RSC Advances

REVIEW

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Cite this: *RSC Adv.*, 2024, **14**, 11284

Comprehensive assessment of carbon-, biomaterial- and inorganic-based adsorbents for the removal of the most hazardous heavy metal ions from wastewater

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Received 7th February 2024
Accepted 21st March 2024

DOI: 10.1039/d4ra00976b

rsc.li/rsc-advances

Owing to the high cost of recycling waste, underdeveloped countries discharge industrial, agricultural, and anthropogenic effluents without pretreatment. As a result, pollutant-loaded waste enters water bodies. Among the diverse toxic contaminants, heavy metal ions are the most detrimental because of their chronic toxicity, non-degradability, prevalence, and bioaccumulation. The growing shortage of water resources demands the removal of heavy metal ions from wastewater. Three SDGs of the sustainability agenda of the United Nations appeal for clean water to protect life beneath water and on land depending on the water sources. Therefore, efficient environmentally friendly approaches for wastewater treatment are urgently required. In this regard, several methods have been developed for the removal of heavy metal ions from wastewater, including adsorption as the most widely used method owing to its eco-friendly, cost-effective, and sustainable nature. The present review discusses the progress in the preparation and application of various adsorbents based on carbon, micro-organisms, agricultural waste and inorganic materials for the extraction of toxic metal ions such as Pb^{2+}, Cr^{6+}, As^{3+}, As^{5+}, Hg^{2+} and Cd^{2+}. Herein, we provide information on the role of the homogeneity and heterogeneity of adsorbents, kinetics of the adsorption of an adsorbate on the surface of an adsorbent, insights into adsorption reaction pathways, the mechanism of the sorption process, and the uptake of solutes from solution. The present review will be useful for researchers working on environmental protection and clean environment.

1. Introduction

The pervasive presence of toxic heavy metals in different ecosystems poses environmental challenges, which needs to be promptly addressed to safeguard both human health and ecological balance. It is a public obligation to develop methods for treating wastewater to protect water dwelling species and human life. Heavy metal ion water contamination is one of the most serious environmental issues. It is the result of inappropriate, unregulated industrial wastewater and agricultural and irrigation drainage schemes that dump sewage directly into water bodies. This irresponsible approach of waste disposal has led to the concentrations of water pollutants exceeding the recommended safety limit. For example, the steel sector releases lead ions. Lead is also released into the environment from acid batteries, the combustion of leaded gasoline, the illegal use of tetraethyl lead as an anti-knock agent in gasoline, volcanic eruptions and natural weathering of rocks.[1] Cadmium enters the environment through mining activities, coal combustion and excessive use of chemical fertilizers.[2] The eruption of volcanoes and weathering of rocks are natural sources introducing heavy metals into the environment. Anthropogenic sources include industrial waste, combustion, mining, casting, and the use of pesticides and fertilizers. Water contamination has serious consequences on marine life, public health, and food quality. Accordingly, if proper pretreatment approaches are not adopted, then the scarcity of clean water and toxicity of seafood will become a global challenge in the near future.

The advent of industrialization and urbanization is significantly beneficial to the society, but together with its numerous advantages, it also poses serious problems.[3,4] Toxic metal ions not only contaminate the water present in seas, lakes, ponds and reservoirs but also reach the underground water. Heavy metals can be absorbed by living organisms due to their high solubility in the aquatic environment. Consequently, heavy metals enter the food chain, posing a serious threat to the ecological balance. Even minor exposure to heavy metals can lead to dermatological problems and respiratory diseases. Furthermore, when the uptake of these metals exceeds the

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permissible limits, they cause serious health disorders.[5–7] Hence it is crucial to monitor and regulate heavy metal exposure to safeguard human well-being. The World Health Organization (WHO) and US Environmental Protection Agency (US EPA) have set permissible limits for heavy metals in drinking water. These guidelines are crucial for ensuring the safety of communities by minimizing exposure to harmful substances. Numerous elements fall into the category of heavy metals but in this review, we focus on the top five toxic metals including mercury, cadmium, lead, arsenic and chromium and understanding their impact, which is crucial for effective management and mitigation strategies.

Cadmium is present in the Earth's crust, but anthropogenic activities such as electroplating, mining, stabilizing plastics, alloy, cement, pigment, and battery manufacturing, fossil fuel combustion, use of high-phosphate fertilizers, and municipal and sewage sludge incineration yield a huge amount of cadmium. Specifically, 150–2600 tons of cadmium is released into the environment annually.[8] Similarly, due to the volatile nature of mercury, it is mostly used in batteries, thermometers, barometers, and dental amalgams. Mercury can exist in three forms, *i.e.*, elemental form (Hg), organic form (CH_3Hg), and inorganic form (Hg^{2+}). It was reported by the United Nations Environment Program (UNEP) that in 2015, around 2200 tons of mercury was emitted from anthropogenic sources, which included the iron and steel industry, gold industry, and direct mercury production industries. Forest fires and volcanos are natural sources of mercury.[9,10] Arsenic is a naturally occurring metalloid having a germicidal nature and resistance to decay. Due to this property, it is used as an insecticide, herbicide, and also the preservation of wood.[11] Similar to mercury, chromium also exists in three thermodynamic stable forms Cr(0), Cr(III), and Cr(VI). The metallic form of chromium is chiefly used in iron-based alloys. The chemical industry, production of dyes, wood preservation, leather tanning, chrome plating, and manufacturing of various alloys utilize chromium, and then discharge it without processing, leading to environmental pollution.[12] Lead is widely applied in various industries such as production of acid batteries, production of lead additives for gasoline, ceramic and glass manufacturing, metal planting and finishing, printing, and tanning.[13,14] This is the first report presenting the sources of metal-based water contaminants, their toxicity mechanisms and methods for their efficient removal by recoverable adsorbents to avoid any chances secondary pollution. The current review presents remediation technology based on environmental-friendly protocols and is expected to advance renewable and sustainable water treatment strategies. This review is expected to play a critical role in the implementation of solutions for controlling pollution levels, which is necessary to protect human health and ensure the quality standards of aquatic environment.

2. Harmful effects of heavy metal ions

Various routes facilitate the entry of heavy metals into the human body including dermal exposure, inhalation and ingestion *via* contaminated food or drinking water. Overall, the effects of heavy metal ions on different parts of human body are shown in Fig. 1.[15] Once inside the body, these metals can react with chlorine or oxygen and exert toxic effects. Prolonged exposure to heavy metals may result in their substitution for vital elements within the body such as calcium substituting lead, zinc replacing cadmium and the majority of trace elements substituting aluminum. The accumulation of heavy metals causes an imbalance in antioxidants. Enzymatic function and hormonal activity are also influenced by exposure to heavy metals. Studies have reported that oxidative stress is produced due to the generation of reactive oxygen species irrespective of which molecular pathway is undertaken. Oxidative stress leads to kidney damage, cancer, neurological disorders and abnormalities related to the endocrine system.[16] Besides the various benefits of heavy metals in plants and humans, these heavy metals are also responsible for the malfunctioning of cells by displacing the original metals from their natural binding sites in proteins, which ultimately leads to toxicity. The binding of heavy metals to the nuclear protein and DNA is the prime reason for the oxidative deterioration of biological macromolecules.[17]

Cadmium (30 mg kg^{-1}) has been reported to cause acute toxicity, which primarily includes abdominal discomfort, headaches, muscle cramps, fatigue, and even death. However, its dangerous effect on various organs in the body such as the lungs, liver, placenta, and endocrine tissues, kidney damage, skeletal and cardiovascular dysfunctions, and reproductive problems at higher concentration has also been reported. Cadmium replaces calcium in minerals due to their comparable ionic radius and chemical behavior, consequently reducing the uptake of Ca and affecting the bones.[8] Cd also affects the biological activity of terrestrial and aquatic organisms. In plants, cadmium causes chlorosis and stunted growth. Moreover, it not only decreases the chlorophyll content and photosynthetic activity but also inhibits carbon fixation in plants. Osmotic stress in plants is also induced due to exposure to Cd in soil. This results in a decrease in the relative water content in leaves, stomatal conductance, and transpiration. Damage to plant membranes and destruction of cell biomolecules and organelles are consequences of the overproduction of reactive oxygen species (ROS) induced by the presence of cadmium.[18] The oxidative stress may be attributed to an imbalance in the production of ROS and the ability of plants to detoxify them.

Mercury can exist in three forms, *i.e.*, elemental form (Hg), organic form (CH_3Hg), and inorganic form (Hg^{2+}). Elemental mercury in vapor form can easily be absorbed by the lungs and causes damage to the body. Among the three different forms of mercury, the organic form (CH_3Hg) causes neurological alterations in humans due to the increase in reactive oxygen species. Reactive oxygen species are also responsible for injuries in the central nervous system (CNS). The organization of microtubules, which is important in CNS development, is also inhibited by methylmercury. Inorganic mercury mainly causes cardiotoxicity.[9,10] Heavy metals also affect the biological activity of terrestrial and aquatic organisms. For instance, Cd and Hg cause chlorosis and shunted growth in plants. The fixation of carbon is also inhibited due to presence of Cd, together with

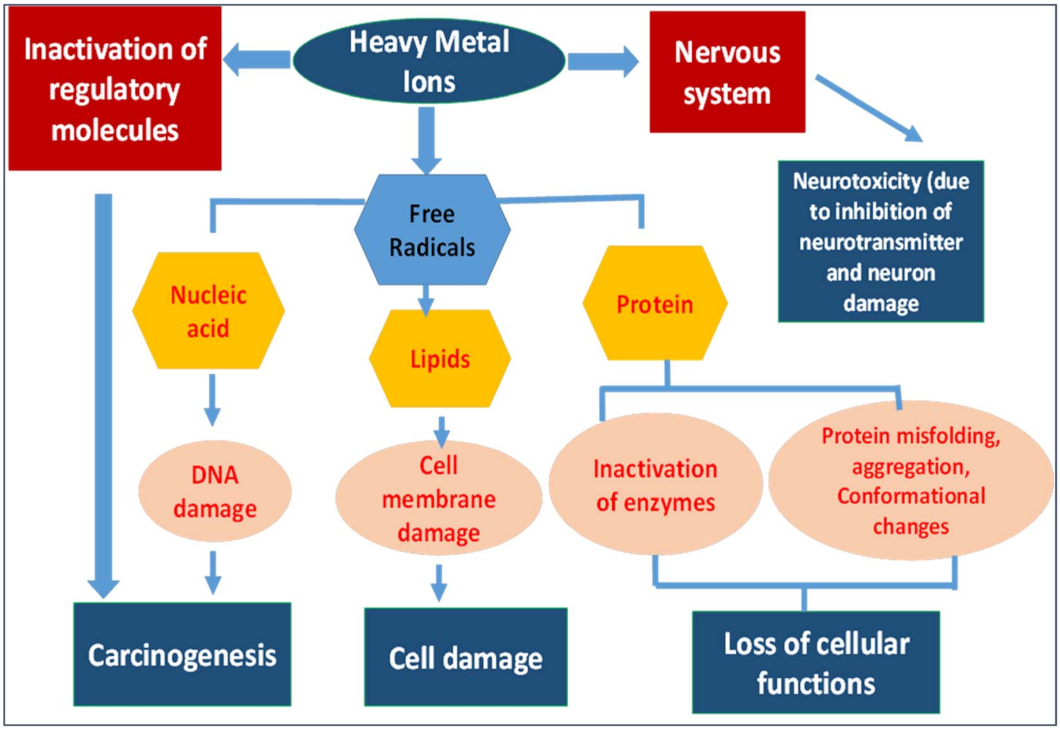


Fig. 1 Harmful effects of heavy metal ions on human beings.[15]

a decrease in chlorophyll content and photosynthetic activity. Osmotic stress in plants is also induced due to exposure to Cd in soil. Damage to plant membranes, destruction of cell biomolecules and organelles is also reported due to the excessive generation of reactive oxygen species. Boston fern (*Nephrolepis exaltata*) and Indian mustard (*Brassica juncea*) after exposure to Hg show loss of cell shape, decrease in intercellular spaces, and vascular abnormality in their leaves. The amount of chlorophyll is also reduced because the biosynthesis of chlorophyll depends on the activity of NADPH, where protochlorophyllide oxidoreductase (POR) is inhibited by Hg stress.[19,20]

Arsenic has the ability to attach to small particles in the air and remain suspended in the air for prolonged periods. It can change its forms and interaction with oxygen or other molecules present in the air, water, or soil, as well as with soil bacteria. The toxicity of arsenic depends on its oxidation state. The toxicity of arsenic has been reported to follow the order of AsH_3 > As(III) > As(V) > organic As.[11] Arsenic is classified as a class 1 human carcinogen by The International Agency for Research on Cancer. Drinking water containing arsenic causes skin cancer and lung, bladder, liver, and kidney damage. Non-insulin-dependent diabetes mellitus is also caused by increased exposure to arsenic.[21] Peripheral neuropathy is the consequence of long-term exposure to inorganic arsenic. Changes in behaviors, confusion, disorientation, memory loss and cognitive impairment are other effects associated with arsenic.[22]

Chromium(VI) is carcinogenic and the most mobile form of chromium in the environment. The chemical form of this metal, its oxidation state, and the route of exposure determine the type of toxicity in humans. Cr^{6+} reacts spontaneously with intracellular reductants after entering the cell and generates Cr^{5+} or Cr^{4+}, free radicals, and Cr^{3+} eventually. The limited membrane permeability of Cr^{3+} causes it to be retained inside the cell and interact with DNA. Reactive oxygen species are generated after the one-electron redox reaction of Cr^{5+}, which react with DNA–protein multiplexes, triggering multiple possible apoptotic signaling pathways in various cell types. Also, Cr causes irritation and inflammation of the skin.[23]

Lead poisoning has common impacts, which include severe damage to the kidneys, liver, brain, reproductive system, and nervous system. Sterility, abortion, and neonatal death are caused by long-term exposure to lead. An elevated blood-lead level is the root cause of the rise in mortality and alteration of puberty in girls. In children, it is reported that exposure to lead causes impaired development, lower intelligent quotient, shortened attention span, hyperactivity and mental systolic blood pressure together with causing hearing impairment, intelligential impediments, and deterioration.[14,24]

When heavy metals enter the body through ingestion, upon reaching the stomach, they undergo conversion into their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, and Hg^{2+}) due to the presence of acid in the stomach. These stable oxidation states react with the biomolecules in the body and form stable bonds. One of the most common bonding groups is the thiol group. This interaction plays a crucial role in the bioavailability and toxicity of heavy metals within the body.

Heavy metals have been reported to replace hydrogen or the methyl group in enzymes or proteins and inhibit their normal functioning.[21] Heavy metal-bound enzymes are not utilized by the body. Consequently, these enzymes are inactivated and their persistence in the body causes various abnormalities and internal damage.[25,26] The aggregation of proteins is also caused by heavy metals.[25,26] Hence, to protect living organisms, it is imperative to find effective approaches for wastewater purification from lethal heavy metal ions. Herein, we present numerous adsorbents for addressing the challenges related to the removal of heavy metal ions, which are potential hazards for creatures living on land and in water bodies.

3. Techniques for the removal of heavy metals

To mitigate the effects of heavy metals, various methods have been employed for their removal. The methods used for the removal of contaminants include biological treatment, coagulation membrane, filtration, electrochemical treatment, electrodialysis, ion-exchange, photocatalysis, oxidation and adsorption, as shown in Fig. 2.[27–29] Over the past few decades, intensive efforts have been devoted to the development of cheaper and more effective technologies and sorbent materials to improve the quality of treated effluents.[6] Each method has its own advantages and disadvantages. Conventional methods have major disadvantages such as incomplete removal, high-energy requirements, and production of toxic sludge. Thus, the selecting of a suitable technique depends on the characteristics of the effluents, targeted specific heavy metal, scale of treatment, standards promulgated by government agencies and cost effectiveness. Fig. 2 presents the various treatment techniques for water purification.[30]

This work reviews the adsorption method for the removal of heavy metals ions from wastewater. This water treatment approach has garnered significant attention in recent years. Adsorption treatment of heavy metals is preferred due to its significant metal removal efficiency, easy operation, low sludge production, and utilization of low-cost adsorbents.[31,32] However, the adsorbents eventually become saturated with metal ions, and hence developing efficient regeneration methods is crucial. This is a comprehensive review on the removal of five hazardous heavy metals (Pb^{2+}, Cr^{6+}, As^{3+}, As^{5+}, Hg^{2+} and Cd^{2+}) *via* synthetic and natural adsorbents.

4. Adsorption process

Adsorption is a surface phenomenon in which pollutants are adsorbed on the surface of a solid substance. The substance that becomes adsorbed on the solid surface is termed the adsorbate, while the solid surface itself is referred to as the adsorbent. Adsorption can be monolayer or multilayer depending on the applicable model (Langmuir or Freundlich). The Langmuir isotherm describes a monolayer adsorption process, in which the adsorbate is directly attached to the surface of the adsorbent. Alternatively, the Freundlich isotherm is a widely used model to describe the multilayer adsorption on heterogeneous surfaces. Typically, physical forces drive adsorption although weak chemical bonds may also play a role. Three major steps are involved in adsorption including diffusion of the adsorbate from solution towards the surface of the adsorbent, adsorption on the solid surface and diffusion inside the adsorbent particles.

Adsorption is broadly classified into two types, *i.e.*, physico-sorption and chemisorption, as shown in Fig. 3.[33] In the case of physico-sorption, the adsorbate adsorbs on the surface of the adsorbent through weak van der Waals forces. This type of

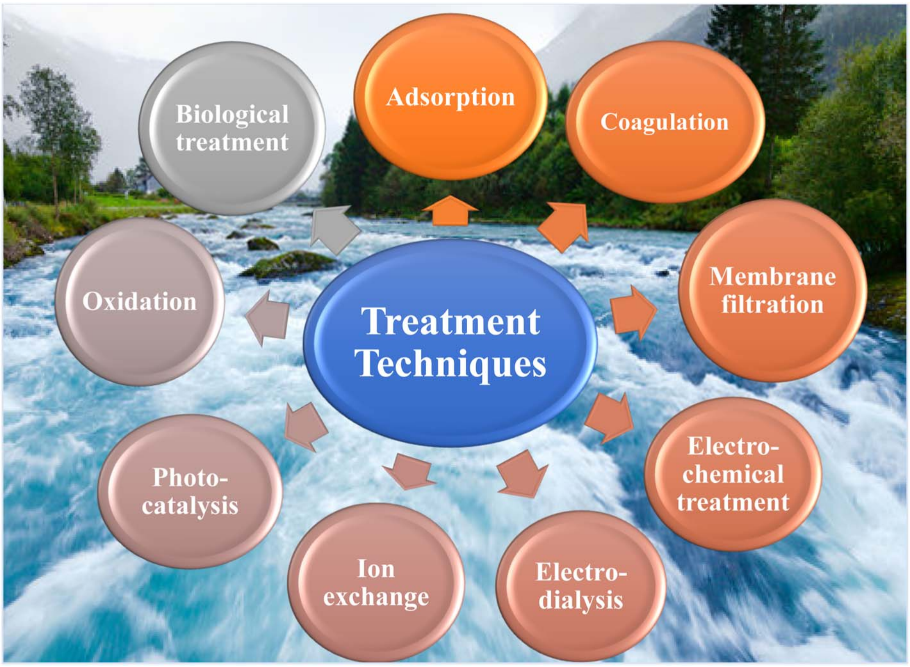


Fig. 2 Treatment techniques for the removal of heavy metals from water.

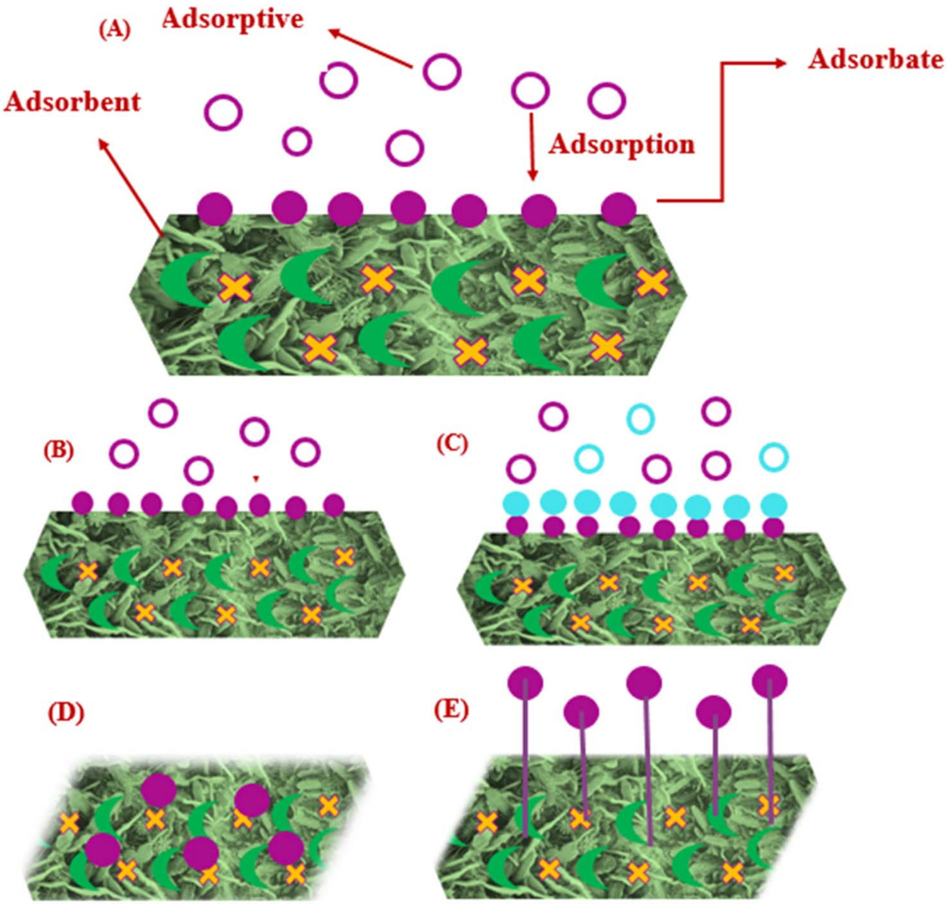


Fig. 3 (A) General mechanism of adsorption, (B) monolayer adsorption, (C) multilayer adsorption, (D) physical adsorption, and (E) chemical adsorption.

adsorption is reversible but not specific. Alternatively, in chemisorption, chemical bonds (ionic or covalent bond) are formed between the adsorbate and adsorbent, which make them irreversible due to chemical reaction. In the adsorption process, different adsorbing materials are used such as synthetic and natural materials. The term bio-sorption is used for the type of adsorption in which the adsorbate adsorbs on natural materials (biological systems).[34] Herein, we focus on carbon-based materials, biomaterials and inorganic materials for the removal of the five most hazardous heavy metals for wastewater treatment.

4.1. Factors affecting the adsorption process

The adsorption process is influenced by several key parameters including temperature, nature of the adsorbate and adsorbent, pH, concentration of pollutants, contact time, synthesis route, and particle size.

4.1.1. Influence of pH. The adsorption capacity of heavy metals is affected by a change in pH. The pH value at which the charge on the adsorbent surface is zero is termed pH_{PZC} (point of zero charge). When the pH is lower than pH_{PZC}, the adsorbent surface becomes positively charged. As a result, it attracts anionic species from the solution. Alternatively, when the pH is greater than pH_{PZC}, the adsorbent surface becomes negatively charged. This charge facilitates electrostatic interactions, particularly with cationic species such as heavy metals. Consequently, the adsorption capacity of metals is enhanced at higher pH compared to lower pH.[35] Understanding this pH-dependent behavior is crucial for optimizing the adsorption process in water treatment and environmental remediation.

4.1.2. Influence of contact time. The removal of heavy metals is also affected by the contact time. Initially, the removal efficiency increases with an increase in contact time, but after reaching the maximum value, a further increase in contact time does not yield significant improvements. This phenomenon occurs because initially, the concentration gradient is high and the adsorption sites are vacant.[36] However, as saturation occurs, additional contact time does not lead to a substantial enhancement in adsorption. During the adsorption of Pd(II) on a cryogel, it was observed that in the first 2 h, the adsorption capacity reached 140 mg g^{-1}, while 360 min was the longest time to reach the point of equilibrium. The results of this test prove that during the initial stages, the adsorption capacity increases with an increase in contact time because of the greater availability of binding sites, and finally reaches equilibrium when the active sites are fully occupied.[37]

4.1.3. Influence of porosity of adsorbent. Various porous materials have been employed for the adsorption of pollutants from water bodies. Porosity is an important factor to be considered during the development of any adsorbent because large pores can facilitate the diffusion of pollutants, which is beneficial to reach the targeted functional groups.[38]

4.1.4. Influence of adsorbent dose. To obtain economical optimization in an adsorption system, the adsorbent dose plays a crucial role. Generally, the removal efficiency increases with higher adsorbent doses due to the enhanced availability of adsorption sites.[39] However, at the same time, a decrease in metal adsorption capacity has also been reported at a very high adsorbent dose. For instance, the copper adsorption capacity decreased when the concentration of the adsorbent increased up to 40.5 mg g^{-1}. This is due to the partial aggregation of the adsorbent particles.[40]

4.1.5. Influence of temperature. Temperature significantly influences adsorption and its effects vary based on whether the process is exothermic or endothermic. When the process is exothermic, an increase in temperature retards the adsorption capacity. Specifically, higher temperatures hinder the adsorption of substances. Conversely, in an endothermic process, an increase in temperature increases the adsorption capacity. At elevated temperatures, heavy metal ions exhibit mobility, and more active sites are available for adsorption.[41]

4.1.6. Influence of initial concentration of adsorbate. The initial concentration of heavy metals significantly influences the extent of adsorption and is considered a key parameter for evaluating the efficiency of an adsorbent. Generally, with an increase in the initial concentration of heavy metal ions, the removal percentage decreases. However, an increase in the initial concentration of heavy metal ions corresponds to an increased adsorbent capacity. This inverse relationship between removal percentage and initial concentration stems from the saturation of the adsorption sites on the adsorbent surface. The direct relation between the adsorbent capacity and initial concentration of heavy metal ions originates from the strong driving force for mass transfer.[42]

4.1.7. Influence of particle size. Particle size has a prominent effect on the adsorption performance. Particles with a smaller size have greater adsorption efficiency in comparison to larger particles. This foundation is based on surface area. Smaller particles have a greater surface area in comparison to larger particles. Therefore, smaller particles are always considered more suitable for adsorption in comparison to larger particles.[43]

4.1.8. Influence of synthesis route. The synthesis route is a prominent factor that affects the adsorption performance. This factor can be explained as follows: in the case of conventional polymers synthesis, higher or room temperature is used but the fabricated polymers have a condensed and packed structure, in which the diffusion of pollutants is very difficult to reach the targeted functional groups. Alternatively, cryogels (porous polymers) prepared at a negative temperature (temperature below the freezing point of the solvent) have the ability to facilitate the easy transport of pollutants to the targeted point. This observation confirms that the synthesis route has a prominent effect on the adsorption process.[44]

4.2 Equations related to isotherms, kinetics and thermodynamic study of adsorption

Isotherm studies explore the homogeneity and heterogeneity of adsorbents. An adsorption isotherm represents the relationship between the amount of pollutant adsorbed and its concentration in water at equilibrium.[45] Specifically, the Langmuir adsorption isotherm assumes that the active sites are homogenously distributed. When a site is occupied, further adsorption ceases. This model is particularly applicable to monomolecular layers.[46] The separation factor R_L is used to access the favorability of adsorption based on the initial concentration of the adsorbate, which can be defined as follows:

$$R_L = \frac{1}{(1 + bC_o)}$$

where R_L is a dimensionless constant. If R_L is between 0 and 1, it means that the process is favorable, whereas if equal to zero, then adsorption is irreversible. Linear adsorption is indicated by R_L equal to 1. R_L greater than one shows that the process is unfavorable.[47] Similarly, adsorption occurring on a heterogeneous surface is investigated using the Freundlich isotherm. According to Freundlich, the adsorption isotherm becomes linear, indicating favorable adsorption when $n = 1$, favorable when $n < 1$, and unfavorable when $n > 1$.[48] The distribution of the binding energy can be explained by the Temkin model. This model considers the variation in the heat of adsorption across the surface. The temperature dependence is related to the Dubinin–Radushkevich isotherm. It also estimates the free energy of a heterogeneous surface and porosity of the adsorbent. The nature of biosorption can be determined, which refers to the adsorption of biological materials on surfaces. If the sorption energy value is in the range of 8 to 16 kJ mol^{-1}, it suggests chemical or ion exchange, whereas for energies less than 8 kJ mol^{-1}, physical adsorption is dominant.[41] The value of the linear regression correlation coefficient R^2 indicates which model is appropriate to give the best fit.

To understand the adsorption process, investigating the rate at which the adsorbate adsorbs on the surface of the adsorbent is crucial. The major kinetic models employed in adsorption studies include pseudo-first-order, pseudo-second-order, intraparticle model, and Elovich model. Additionally, thermodynamic studies estimate the changes in enthalpy, entropy and Gibbs free energy, which are essential for evaluating the feasibility of the process.[49] The linear forms of different isotherms, kinetics models, and thermodynamic study used to determine the different parameters related to adsorption are presented in Table 1.

A variety of techniques such as UV-visible spectrophotometry, atomic absorption spectrophotometry, and inductive coupled plasma spectrometry is used for the measurement of the adsorbate concentration in the liquid phase. UV-visible spectrophotometry is based on the principle of the Beer–Lambert law and is the simplest and most cost-effective method

Table 1 Linear forms of different equations used in isotherm, kinetic, thermodynamic and batch studies

Equations used in adsorption study			
Isotherms	Kinetic equations	Batch study	Thermodynamic equations
Langmuir isotherm $\frac{C_e}{q_m} = \frac{1}{q_m K_l} + \frac{C_e}{q_m}$	Pseudo-first-order $\ln(q_e - q_t) = \ln q_e - K_1 t$	$q_e = \frac{(C_i - C_e)}{m} \times V$	$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{RT}$
Freundlich isotherm $\log q_e = \log K_F + \frac{1}{n(\log C_e)}$	Pseudo-second-order $\frac{1}{q_t} = \frac{1}{{q_e}^2 K_2} + \frac{1}{q_e} t$	$\%R = \left(\frac{C_i - C_e}{C_i}\right) \times 100$	
Temkin isotherm $q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	Elovich model $q_e = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} t$		
Dubinin Radushkevich isotherm $\ln q_e = \ln q_m - K_{DR}\, \varepsilon^2$	Intraparticle model $q_e = K_{id}\sqrt{t} + C$		

for the detection of heavy metals. The common heavy metals quantified using this technique include Ni^{2+}, Cu^{2+}, Cr^{3+}, Cr^{6+}, Fe^{2+}, and Fe^{3+}.[50] Atomic absorption spectrophotometry requires the sample to be in atomic gas form and can determine concentrations of over 65 elements. It exhibits high sensitivity, especially when measuring at parts per million (ppm). Another method employed for measuring the concentration of adsorbates in the liquid phase is inductively coupled plasma spectrometry. It is comprised of two further modifications, *i.e.*, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). ICP-MS is 10–100 times superior to ICP-AES.[43] The adsorbents utilized can originate from mineral, organic or biological sources, including zeolites, industrial by-products, agricultural waste, biomass, and polymeric materials. Adsorbents can be broadly classified into natural adsorbents, bio-adsorbents, commercially available adsorbents and adsorbents made from agriculture and industrial waste, as depicted in Fig. 4.[51]

Commercially available adsorbents predominantly consist of carbon-based adsorbents such as graphene, carbon nanotubes, and activated carbon. Graphene has a two-dimensional (2D) structure and is available in various forms such as pristine graphene, graphene oxide and reduced graphene oxide. When rolled up, graphene sheets form carbon nanotubes, which may be single walled or multi-walled depending on the number of rolled-up graphene sheets. All these materials fall in the category of nanomaterials and can be employed as adsorbents for the removal of heavy metals due to their stable nature and high surface properties.

Inorganic-based adsorbents primarily include natural adsorbents such as clays, zeolites and silica. Mesoporous silica is characterized by a regular two-dimensional hexagonal array of channels. It has a highly ordered structure, which can be

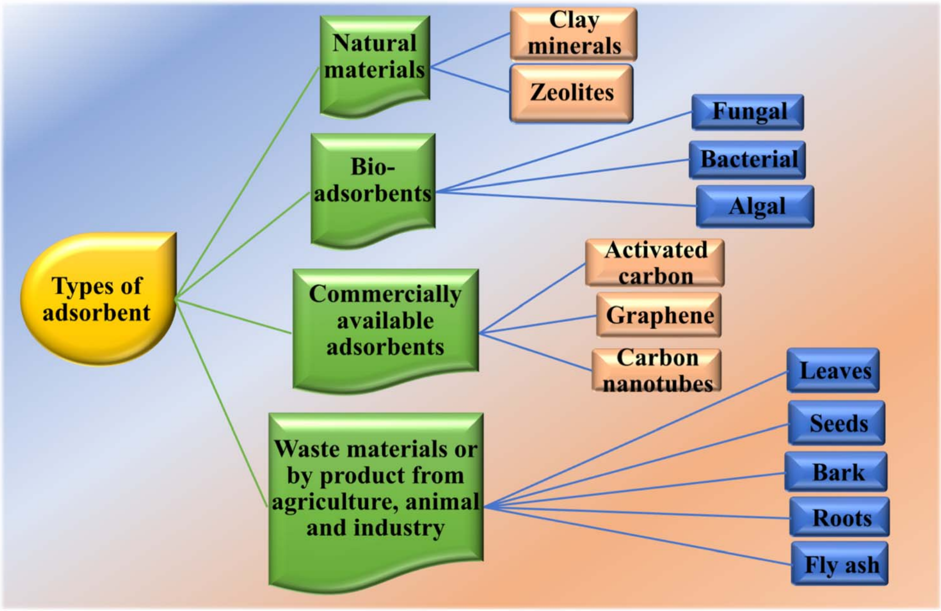


Fig. 4 Types of adsorbent and their sources.

modified with functional groups such as carboxylic acid and sulfonic acid. Zeolites are employed as adsorbents due to their good ion exchange properties, high surface area and hydrophilic character, which make them suitable for the removal of metals, *e.g.* cadmium. It has been observed by researchers that modified zeolites show better efficiency compared to natural zeolites.[52]

Adsorbents made from agriculture waste are used as alternatives to conventional methods for the removal of pollutants from water bodies due to their cost effectiveness, highly efficient and environment-friendly nature, reduction of biological or chemical sludge, absence of need for extra nutrients, biosorbent regeneration, and potential for metal recovery. Ionizable functional groups such as carboxyl, amine, and hydroxyl create possible adsorption binding sites. The major components of agricultural waste biomass include hemicellulose, proteins, simple sugars, lignin, extractives, lipids, water hydrocarbons, and starch, which contains different functional groups that facilitate the formation of complexes with metals. To enhance the adsorption capacity of adsorbents, some researchers also modified the adsorbents by functionalizing them. Because coal-based AC is limited in its usage due to its high cost, multiple strategies have been used to create activated carbon from diverse agriculture-based sources. The selection of agriculture waste-based adsorbents is based on many factors such as local availability, easy desorption, high regeneration capability, high binding capacity and selectivity for heavy metals, cost-effectiveness, and the negligible release of unrequired compounds into aqueous solutions.[53,54]

Algae, fungi, bacteria and yeast can also be used as adsorbents, which are termed as bio-adsorbents. These microorganisms play a crucial role in sequestrating pollutants from water bodies. Their enzymatic activity enables them to transform or degrade pollutants. Non-living biomass needs simple and cost effective treatment. Whether free or immobilized, both forms can be used as microbial biomass. The resultant efficacy rates are influenced by environmental factors, physicochemical characteristics of the microbes used, and the target environments.[55,56]

Various other materials serve as adsorbents including biopolymers, biopolymeric nanocomposites, metal organic frameworks, covalent organic frameworks, and organic membranes. Biopolymers are more selective towards the adsorption of heavy metal ions with cellulose derived from the cell wall of various plants, being a common choice as a biopolymer. Chitosan, which is obtained by de-acetylating chitin, and sodium alginate, extracted from brown algae, are also notable adsorbents for heavy metal ions.[57] Employing cheap and renewable materials such as chitosan-calcium carbonate nanocomposites (Cs/$CaCO_3$) show significant adsorption capacity of 62.11 mg g^{-1} for Cr(III), 83.33 for Cd(II), and 98.03 for Pb(II) within short removal times.[58]

Metal organic frameworks (MOFs) are organic–inorganic hybrids composed of metal clusters and organic linkers. MOFs have variable porosity and high surface area, making them versatile for applications such as sensing, drug delivery, adsorption and water splitting. Shi-Wen Lv *et al.* synthesized MIL-101-NH_2, which showed an adsorption capacity of 1.1 mM g^{-1} for Pb(II) ions.[59,60] Similarly, UiO-66-NHC(S)NHMe exhibited a remarkable uptake capacity of 769 mg g^{-1} for Hg(II) ions.[61] Nathan D. Rudd *et al.* synthesized luminescent metal–organic frameworks (LMOFs) for the detection and removal of the metal ions. The as-synthesized LMOF-263 was reported to demonstrate an adsorption capacity of 380 mg g^{-1} for Hg(II) ions.[62] The rapid and selective removal of Hg(II) and Pb(II) ions were achieved using a metal–organic framework/polymer composite, *i.e.*, Fe-BTC/PDA. This cos-effective and water-stable composite exhibited an uptake efficiency of 1634 mg g^{-1} for Hg(II) and 394 mg g^{-1} for Pb(II) ions.[63] Similarly, covalent organic frameworks (COFs) typically consist of low molecular weight elements with robust covalent linkages. Their porous nature, tunable pore size, crystallinity, and easily tailored functional groups enable them to be used as adsorbents for heavy metal ions. In this regard, TPB-DMTP-COF-SH showed the highest adsorption capacity reported thus far for the removal of Hg(II) and Sn(II) ions at rates of 4395 and 4350 mg g^{-1}, respectively.[64]

Membrane technology offers promising avenues for the separation of a wide variety of pollutants from wastewater due to their tailored pore size. However, many commercial membranes currently available are non-degradable, posing environmental concerns. Biodegradable plastics have gained attention owing to their ability to degrade under controlled conditions. Although biodegradable plastics have superior properties compared to conventional polymer membranes they have low mechanical, thermal and water stability. Thus, to overcome these limitations, novel approaches for membrane development are being explored, including blending of nanoparticles with polymers, copolymerization and cross-linking. Additionally, emerging biodegradable plastics other than cellulose and chitosan are gaining attention for their potential applications in wastewater treatment, including poly(butylene succinate)-based membranes, poly(ε-caprolactone)-based membranes, poly(lactic acid)-based membranes and poly(hydroxyalkonate)-based membranes.[65] These advancements hold promise for the development of more sustainable and effective membrane technologies.

5. Carbon-based adsorbents

Carbonaceous materials such as activated carbon (AC), biochar, carbon nanotubes (CNTs), and graphene oxide (GO) are considered the most cost-effective and highly efficient materials for the removal of heavy metals from various environmental matrices. Their favorable surface properties, uniform adsorption, non-toxic nature, ease of synthesis, and high adsorption capacities have prompted researchers to investigate the use of carbon-based materials as adsorbents.[66] CNTs exhibit a stable nature, large specific area and excellent mechanical and electrical properties. These attributes have attracted attention from researchers for utilizing them for the removal of heavy metals.[67] Similarly, GO possesses a huge surface area and oxygenated functional groups. Researchers are keen on employing GO as an adsorbent for the removal of heavy metals. Coal-based AC is expensive, limiting its widespread use. Thus, concerted efforts have been employed to develop AC from various sources beyond coal. Any material with a high carbon content can potentially yield activated carbon.[68] The adsorption of heavy metals on carbon-based adsorbents can take place *via* different mechanisms, which are influenced by the functional groups present on the surface of adsorbents. The major functional moieties include hydroxyl, amine and carboxyl groups (see Fig. 5). These carbon-based materials offer diverse options for efficient heavy metal removal, each with their unique advantages and applications. Adsorption can be physisorption or chemisorption depending on the type of interaction the between adsorbent and adsorbate. The large surface area and highly porous nature of carbon-based adsorbents are helpful for the formation of van der Waals interactions between heavy metal ions and adsorbents. Functional groups such as carboxyl, which bear the opposite charge to the adsorbate (heavy metal ions) are responsible for the electrostatic interaction between them. Sometimes the functional moieties present on the surface of adsorbents have exchangeable ions, for example, in the carboxyl group, hydrogen can be replaced by the neighboring metal ions, which is known as the ion exchange mechanism. To enhance the adsorption capacity of carbon-based adsorbents, metal binding agents are used to modify their surface. These modifications lead to the precipitation and redox mechanisms. If the thiol group is attached on the surface of adsorbent, it will facilitate the precipitation of lead ions. If the surface is modified by a reducing agent or oxidizing agent, then the metal ion will either oxidize or reduce itself, respectively.[69]

Numerous researchers have implemented carbon-based materials for the removal of heavy metal ions for wastewater. Bandaru *et al.* synthesized thiol-derivatized single-walled carbon nanotubes (SWCNT-SH) and investigated their potential as an adsorbent for the removal of Hg(II) ions. Notably, the Langmuir parameter showed a maximum adsorption capacity of 131 mg g^{-1} for the functionalized SWCNTs, highlighting their effectiveness to treat mercury pollution. The enhanced adsorption capacity for Hg(II) ions is due the presence of thiol groups, which undergo the selective formation of a complex with Hg(II) ions *via* soft acid-soft base interaction.[70] Another study highlighted the efficacy of calf/cow bone charcoal (CBC) as an adsorbent for removing Hg(II) ions from water. With a surface area of 112 m^2 g^{-1}, CBC demonstrated the maximum adsorption capacity of 38.08 mg g^{-1}. The thermodynamic study showed the endothermic, spontaneous and reversible nature of adsorption.[71] Similarly, many other carbonaceous materials demonstrate the ability to remove Hg(II) ions by adsorption including camel bone charcoal,[72] sheep bone charcoal,[73] and coconut shell-based granulated activated carbon.[74]

Janik *et al.* synthesized various amino silanes containing one, two, or three nitrogen atoms in the molecule for the modification of GO. Interestingly, despite having a different number of nitrogen atoms, the resulting GO derivatives exhibited similar maximum adsorption capacities for Cr(VI) in the range of 13.3–15.1 mg g^{-1}. The detection limit was found to be 0.17 ng mL^{-1}. The adsorption process followed a pseudo-second-order rate kinetic model, and the Langmuir and Freundlich isotherm data showed that adsorption is monolayer. Specifically, the anionic species of Cr(VI) form electrostatic interactions with the protonated amino groups on the surface of GO derivatives.[75] Similarly, AC-functionalized multi-walled carbon nanotubes (AC/f-MWCNTs) have excellent potential for chromium resistance. The highest adsorption capacity achieved

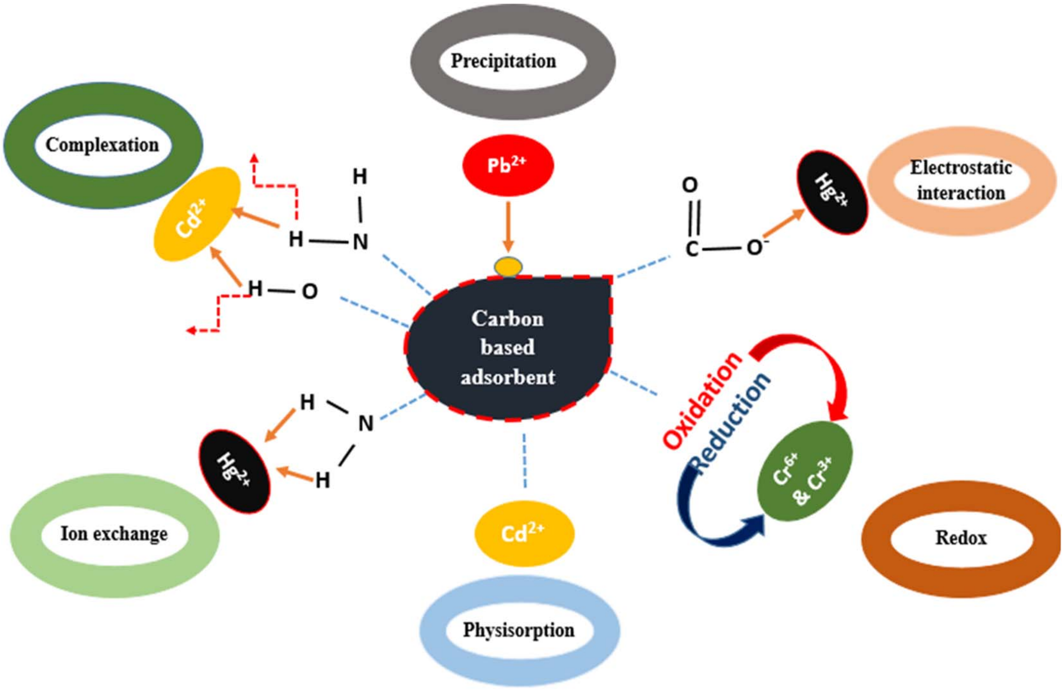


Fig. 5 Mechanism of adsorption of heavy metals on carbon-based adsorbents.

using AC/f-MWCNTs as an adsorbent was 113.29 mg g^{-1}.[76] Another study reported that GO prepared from the chemical exfoliation and oxidation of layered graphite showed the adsorption capacity of 240.3 mg g^{-1}. The strong adsorptive interaction between the GO surface and Cr(VI) is confirmed by the adsorption energy (290.32 kcal mol^{-1}) for Cr(VI).[77] Similarly, graphene oxide functionalized with alpha cyclodextrin and modified with polypyrrole (GO-αCD-PPY NC) showed the maximum adsorption capacity of 666.67 mg g^{-1} at 45 °C for the removal of Cr(VI) ions.[78]

Šolić *et al.* reported that ox-MWCNTs act as an effective adsorbent for the removal of Cd(II). The duration of the functionalization processing impacted the capacity of the adsorbent. Thus, ox-MWCNTs functionalized for 6 h showed the maximum adsorption capacity of 13.5 mg g^{-1} for Cd(II).[79] In another study, MWCNTs used as an adsorbent demonstrated an impressive adsorption capacity of 181.81 mg g^{-1} for the removal of Cd(II) ions.[80] Alsaadi and team synthesized novel adsorbents for the removal of As^{3+} from water. This study used a deep eutectic solvent (DES) as the functionalization agent for CNTs. KM-CNTs (CNTs functionalized with $KMnO_4$ and MTPB-based DES) showed the maximum adsorption capacity of 23.4 mg g^{-1}.[81] Besides this, microwave-assisted economic MWCNTs having a surface area of 9.1 m^2 g^{-1} showed 92% and 91% removal of arsenate and arsenite, respectively.[82] Additionally, many other carbonaceous materials have been employed to adsorb As ions including iron oxide nanoparticle-coated SWCNTs,[83] chitosan magnetic graphene oxide (CMGO),[84] iron oxide–graphene oxide nanocomposite,[85] and graphene oxide/copper ferrite foam (GCFF).[83]

Momčilović *et al.* used AC prepared from the cones of European black pine as an adsorbent for the removal of lead(II) ions, which showed the maximum adsorption capacity of 27.53 mg g^{-1}.[13] Another study investigated hybrid nanofibers based on ZnO-loaded activated carbon nanofibers (ZnO-ACNFs). These activated NFs exhibited an adsorption capacity of 92.59 mg of Pb(II)/g within a contact time of 45 min.[86] Moreover, GO prepared from waste dry cell batteries showed an impressive performance for the removal of Pb(II) ions, achieving a 98.87% removal efficiency. The oxygenated groups present on the surface of GO were responsible for the adsorption of Pb ions.[87] Similarly, diethylenetriamine-modified MCNTs(d-MWCNT),[88] CNT modified with four generations of poly-amidoamine dendrimer (PAMAM/CNT),[89] graphene oxide–$MnFe_2O_4$ magnetic nanohybrids (GO–$MnFe_2O_4$ nanohybrids)[90] were reported as carbon-based adsorbents for the removal of Pb(II) ions from water. The above-mentioned literature survey confirmed that carbon-based materials are excellent sorbents for the removal of heavy metals from water bodies due to the presence of various functionalities in their network. These studies underscore the importance of optimizing the functionalization process to enhance the adsorption efficiency. Carbon-based materials and the different factors affecting their performance such as pH, adsorption capacity, applicable isotherms and kinetic models are shown in Table 2.

6. Agriculture waste-based adsorbents

Different parts of plants such as their bark, stem, leaves, root, flower, fruit biomass, husk, hull, skin, shell, bran and stone fall under the category of agriculture waste, as shown in Fig. 6.[93] These types of adsorbents have the ability to remove organic and inorganic pollutants through different interaction modes owing to their various functional moieties. Adsorbents derived from agriculture waste exhibit abundant availability of binding groups, demonstrating a strong affinity and selective capability to attach heavy metals. These adsorbents contain structural polysaccharides and various functional groups such as carboxyl, phenolic, amido, amino, and sulphydryl carboxyl groups. These groups have the ability to effectively bind heavy metals either by substituting hydrogen with metal ions or by donating electron pairs to form complexes.[94] Agriculture waste-based adsorbents can be used directly as well as modified with acids, such as hydrochloric and phosphoric, or with alkaline solutions, such as sodium hydroxide, and potassium hydroxide, or cross-linked with other materials. Due to the high selectivity, porosity, and surface area of activated carbon, biochar, and charcoal produced from agricultural solid residuals, they have become emerging adsorbents for the removal of heavy metals.[95]

Jeyaseelan *et al.* utilized green tea leaves (*Camellia sinensis*) as a natural adsorbent for the removal of Cr(VI) from water, achieving an impressive 99% removal efficiency under the optimized conditions including pH of 2, contact time of 180 min, and adsorbent dosage of 0.8 g L^{-1}.[96] Similarly, Eucalyptus bark (*Eucalyptus globulus* tree species) showed more than 99% removal efficiency at a concentration of 200 ppm. Furthermore, at a Cr(VI) concentration of 250 mg L^{-1} in the effluent, the adsorption capacity was reported to be 45 mg g^{-1} of adsorbent.[97]

In another study, Jatropha oil cake demonstrated a remarkable removal efficiency of 97% at pH 2. The adsorption capacity was reported to be 4.76 mg g^{-1} at an adsorbent dose of 2.5 g L^{-1}. Additionally, FTIR analysis conducted before and after the adsorption showed a significant shift in the position and shape of the –OH group, indicating that Cr(VI) binding primarily occurs with –OH groups.[98] Other agriculture waste bio-adsorbents include *Caesalpinia bonduc* plant leaves and their ashes,[99] magnetic biochar derived from peanut hull,[100] and leaves and stems of *Eclipta prostrata*,[101] all of which have the ability to remove Cr(VI) ions. In the case of magnetic biochar derived from peanut hull, it was observed that there was no change in the crystal lattice of γ-Fe_2O_3 and no new shape crystals were formed. This observation clearly suggests that the maghemite layer attracts Cr(VI), leading to the formation of a monolayer.

Dubey *et al.* reported that *Portulaca* plant biomass (PPBM), obtained from its leaves and stems, has significant potential to remove Cd(II) ions from water, achieving 72% maximum adsorption efficiency at pH 6. The R_L value of 0.429 indicates the favorable adsorption of Cd(II) ions.[102] Similarly, another study revealed that the sawdust of *Pinus sylvestris* also has the capacity

Table 2 Comparison of different carbon-based adsorbents for the removal of heavy metals

Adsorbate	Adsorbent	pH	Maximum adsorption capacity (mg g^{-1})	Applicable isotherm models	Applicable kinetic models	Ref.
Hg(II)	(SWCNT-SH)	5	131	Langmuir	A first-order rate model	70
	(CBC)	4	38.08	Langmuir isotherm	Pseudo-second-order kinetic	71
	Camel bone charcoal	2	28.24	Langmuir		72
	Sheep bone charcoal	2	12.550	Freundlich isotherm model		73
	Coconut shell-based granulated activated carbon	4.5	15.19	Langmuir		74
Cr(VI)	AC/f-MWCNTs	2.2	113.29	Langmuir equation		76
	GO		240.3			77
	GO-αcd-PPY NC		666.67	Langmuir models		78
Cd(II)	Oxidized multiwalled carbon nanotubes	8	13.5	Freundlich		79
	MWCNTs	7	181.81			80
	Graphene magnetic composite nanoparticles (Fe_3O_4-GS)	6–7	163.6	Freundlich equation	Pseudo-second-order model	91
	(Fe_3O_4 NPs/HPC)		34.22			92
As(III)	KM-CNTs	3.0	23.40	Freundlich	Pseudo-second-order kinetics	81
As(V) and As(III)	Microwave assisted MWCNTs	6	92.0% and 91.0% removal efficiency	Temkin, Dubinin-Radushkevich, Freundlich, and Langmuir models	Pseudo-first order	82
As(V)	Iron oxide nanoparticle-coated SWCNT	8	49.65	Freundlich model	Pseudo-second order	83
As(III)	CMGO	7.5	45	Langmuir isotherm	Pseudo-second-order kinetic model	84
As(III) and As(V)	Iron oxide–graphene oxide nanocomposite		147 for As(III) and 113 for As(V)			85
As(III) and As(V)	Graphene oxide/copper ferrite foam (GCFF)	7	As(III) and As(V) are 51.64 and 124.69	Langmuir model		83
Pb(II)	Activated carbon obtained from cones	6.7	27.53	Langmuir model	Pseudo-second-order kinetic model	13
	ZnO-ACNFs	pH 7	92.59	Langmuir model	Pseudo-second-order kinetic model	86
	GO prepared from waste dry cell battery	4	55.80	Langmuir model	Pseudo-second-order kinetic model	87
	D-MWCNT	6.2	58.26	Langmuir model	Pseudo-second-order kinetic model	88
	PAMAM/CNT	7	4870	Langmuir	Pseudo-second-order kinetic model	89
	GO–$MnFe_2O_4$ nanohybrids		673	Langmuir	Pseudo-second-order kinetic model	90

Fig. 6 Agriculture waste-based adsorbents and their interaction with organic and inorganic pollutants.[93]

to bind Cd(II) ions. At pH 5.5, the maximum adsorption efficiency of 96% was observed. The adsorption process followed pseudo-second-order kinetics.[103] Agriculture waste such as orange residues contains different functional components including cellulose, pectins, hemicellulose, chlorophyll pigments and other low-molecular weight compounds, including limonene. It has been observed that the carboxylic groups in pectins and the alcoholic hydroxyl groups in cellulose act as active binding sites for metals. The maximum adsorption capacity of orange waste was found to be 0.43 mmol g^{-1} at pH 6 for Cd(II) ions.[104] Additionally, other adsorbents derived from agriculture waste including sugarcane bagasse (SCB), maize corncob (MCC) and *Jatropha oil* cake (JOC),[105] bagasse fly ash,[106] cashew nut shell,[107] urea-modified wheat straw (MWS)[108] show enhanced adsorption towards Cd(II) ions. In their investigation, Akbar and colleagues (Fig. 7) studied the use of natural flax fiber tows (FFT) as an adsorbent for removing Cu^{2+}, Pb^{2+} and Zn^{2+} ions from water. The dominant mechanism for the adsorption of heavy metals in natural materials is the ion exchange mechanism. In flax fibers, which are lignocellulosic materials, the bound atoms (Na^{+} and Mg^{2+}) are exchanged with the heavy metal ions present in wastewater and responsible for the good

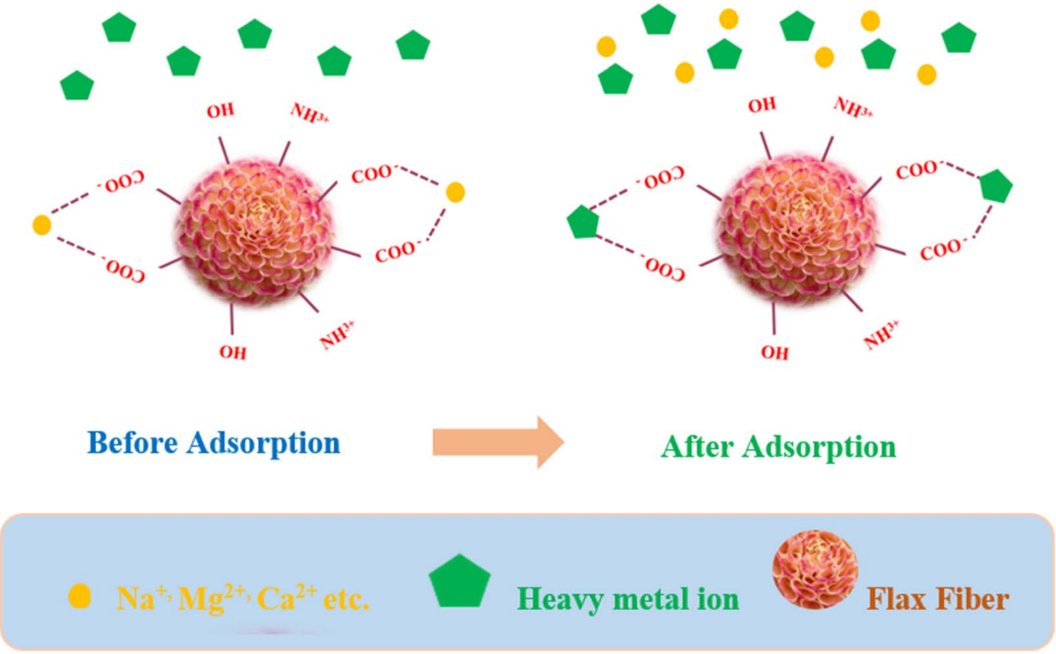


Fig. 7 Schematic illustration of proposed mechanisms for heavy metal adsorption on flax fiber tows.[109]

adsorption capacity of flax fibers tows. It was observed that the adsorption rate for these ions increased rapidly and the optimal removal efficiency was achieved within 60 min. The Langmuir model well-described the adsorption isotherm and a significant reduction in metal levels (97.4% for Pb, 79% for Cu and 73.28% for Zn) after FTT treatment was reported. The economic viability and potential for urban runoff water treatment make FTT a promising bio-based material.

Recent studies highlighted the potential of raw and alkali metal ion-free banana peel as an effective adsorbent for the removal of Hg^{2+} ions, showing a maximum loading capacity of 46.8 and 52.2 mg g^{-1}, respectively. This study emphasized that the protonation step enhances the removal efficiency of Hg^{2+} ions from aqueous solution.[110] Giraldo *et al.* explored calcinated sugarcane bagasse (CSB) as an alternative adsorbent. CSB showed the maximum adsorption efficiency of 13.6 mg of Hg(II)/g. The kinetic studies suggested that the adsorption process follows chemisorption, confirming the strong interactions due to complexation through coordinated bonds.[111] Moreover, magnetic carbon composites (MCC) prepared from pinewood sawdust showed an adsorption capacity of 167.22 mg g^{-1} for Hg^{2+} ions.[112] Palm leaves,[113] *Eucalyptus* leaves,[114] and adsorbents derived from date pits[115] serve as an effective sorbents for the removal of Hg(II) ions.

Rao *et al.* synthesized activated carbon prepared from *Ceiba pentandra* hulls and used them as a sorbent for the removal of lead, exhibiting a maximum removal efficiency of 99.5%.[116] Another study focused on sunflower residue, which showed an adsorption capacity of 182 mg g^{-1} for Pb ions.[117] Recent investigations have shown that banana stem scutcher shows a remarkable adsorption capacity of 179.9 mg g^{-1} for Pb(II) ions. FTIR and XPS analysis highlighted the significance of functional groups (C–OH, C–O–C) as major binding groups.[118] Sugarcane bagasse,[119] *Musa paradisiaca* peels,[120] tea waste and peanut shells,[121] maize cob,[122] orange and banana peel[123] are some other reported agriculture-based adsorbents for the removal of Pb(II) ions.

Javanshir and colleagues synthesized iron nanoparticles using a mixed extract of two plant species, namely *Prangos ferulacea* and *Teucrium polium*. These green nanoparticles showed an arsenic removal efficiency of 93.8% with a maximum adsorption of 61.7 mg g^{-1}.[124] In another study, magnetite nanoparticles were synthesized from onion peel (MNp-OP) and corn silk extract (MNp-CS), having a specific surface areas of 243 m^2 g^{-1} and 261 m^2 g^{-1}, respectively, which demonstrated the ability to effectively remove As from water. The Langmuir isotherm model showed the maximum adsorption capacities of 1.86 mg g^{-1} for MNp-OP and 2.79 mg g^{-1} for MNp-CS.[125] Other agriculture-based sorbents include iron nanoparticles synthesized from black tea leaves (*Camellia sinensis*), oak tree leaves (*Quercus virginiana*), green tea leaves (*C. sinensis*), pomegranate leaves (*Punica granatum*), and eucalyptus leaves (*Eucalyptus globulus*).[126] Additionally, iron nanoparticles (BB-Fe NPs) produced using blueberries extract,[127] modified green tea waste,[128] and nanoparticles synthesized from mint leaves[129] demonstrated the capacity for arsenic removal. Table 3 lists the various reported agriculture waste-based adsorbents together with their capacities for removing different metal ions and relevant parameters.

7. Micro-organism-based adsorbents

Many microbial species such as bacteria, fungi, yeast and algae are known to be capable of adsorbing heavy metals on their surface. These microbial species have special surface properties such as adhesion and flocculation abilities. The number of effective adsorption binding sites increases with the modification of functional groups on the cell surface. Various functional groups such as carboxylic, hydroxyl, amines, and phenolic groups endow microorganisms with a negatively charged cell surface, enabling them to bind various cationic species such as heavy metals. Microbial cells have several protection mechanisms against heavy metal toxicity, such as active efflux of metal ions and reduction of metal ions. Ambient factors, sorbing materials, and metals to be removed are factors affecting the biosorption efficiency of microorganism-based adsorbents.[136,137]

Umer Shafique and team utilized Pleurotus ostreatus as a bioadsorbent for the removal of chromium(VI) owing to its fast metal removal rate, remarkable biosorption capacity and high regeneration ability. The maximum adsorption of Cr(VI) takes place at pH 2.5, while the maximum bio-sorption capacity of fungus was 10.75 mg g^{-1}. FTIR analysis revealed that amine and carboxylic acid groups play a major role in the adsorption process.[138] In another study, *Staphylococcus saprophyticus* bacteria were found to be proficient for the removal of chromium, showing the maximum adsorption of 88.66 mg for Cr(VI) at pH 2, temperature of 27 °C, and an initial ion concentration 193.66 mg L^{-1}.[139] Dadrasnia *et al.* used *Bacillus salmalaya* as a biosorbent, showing a maximum sorption capacity of 20.35 mg g^{-1} for Cr(VI). The adsorption process followed a pseudo-second-order mechanism and the Langmuir isotherm model provided the best fit to the data. The thermodynamic parameters showed that it is an endothermic process.[140] Similarly, *Chlorella vulgaris* was used as an adsorbent for the removal of chromium(VI) ions, showing a removal efficiency of 99.75% under the optimum conditions. The value of R_L confirmed the favorable adsorption process.[141] Moreover, *Spirulina platensis* possesses enriched functional groups, which aid in the adsorption of metal ions. Sulfate, phosphate, hydroxyl, carbonyl and other charged groups present in algae contribute to heavy metal binding. Waste algal biomass of *Spirulina platensis*, obtained after biodiesel production, was successfully employed as an adsorbent for the removal of chromium(VI) ions with an adsorption capacity of 45.5 mg g^{-1}. This approach demonstrated the potential for reusing algal biomass waste as an adsorbent.[142]

Mahmood *et al.* reported the adsorption potential of dead biomass of *Sargassum* sp., a brown marine alga, for the removal of heavy metals, specifically Cd(II). Remarkably the removal efficiency reached 95.3%.[143] Additionally, *Bacillus subtilis* coated with maghemite nanoparticles was used as a biosorbent for the removal of Cd(II) ions. It showed a maximum removal efficiency of 84% and a high recovery percentage (76.4%), making it a sustainable method. The adsorption data correlated well with

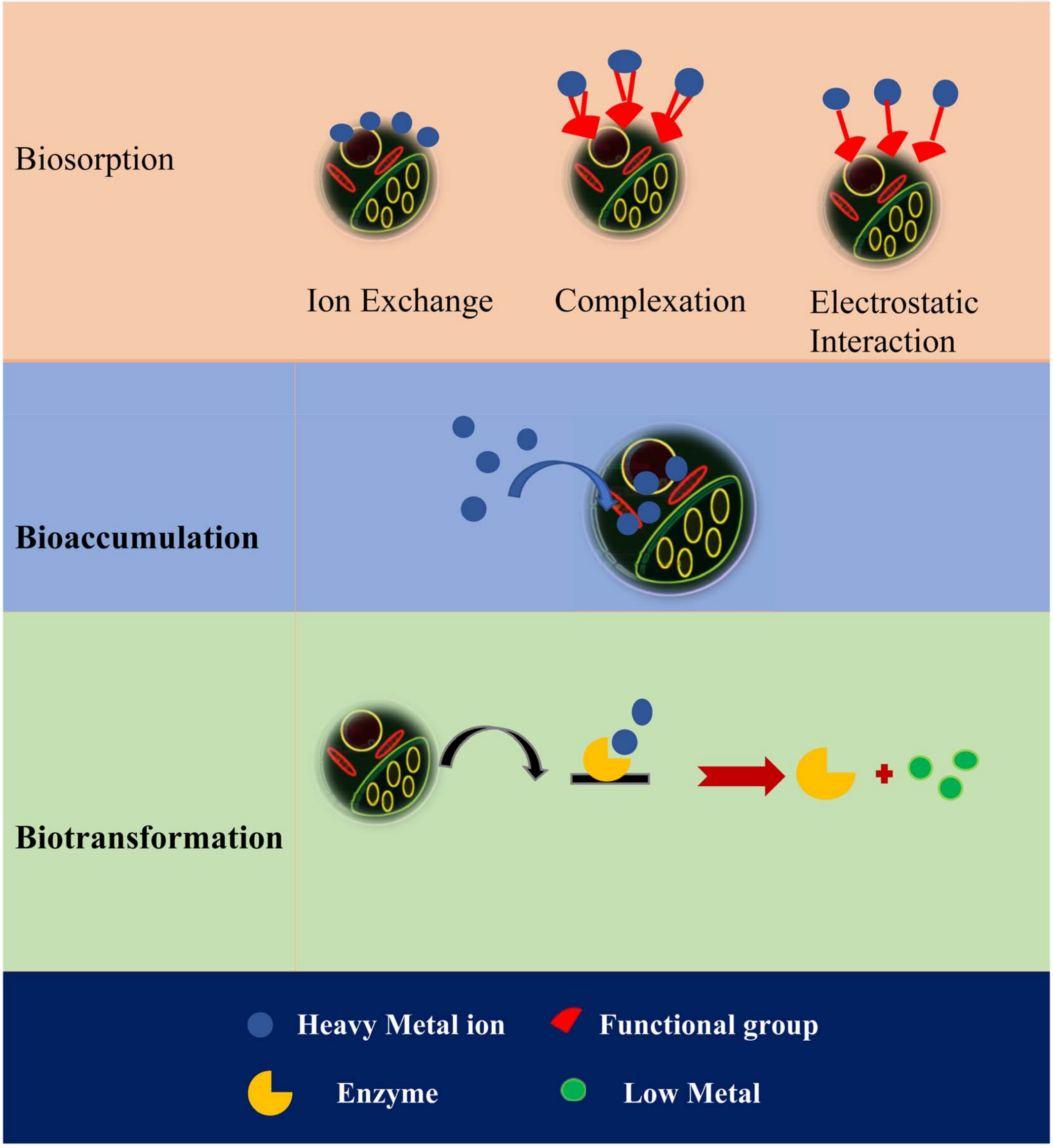
Table 3 Comparison of different agriculture waste-based adsorbents for the removal of heavy metals

Adsorbate	Adsorbent	pH	Adsorption capacity (mg g^{-1})	Isotherm	Kinetics	Ref.
Cr(VI)	Eucalyptus bark	2	45	Freundlich isotherm	First order	97
	Caesalpinia bonduc		19.6 with ash 12.7 with leaves			99
	Magnetic biochar derived from peanut hull		77.54	Elovich model		100
	Jatropha curcas seed cake	2.0	4.76	Freundlich isotherm		98
Cd(II)	Coffee grounds	5	16.2	Langmuir and Freundlich models	Pseudo-second-order	130
	Wheat straw	5	31.6	Langmuir and Freundlich models	Pseudo-second-order	130
	Cashew nut shell	5	22.11	Freundlich	Pseudo-second order	107
	Urea-modified wheat straw	6	39.22	Langmuir model	Pseudo-second-order kinetic model	108
	Orange peel	7	35.71	Langmuir model	Pseudo-second-order kinetic model	131
	Orange peel and Fe_2O_3 nanoparticles	7	71.43	Langmuir model	Pseudo-second-order kinetic model	131
	Cashew nut shell	5	436.7	Langmuir isotherm	Pseudo-second-order	132
	Reed plant (*Phragmites australis*) root	10	168.6			133
	Seaweed (*Ascophyllum nodosum*)	10	106.3			133
	Esterified spent grain from brewery	5	473.93	Langmuir isotherm	Pseudo-second order	134
	Raw spent grain from brewery	5	335.57	Langmuir isotherm	Pseudo-second order	134
Hg(II)	SDS-modified bamboo leaf powder	8	31.05	Langmuir isotherm	Pseudo-second-order	135
	SDS-modified bamboo leaf powder(BLP)	8	27.1	Both Freundlich and Temkin isotherms	Pseudo-second-order	135
	Triton X-100-modified BLP	8	28.1	Both Freundlich and Temkin isotherms	Pseudo-second-order and Elovich	135
	Alkali metal ion-free banana peel		52.2	Langmuir	Pseudo-second-order	110
	CSB	6	13.6	Langmuir	Pseudo-second-order and intraparticle diffusion	111
	Pinewood sawdust (MCC)		167.22	Langmuir	Pseudo-second-order	112
Pb(II)	*Ceiba pentandra* hull AC	6.0	25.5	Freundlich isotherm	Second-order rate	116
	Sunflower residue	5	182	Modified two-site Langmuir		117
	Banana stem scutcher		179.9	Langmuir model	Pseudo-second-order kinetic	118
	Sugarcane bagasse	6.0	1.61 mg g^{-1} with 89.31% removal efficiency	Freundlich isotherm	Pseudo-second-order kinetic models	119
	Maize cob	5	95% removal efficiency	Freundlich model	Lagergren first-order kinetics	122
As(III)	Green-synthesised iron nanoparticles using *Prangos ferulacea* and *Teucrium polium* extract	6	61.7	Redlich-Peterson isotherm	Pseudo-second-order kinetic model	124
	(MNp-OP) and (MNp-CS)	8.1	1.86 and 2.79	Freundlich model	Pseudo-second-order model	125
As(V)	Eucalyptus leaf nanoparticles		39.84	Langmuir model	Pseudo-second kinetic model	126
As(V)	Oak tree leaf nanoparticles		32.05	Langmuir model	Pseudo-second kinetic model	126
	BB-Fe NPs		50.40	Langmuir-Freundlich model	Pseudo-second kinetic model	127

the Langmuir and Freundlich isotherm models and the pseudo-second-order equation provided a good correlation with the obtained adsorption data.[144]

Three different mechanisms are observed for the removal of heavy metals by algae.[145] The most common mechanism is the biosorption of heavy metals. The cell wall of algae contains different functional groups such as carboxyl, hydroxyl, sulfate and amino groups, which are responsible for ion exchange, electrostatic interaction and complexation of heavy metals. Cyanobacterial extracellular polymers contain a variety of polymers such as nucleic acid, polysaccharides, and proteins, which play a vital role in biosorption. Polysaccharides help to bind heavy metals to the surfaces, lipids, and proteins of algae. The transport of metal ions across the cell wall is another mechanism for adsorption on algae, which is known as bio-accumulation. Energy is required to accumulate intracellular heavy metals. In this process, as microorganisms grow, they accumulate heavy metals intracellularly and allow metals to concentrate, often exceeding the levels in the surrounding environment. Another type of mechanism used for the detoxification of heavy metals in the cells of algae is biotransformation, which is related to the enzymatic or biochemical transformation of heavy metals. In the case of enzymatic transformation, the enzymes present inside the cells of algae convert the non-degradable heavy metals into less hazardous inorganic complexes. A schematic representation of these mechanisms is shown in Scheme 1.

In a separate study, *Pseudomonas aeruginosa* B237 bacteria exhibited a maximum Cd^{2+} adsorption capacity (q_{max}) of 16.48 mg g^{-1}. The Langmuir isotherm model effectively described the Cd^{2+} ion adsorption by this bacterial biomass with its favorable process indicated by the low R_L value of



Scheme 1 Mechanism for the removal of heavy metals by algae.[34]

0.002.[146] *Aspergillus niger* (*A. niger*)[147] and Spirulina platensis also have the capability to serve as sorbents for the removal of Cd(II) ions. Wen *et al.* synthesized a novel adsorbent by immobilizing the endogenous bacterium *Bacillus licheniformis* with magnetic polyvinyl alcohol (PVA) and sodium alginate for the removal of lead ions, showing a maximum adsorption capacity of up to 113.84 mg g^{-1}.[148] Furthermore, the fungus *Mucor indicus* was found to have the ability to remove lead with a maximum biosorption capacity of 22.1 mg g^{-1}.[149] Similarly, the red marine algae *Jania rubens* pretreated with formaldehyde showed the highest adsorption capacity of 774 mg g^{-1} for Pb(II) ions and that for *Jania* pretreated with $CaCl_2$ reached 1089.6 mg g^{-1}.[150] Other microorganism-based biosorbents including *Aspergillus niger* and *Aspergillus terreus* fungus isolates on luffa sponge,[151] Cystoseira compressa, Sargassum vulgare, Turbinaria, Agaricus campestris,[152] as well as the green alga Ulva lactuca[153] have been used for removal of lead ions.

Ahmet Sarı and coworkers investigated the efficiency of dead green algae (*Mougeotia genuflexa*) biomass for the removal of As(III) from water. The Langmuir model showed a maximum monolayer biosorption capacity of 57.48 mg g^{-1}. Additionally, the mean free energy calculated from the D–R model (10.2 kJ mol^{-1}) indicated that the adsorption occurred through chemical ion exchange.[154] A mixture of green (Chlorophyta) and blue-green (Cyanobacteria) algae showed the maximum sorption capacity of 35 mg g^{-1} for As(III). FTIR confirmed the presence of hydroxyl and carboxyl groups on the surface of the adsorbent, thus playing a key role in capturing metals.[155] Similarly, some bacterial stains such as *Yersinia* sp. strain SOM-12D3 showed the adsorption capacity of 159 mg g^{-1} towards As(III).[156] Other microbial adsorbents including *Bacillus thuringiensis* strain WS3,[157] mixed dried biomass of *Bacillus thuringiensis* strain, *Pseudomonas* stutzeri strain and Micrococcus yunnanensis strain,[158] and *Saccharomyces cerevisiae*[61] exhibited enhanced ability to remediate As(III) ions.

Xia *et al.* reported that extracellular polymeric substances (EPS) extracted from Klebsiella sp. NT8 and Bacillus sp. NT10 (EPS-K and EPS-B) have the maximum sorption capacity of 2597.62 and 2617.23 mg g^{-1}, respectively, for Hg(II) ions. The adsorption followed pseudo-second-order kinetics and fit the Langmuir isotherm model.[159] Another study showed that Brevundimonas species IITISM22 has the potential to remove Hg ions, achieving a maximum adsorption capacity of 666.6 mg g^{-1} at pH 6.5.[160] Additionally, yeast *Yarrowia* spp.,[161] *Sargassum glaucescens* (brown algae),[162] *Sargassum bevanom*,[163] *Chlorella vulgaris*,[164] *etc.* show promise as effective sorbents for Hg(II) ions. Table 4 provides a comparison of various microorganism-

Table 4 Comparison of different microorganism-based adsorbents for heavy metals

Adsorbate	Type	Adsorbent	pH	Adsorption capacity (mg g^{-1})	Ref.
Cr(VI)	Fungi	*Pleurotus ostreatus*		10.75	138
	Bacteria	*Bacillus salmalaya*		20.35	140
	Chemically modified algae/waste algal biomass	Biodiesel-extracted *Spirulina platensis*		45.5	142
		Rhizoclonium hookeri (0.1 M HCl)		67.3	142
		Sargassum siliquosum		66.4	142
		Sargassum sp.		58.2	142
	Bacteria	*Bacillus megaterium*		30.7	165
	Yeast	Yeast		86.95	166
Cd(II)	Bacteria	*Bacillus subtilis* coated with maghemite nanoparticles	4	71.4	144
		Pseudomonas aeruginosa	6	16.48	146
	Fungi	*Aspergillus niger* (*A. niger*)	4	15.50	147
	Algae-based bioadsorbents	Red algae *Galaxaura oblongata*	5	85.5	167
		Red algae *Chondracanthus chamissoi*	4	85.4	168
		Red algae *Hypnea valentiae*	6	28.6	169
		Alginate-PEI modified with *Fucus vesiculosus* (brown algae)	3.5	97.8	170
Pb(II)	Bacterium	*Bacillus licheniformis*-based adsorbent	6	113.8	148
	Fungus	*Mucor indicus*	5.5	22.1	149
	Algae	*Jania rubens* pretreated with formaldehyde		774	150
	Algae	*Jania* pretreated with $CaCl_2$		1089.6	150
As(III)	Algae	*Mougeotia genuflexa*	6	57.48	154
	Algae	Mixture of green (Chlorophyta) and blue-green (Cyanobacteria) algae	4–5	35	155
	Bacteria	*Yersinia* sp. strain SOM-12D3	7	159	156
	Bacteria	*Bacillus thuringiensis* strain WS3	7	95.238	157
	Fungus	*Saccharomyces cerevisiae*		113.9	61
Hg(II)		EPS-K and EPS-B		2597.62 and 2617.23	159
	Bacteria	*Brevundimonas species* IITISM22	6.5	666.6	160
	Yeast	*Yarrowia* spp.		32.2	161
	Algae	*Sargassum glaucescens*	5,7	147.05	162
	Algae	*Chlorella vulgaris*	6	42.0	164

based adsorbents used for the removal of heavy metal ions together with their important parameters.

8. Inorganic-based adsorbents

Inorganic-based adsorbents are ideal and effective adsorbents for the removal of heavy metal ions, which include clay, soil, minerals and zeolites. Their high affinity for heavy metal ions stems from their properties such as solubility (K_{sp}), charge density, electronegativity, and hydrolysis constant (pK_H). Minerals and soil readily precipitate metal carbonates and hydroxides due to these properties.[171] Ahmadi *et al.* investigated bentonite clay (BC) and bentonite clay@$MnFe_2O_4$ composite (BCMFC) for the removal of Cr(III) and Cr(VI). The adsorption followed the Freundlich isotherm model and quasi-second-order kinetic model and demonstrated physical, spontaneous, and exothermic nature of adsorption.[172] Similarly, red mud,[173] natural clay and clay/Fe–Mn composite,[174] and iron oxide-coated acid-treated activated red mud[175] have been proven to be effective for the removal of heavy metals ions.

Natural and modified zeolites also contribute to the remediation of heavy metals. Their ion exchange properties and molecular sieve-type structures make them suitable candidates for the removal of heavy metals. Further, they offer advantages such as selectivity, low sludge production and compliance with strict discharge standards. Modification of natural zeolites enhances their surface properties.[176] Thus, Neolaka *et al.* reported the use of an activated natural zeolite-magnetic composite (ANZ–Fe_3O_4) as an adsorbent material with a Cr(VI) adsorption capacity of 2.850 mg g^{-1}.[177] Recent studies showed that a zeolite-Ag_2S nanohybrid material exhibited an extraordinary adsorption capacity of 390 mg g^{-1} towards Hg(II) ions in wastewater with higher removal rates than pure zeolite.[178] It was found that the zeolite component of the nanohybrid material provided a porous structure with high surface area, while the Ag_2S NPs enhanced its adsorption capacity, as shown in Fig. 8. Thus, Ag_2S interacted with Hg(II) ions, forming stable complexes *via* $–OH^-$ and $–COO^-$ groups on the nanohybrid surface. The sulphur atom can act as a ligand and attach the Hg(II) ion. Electrostatic interactions are responsible for the stabilization of metal ions on the surface of nanohybrids. Zeolites are aluminosilicates and the interaction of Hg(II) with the oxygen atom present in zeolites or with the sulphur atom present in metal sulfides represents physisorption, as shown in pathway 1 and 2. In pathway 3, the hydrogen atom from one hydroxyl group is removed and metal ions form a bond between two hydroxyl atoms, which represent chemisorption.

Due to chemisorption, strong chemical bonds are formed between Hg(II) ions and the functional groups on the nanohybrid surface. The simple synthesis, high effectiveness and stability of functionalized nanohybrids make them excellent candidates for wastewater remediation.

Similarly, an Na–Y zeolite demonstrated the maximum adsorption capacity of 0.81 mmol g^{-1} for Cd(II) ions. The adsorption process is favorable, as indicated by the separation factor. Physical sorption mechanisms were responsible for the process, as supported by the mean free energy value of less than 8 kJ mol^{-1}.[179] Other zeolite-based adsorbents including zeolites/MgAl-LDHs,[180] magnetic zeolite,[181] and dithizone-immobilized natural zeolite (DIZ)[182] have been employed for the removal of heavy metals *via* the adsorption process.

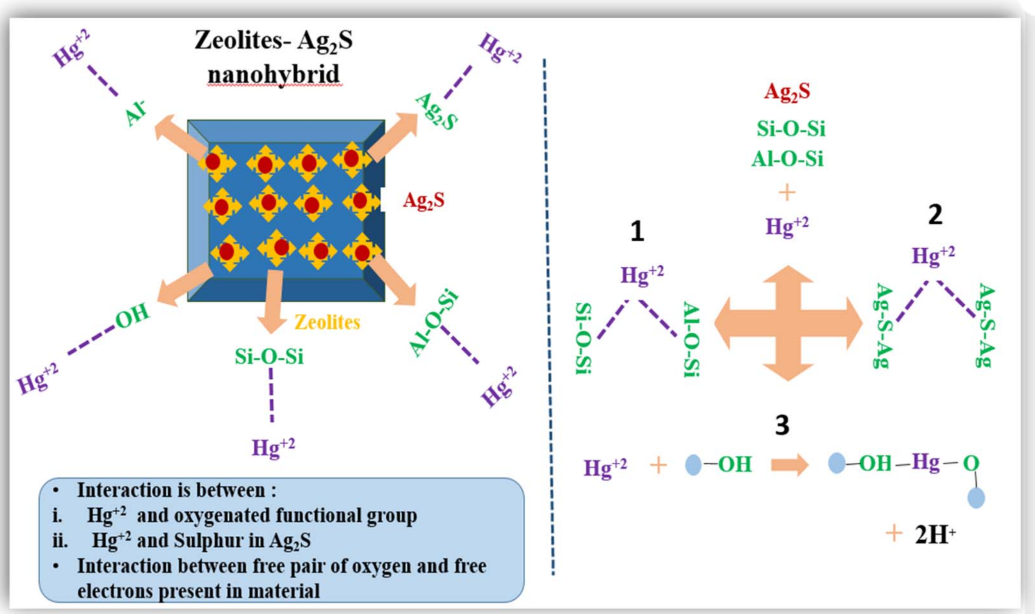


Fig. 8 Major processes of mercury adsorption in zeolite-Ag_2S nanohybrid materials from wastewater. The proposed chemical reaction mechanism: (1) and (2) represent physisorption and (3) represents chemisorption. Reproduced with permission from ref. 178. Copyright [2023], Elsevier. All rights are reserved.

Additionally, silica-based materials such as mesoporous silica as adsorbents offer advantages due to their porosities, large surface areas, and reasonable mechanical thermal stabilities.[183] Snoussi and coworkers employed polyethylenimine-functionalized mesocellular silica foam as an adsorbent, showing more than 90% removal efficiency towards Cd(II) ions.[184] Another study showed that a silica gel material modified with nitrilotriacetic acid (NTA-silica gel) exhibited the maximum adsorption capacity of 76.22 mg g^{-1} for Pb(II) ions. Equilibrium and kinetic studies confirmed that the adsorption followed the Freundlich and Langmuir isotherm models together with a pseudo-second-order kinetic model. The positive $\Delta H°$ values and negative $\Delta G°$ values show that the adsorption of lead is an endothermic and spontaneous process, respectively.[185] Bao *et al.* reported the use of mercaptoamine-functionalised silica-coated magnetic nanoparticles (MAF-SCMNPs) as an adsorbent for the removal of Pb(II) ions. The mechanism involved chelation through the amine group and ion exchange between heavy metal ions and the thiol functional groups on the nanoadsorbent surface. The maximum adsorption capacity of 292 mg g^{-1} for Pb(II) ion showed that silica-based adsorbents can play a role in removing inorganic pollutants such as heavy metals from aqueous medium.[186]

Fig. 9 (ref. 187) shows the mechanism of adsorption and desorption of Pb(II) on mesoporous silica. The understanding of adsorption and regeneration is vital for the synthesis of new adsorbents in the future. Electrostatic interaction is responsible for the adsorption of positively charged lead ions and negatively charged silica. The pH_{zpc} of mesoporous silica is 3.2, above which, it is negatively charged and the concentration of H^+ decreases. The maximum adsorption of Pb(II) takes place at pH 6 through electrostatic interactions. When the pH of the solution is lower than the pH_{zpc} value, the process of desorption from lead-loaded mesoporous silica is dominant.

The other reported silica-based adsorbents include mesoporous silica modified by iron-manganese binary oxide (FeMnOx/SBA-15) with 76.5% FeMnOx mass fraction,[188] silica-based hybrid organic–inorganic adsorbent (MNPs@SiO_2-TSD-TEOS),[189] diatom silica microparticles functionalized with *n*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS),[190] and functionalized mesoporous silica/poly(*m*-aminothiophenol) nanocomposite[191] for the removal of heavy metal ions. Table 5 summarizes the different inorganic-based adsorbents for the removal of heavy metals, together with their important adsorption parameters.

9. Advantages and disadvantages of different adsorbents

- The possibility of regeneration and recovery of metal ions are major benefits associated with biological adsorbents. These adsorbents are eco-friendly, easily accessible, and depending on the biomass source and pretreatment techniques, their adsorption capacities may vary, impacting their selectivity. Mechanical instability and challenges in separating biomass after the removal process are the major disadvantages associated with using microorganisms. Thus, to eliminate these disadvantages, the method of immobilization of microorganisms on a carrier is used which, increases the productivity,

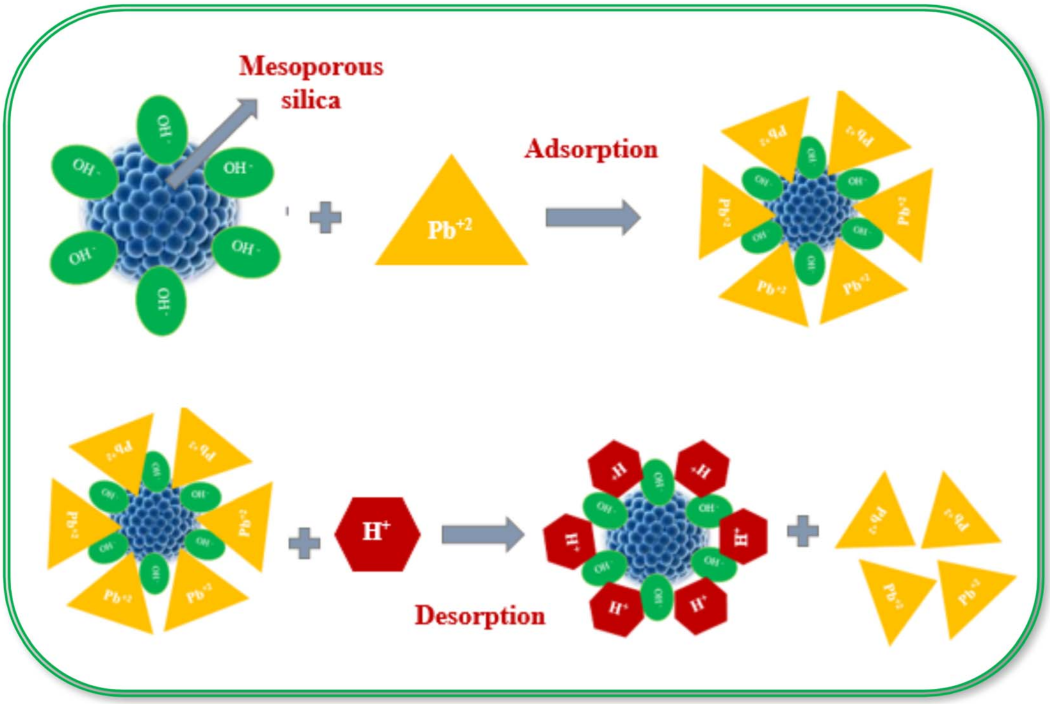


Fig. 9 Mechanism of the adsorption and regeneration of Pb(II) on mesoporous silica. Reprinted with permission from ref. 187. Copyright [2015], Elsevier. All rights are reserved.

Table 5 Comparison of various inorganic-based adsorbents for the removal of heavy metals

Adsorbate	Adsorbent	pH	Adsorption capacity	Ref.
Cr(VI)	Bentonite clay (BC)	3	95.74% 161.3 mg g^{-1}	172
	Bentonite clay@$MnFe_2O_4$ composite (BCMFC)	3	98.65% 178.6 mg g^{-1}	172
	Activated natural zeolite-magnetic composite (ANZ-Fe_3O_4)	2	2.850 mg g^{-1}	177
	Zeolites/MgAl-LDHs		121.85 mg kg^{-1}	180
	Zeolites/ZnAl-LDHs		272.10 mg kg^{-1}	180
Cd(II)	MgO-ATP	5	25.3 mg g^{-1}	192
	Magnetic zeolite		204.2 mg g^{-1}	181
	Na–Y zeolite	5–6	0.81 mmol g^{-1}	179
	Polyethylenimine-functionalized mesocellular silica foam	5	90%	184
As(III) and As(V)	Mesoporous silica modified by iron-manganese binary oxide ($FeMnO_x$/SBA-15) with 76.5% $FeMnO_x$ mass fractions	Below 9	90% of As 32.89 mg g^{-1} As(III) 35.71 mg g^{-1} As(V)	188
	Red mud	7.25 for As(V)	96.52% for As(V)	173
	Natural clay and clay/Fe–Mn composite	3–4	86.86 mg g^{-1} and 120.70 mg g^{-1} for As(V)	174
	Zeolitic imidazolate framework-8 (ZIF-8)	7	As(III) and As(V) were 49.49 and 60.03 mg g^{-1}, respectively	185
Pb(II)	Iron oxide-coated acid-treated activated red mud	6	27.02 mg g^{-1}	175
	Mercaptoamine-functionalised silica-coated magnetic nanoparticles	6–7	292 mg g^{-1}	186
	NTA-silica gel		76.22 mg g^{-1}	185
	(MNPs@SiO_2-TSD-TEOS)	5	417 mg g^{-1}	189
Hg(II)	Diatom silica microparticles functionalized with *n*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS)		169.5 mg g^{-1}	190
	Functionalized mesoporous silica/poly(*m*-aminothiophenol) nanocomposite		242.42 mg g^{-1}	191
	Dithizone-immobilized natural zeolite (DIZ)	5	13.1 μmol g^{-1}	182
	Zeolite-Ag_2S nanohybrid		390 mg g^{-1}	178

improved mechanical strength, and increased chemical resistance.

- Nanomaterial-based adsorbents have a high surface area and enhanced reactivity. However, modified carbonaceous materials face challenges related to complexity, their modification and the need to balance their high adsorption capacity with other desirable properties. Difficulty in the recovery of nanoparticles after adsorption is another limitation associated with nanomaterials. However, magnetic nanoparticles allow easy separation when a magnetic field is applied. Biopolymers such as chitosan are valuable for wastewater treatment due to their hydroxyl and amino groups, facilitating the adsorption of contaminants from wastewater. However, they suffer from drawbacks such as instability, low selectivity, solubility in acidic media, poor mechanical properties and challenges in controlling their pore size. Thus, to address these limitations and capitalize on the strengths of both nanomaterials and biopolymers, bio-nanocomposites have emerged. Examples include cyclodextrin-polycaprolactone/TiO_2-NPs, chitosan/clay, and cellulose nanocrystal/ZnO-NPs, which offer combined properties for effective wastewater treatment.

- Agriculture-based adsorbents such as vegetable and fruit peels are easily available, cost effective, and have abundant functional groups and high metal adsorption capacity, which make them popular adsorbents nowadays. Moreover, they are easily processed, applied, and recovered without causing any harmful effect to the environment. Chemical modification of agricultural waste-based adsorbents improves their adsorption capacity by exposing functional groups. This process involves removing lower molecular weight lignin, waxes and natural fats from the adsorbent, while also creating surface roughness. However, it is important to note that modifying agriculture-based adsorbents can sometimes lead to environmental toxicity. Also, it is worth noting that employing green technology for the treatment of wastewater must not compromise agricultural production, which can potentially exacerbate the food shortage. Thus, the adsorbent from green resources should be carefully selected to ensure they have no value as food sources.

- The abundant clays and clay-based composites have natural physicochemical properties, high specific surface area, extraordinary cation exchange capacity (CEC), surface hydrophilicity, surface electronegativity and cation exchange selectivity, due to which they have gained attention for the remediation of pollutants from water bodies. However, despite the easy availability, low cost and high surface area of clay-based adsorbents, the regeneration of these adsorbents through desorption techniques is not feasible. One more disadvantages is controlling the pH of clay.[34,58,193,194]

- MOFs have a high surface area, highly ordered pore size and shape, which can be tuned by changing the linkage and the type of linkers used. However, despite their remarkable efficacy and selectivity in adsorbing heavy metal ions, many MOFs suffer from poor water and chemical stability.[61]

- Naturally available inexpensive resources for biopolymers have multiple active sites for adsorption but the efficiency of the adsorption process is hindered by their low mechanical strength, low surface areas, and poor stability.[57] Also, biopolymers may undergo degradation under harsh treatment conditions, compromising their effectiveness. Although biopolymers offer sustainability benefits, their drawbacks must be addressed to ensure efficient contaminant removal in wastewater treatment.

10. Conclusion, future prospective and challenges

Among the variety of wastewater treatment methods, the adsorption process is the preferred choice owing to the adsorption potential of different adsorbents for the removal of heavy metals. Among the various carbon-based adsorbents, CNTs modified with four generations of poly-amidoamine dendrimer demonstrated the highest adsorption capacity (4870 mg g^{-1}) towards Pb^{2+} ions. It was found that adsorbents based on micro-organisms such as extracellular polymeric substances (EPS) extracted from Klebsiella sp. NT8 and Bacillus sp. NT10 (EPS-K and EPS-B) exhibit the maximum sorption capacity of 2597.62 and 2617.23 mg g^{-1} for Hg(II) ions, respectively. This review concludes that efficient adsorption depends strongly on the interaction between the adsorbate and the adsorbent, which is mostly influenced by various factors such as pH, initial adsorbate concentration, adsorbent mass and temperature. The majority of the adsorption process data best fit the pseudo-second-order kinetic model, which follows either the Langmuir or Freundlich isotherms. By utilizing low-cost adsorbents such as waste materials and agriculture residues, the environmental hazards associated with heavy metal ion removal can be addressed to meet the WHO standards for drinking water quality. Waste materials can serve as an alternative to replace activated carbon for application in water purification due to their easy availability and low cost. It is expected that low-cost adsorbents will become important for the removal of heavy water from wastewater in the near future. Overall, this review offers guidelines to new researchers on how to develop useful adsorbents with a better adsorption capacity for heavy metal ions in wastewater.

Due to the escalating water contamination crisis, a range of adsorbents is under extensive investigation for treating metal-contaminated waters owing to their extraordinary properties, as outlined in this review. However, despite the advancements, further studies are necessary to optimize the performance of adsorbents. In the future, potential directions for improving adsorbent development and utilizing the adsorption process for industrial applications include:

- A comprehensive investigation into the mechanisms behind the selective and specific adsorption of metal ions is imperative. This endeavor will facilitate the design of targeted removal strategies for the treatment of wastewater, thereby enhancing the efficiency in addressing water contamination issues.
- Although researchers primarily emphasize the exceptional adsorption capacity of various adsorbents, they often overlook their potential environmental impacts. Thus, to address this oversight, it is recommended that the biodegradability of these materials, together with the conditions for their degradation and proper disposal post-use be thoroughly investigated. This holistic approach will contribute to the development of environmentally sustainable adsorption technologies.
- Current studies show that modified adsorbents are more effective compared to unmodified adsorbents. However, the high cost of modification and the use of toxic additives impose limitations on their widespread usage. Therefore, future studies should prioritize the development of alternative modification methods that are both cost effective and environmentally benign.
- The complexity of the adsorption process compounded by the presence of mixed pollutants poses a significant challenge to practical applications. Currently, research efforts focus on single pollutants, thereby limiting the applicability of findings. However, industries are now actively pursuing low-cost adsorbents capable of simultaneously removing multiple coexisting pollutants. This area of research is currently highly active and aims to address the pressing need for comprehensive pollution mitigation solutions.

Conflicts of interest

Authors declare no conflict of interest.

Acknowledgements

Afzal Shah acknowledges the support of Quaid-i-Azam University and the Higher Education Commission of Pakistan.

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