g uptake capacities in single Cu^{2+} (1.6 mmol/L) and Cr(VI) (4.0 mmol/L) systems, respectively.

Sharma et al. produced copper oxide/zinc oxide-tetrapods (CuO/ZnO-T) nanocomposite for wastewater treatment [163]. The synthesized CuO/ZnO-T nanocomposite exhibited high total pore volume, (0.021 cm^3/g) and a large surface area (802 m^2/g). The CuO/ZnO-T nanocomposite showed a high adsorption capacity (99% chromium(VI) removal and 97% lead(II) removal) in comparison to pristine ZnO-T. This study suggested that CuO/ZnO-T nanocomposite is an effective adsorbent for the removal of various wastewater contaminants.

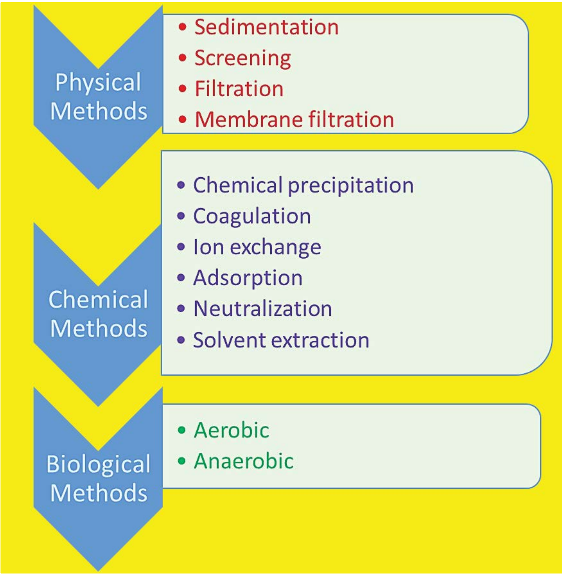

Fig. 1. Conventional technology for heavy metal removal [11].

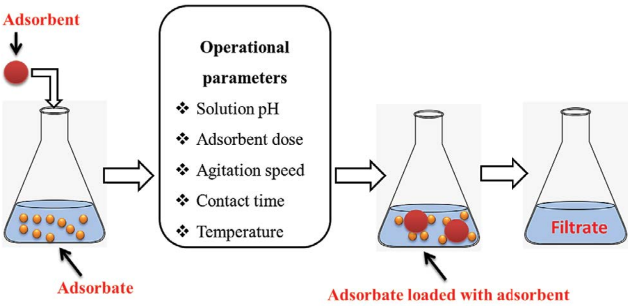

Fig. 2. Schematic of adsorption process.

Novel micro-nano FeOx- and MnOx-modified bone biochars were studied for the removal of Cd(II), Cu(II), and Pb(II) from aqueous solutions [164]. This material was derived from a waste bone meal and applied to remove heavy metals. Based on the results, the pyrolysis temperature greatly influences the specific surface area (SSA), micropore creation, and heavy metal sorption capacities of FO-BCs, and MO-BCs. The maximum sorption capacities were Cd(II) (151.3 and 163.4 mg/g), Cu(II) (219.8 and 259.0 mg/g) and Pb(II) (271.9 and 407.2 mg/g), respectively. Other composites of metal oxides like Mg–Al, Ti–Fe, Fe–Ni, and ferric oxides were investigated to utilize them as an efficient adsorbent to remove heavy metal ions [34].

3.4. Clay-based nanocomposites for adsorption

Nanocomposites are created by the nanoscale dispersion of nanoparticles in matrix-like clay. Clay-based nanocomposites have several advantages, including high ion sorption capacity, high specific surface area, low cost, and chemical stability. Several researchers focused on clay-based nanocomposites to remove various heavy metals from water and discovered that adsorption efficiency is influenced by several parameters such as adsorbent dosage, pH, temperature, and initial concentration among others [175].

Hydroxyapatite-bentonite clay nanocellulose (CHA-BENT-NCC) composite material was synthesized as an efficient adsorbent for the removal of Ni^{2+}, Cd^{2+}, and $(PO_4)^{-3}$ from aqueous solutions [176]. The effect of pH, contact time, temperature, and initial adsorbate concentration were studied to improve the removal capacity. The maximum adsorption capacity for Ni^{2+}, Cd^{2+}, and PO_4^{3-} was estimated to be 29.46, 10.34, and 4.90 mmol/g, respectively. Five adsorption–desorption cycles were performed without a significant decrease in adsorption capacities. The obtained result suggested that CHA-BENT-NCC material is a very effective adsorption material for the treatment of mining water.

Chitosan-clay nanocomposite was studied to remove Cd(II) and Cr(III). The obtained maximum sorption capacity was 72.31 and 0.25 mg/g, respectively. Bentonite-nZVI nanocomposite has also used an adsorbent for Cr(VI) removal, obtaining a maximum uptake ability of 296 mg/g. Various researchers also used acid-immobilized-amine modified polyacrylamide-bentonite (HA-Am-PAA-B) as an adsorbent for Cu(II) removal. From those results, the maximum removal efficiency was 106.2 mg/g. This capacity was obtained by changing the pH value from 6.2 to 5. The HA-AmPAA-bentonite nanocomposite was also used as an adsorbent for Zn(II) and Co(II) and the maximum removal capacity was 96.1 and 52.9 mg/g, respectively [3].

The pH of a given solution can highly influence the adsorption process and capacity. It controls many important aspects such as the surface layer charge of the clay and the exchange capacity. Generally, the removal of heavy metals by the clay and clay-based nanocomposites initially increases with pH, followed by a reduction until a certain point, such as a cutoff value of pH. The adsorption process is also temperature-dependent. Temperature can control the adsorption capacity of heavy metals onto clays and their nanocomposites.

4. Conclusion

In the present review, we have studied various adsorbent materials such as raw and modified clay, raw and modified carbon-based materials, biosorbents, nanocomposites, binary metal oxides, mixed metal oxides, spinel ferrites, etc. have been used separately or in composite form as suitable materials for the elimination of heavy metals pollutants from water and wastewater. Furthermore, the effect of parameters such as contact time, pH of the solution, adsorbent dosage, temperature, and surface area of adsorbent on the adsorption process have also been summarized. In most of the studied cases, the removal rate is high in the first moments of contact time but decreases gradually until reaching equilibrium. Therefore, indicating that the ions occupy the active sites on the adsorbent surfaces after some times. Low and higher pH values are unsuitable for adsorption, favoring H^+ competition, complexation, and precipitation processes. In contrast, maximum adsorption can be obtained at a moderate pH value (pH 4–6). A specific dosage of efficient adsorption is unavailable (for example, adsorbent dosages ranging from 50 mg to 3 g were utilized in this investigation), but in general, a small dosage of adsorbent can be sufficient to adsorb a reasonable concentration of heavy metals. Temperature has a considerable impact on the adsorption process as well. The rate of adsorption reduces with increasing temperature in an exothermic adsorption process, but an endothermic adsorption process leads to greater adsorption capacity at high temperatures. Adsorption is a very victorious and easy physicochemical method to eliminate heavy metal ions from wastewater.

5. Prospects

Various adsorbent materials such as raw and modified clay, raw and modified carbon-based materials, biosorbents, clay minerals, nanocomposites, binary metal oxides, mixed metal oxides, and spinel ferrite metal oxides, among others, have been used separately or in composite form as functional materials for the uptake of heavy metals pollutants from wastewater. However, they also exhibit various drawbacks like high cost, reusability, and agglomeration; due to these problems, several researchers have expected to produce highly efficient water treatment adsorbent materials to enhance the active surface area, pore-volume, cation exchange capacity, etc. We would like to propose a bio-inspired clay/spinel ferrite metal oxide material that may produce a highly efficient adsorbent material. Spinel ferrite metal oxides have magnetic properties due to that separation and reusability are possible. Bio-inspired materials can be extracted from locally available plants, and these materials support the spinel ferrite metal oxide by protecting it from aggregation. So synthesis of these materials may expect a highly efficient adsorbent material.

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