

Review

# Adsorption of Heavy Metals: Mechanisms, Kinetics, and Applications of Various Adsorbents in Wastewater Remediation—A Review

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**Abstract:** Heavy metal contamination in wastewater is a significant concern for human health and the environment, prompting increased efforts to develop efficient and sustainable removal methods. Despite significant efforts in the last few decades, further research initiatives remain vital to comprehensively address the long-term performance and practical scalability of various adsorption methods and adsorbents for heavy metal remediation. This article aims to provide an overview of the mechanisms, kinetics, and applications of diverse adsorbents in remediating heavy metal-contaminated effluents. Physical and chemical processes, including ion exchange, complexation, electrostatic attraction, and surface precipitation, play essential roles in heavy metal adsorption. The kinetics of adsorption, influenced by factors such as contact time, temperature, and concentration, directly impact the rate and effectiveness of metal removal. This review presents an exhaustive analysis of the various adsorbents, categorized as activated carbon, biological adsorbents, agricultural waste-based materials, and nanomaterials, which possess distinct advantages and disadvantages that are linked to their surface area, porosity, surface chemistry, and metal ion concentration. To overcome challenges posed by heavy metal contamination, additional research is necessary to optimize adsorbent performance, explore novel materials, and devise cost-effective and sustainable solutions. This comprehensive overview of adsorption mechanisms, kinetics, and diverse adsorbents lays the foundation for further research and innovation in designing optimized adsorption systems and discovering new materials for sustainable heavy metal remediation in wastewater.

**Keywords:** adsorption; biosorbents; heavy metal; agricultural wastes; traditional and novel adsorbents; wastewater remediation



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## 1. Introduction

The discharge of toxic heavy metals into the environment poses a significant threat to the quality of water and aquatic ecosystems, endangering human health [1,2]. Trace elements such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) are recognized as metallic pollutants in wastewater, industrial effluent, and sewage sludge [3–6]. In surficial environments, the most inorganic stable forms of As and Cr occur as inorganic oxyanions but are frequently referred to as cationic species, e.g., As<sup>3+</sup>, As<sup>5+</sup>, Cr<sup>3+</sup>, and Cr<sup>6+</sup> [7–10]. In general, complete or partial toxic heavy metals removal from wastewater and polluted water is essential to prevent potential health and environmental problems and ensure ecosystem sustainability [11,12]. The World Health Organization has established maximum contaminant or permissible limits for As, Cu, Pb, Cd, Cr, Co, Hg, Ni, and Zn in drinking water at 0.01, 2.5, 0.05, 0.003, 0.05, 0.1, 0.001, 2.0, and 5.0 mg/L, respectively [13]. Traditional methods for removing metal ions from effluents, such as chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction, have limitations, such as insufficient metal removal,

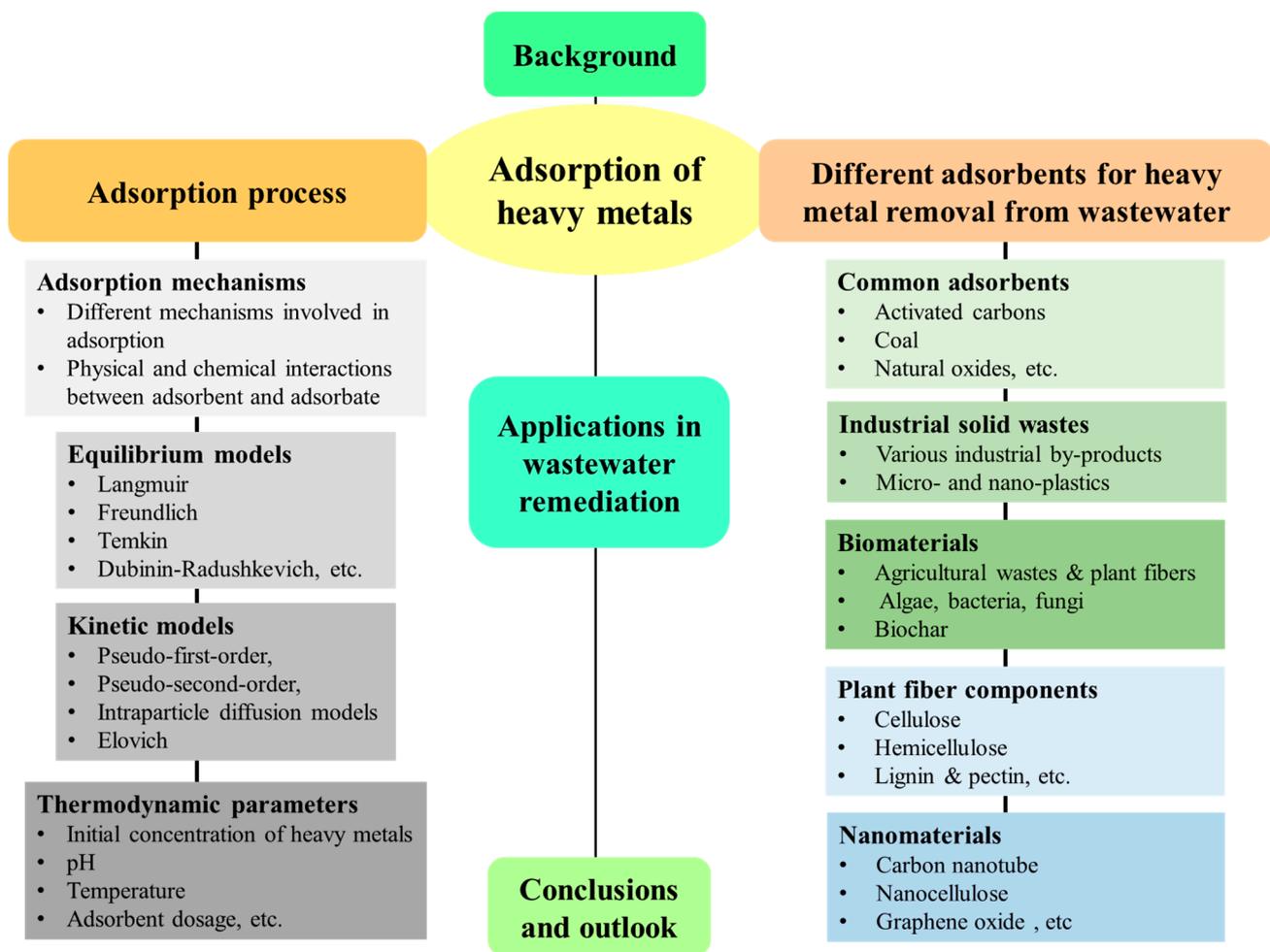
high reagent and energy requirements, and the production of noxious sludge or waste products that require proper disposal [13]. Therefore, it is necessary to devise efficient and environmentally friendly methods for reducing heavy metal content.

Among various methods for removing metal ions, adsorption is regarded as the most promising due to its simplicity of use, high removal efficiency across a wide pH range, and low cost [14]. However, the production of suitable adsorbent materials can be costly, and certain materials, such as commercial activated carbons, cannot be regenerated after use, rendering large-scale applications unsustainable [15]. In order to promote sustainable treatment methods, it is crucial to develop and implement readily available, inexpensive, and renewable adsorbents [16]. The conversion of agricultural waste and residues into value-added sorbents aligns with the circular bioeconomy and green chemistry principles, providing a renewable and environmentally beneficial approach [17]. In this context, the investigation of agricultural, biological, and industrial byproducts as potential metal adsorbents has been motivated by the search for inexpensive and readily available sorbents.

Bioadsorbents have several advantages over traditional techniques. These inexpensive biofilter materials have a high affinity and capacity for metal ions, and they are readily available. Some bioadsorbents exhibit a broad spectrum of metal ion-binding capabilities, whereas others are selective towards particular metal ion types [18]. The use of biological organisms as adsorbents is limited by their intolerance for low pH or high concentrations of toxic metal ions [19]. Plant fibers, in contrast, are chemically and physically more robust, making them appropriate for sorption applications [20]. Metal ions can be effectively adsorbed by plant fibers, which are predominantly made up of cellulose, hemicelluloses, lignin, pectin, and other plant extracts. Metal ions are bonded predominantly to chemical functional groups, such as carboxylic (predominant in hemicelluloses, pectin, and lignin), phenolic (lignin and extractives), hydroxylic (cellulose, hemicelluloses, lignin, and pectin), and carbonyl (lignin and extractives) groups. Through complexation and ion exchange, hydroxyl, carboxyl, and phenolic groups frequently form strong bonds with metal ions [21,22].

Though there are several prospects of bioadsorbents and nanomaterials, such as environmental sustainability, biodegradability, eco-friendliness, high adsorption capacity, etc., issues such as regeneration and reusability, selectivity and specificity, scale-up and practical applications in real-world scenarios, competitive adsorption, and long-term stability and durability still need to be addressed. Moreover, understanding the adsorption process and mechanism, evaluating adsorption kinetics and thermodynamics, designing effective adsorbents, and assessing adsorption capacity are also important in biosorption studies.

This study summarizes the mechanisms, kinetics, and applications of various adsorbents for the removal of heavy metals from an effluent. Bioadsorbents, which include both non-living detritus and living plants and microorganisms, are also studied as alternatives to conventional practices. A schematic representation of this article is presented in Figure 1.



**Figure 1.** A schematic representation of the current review.

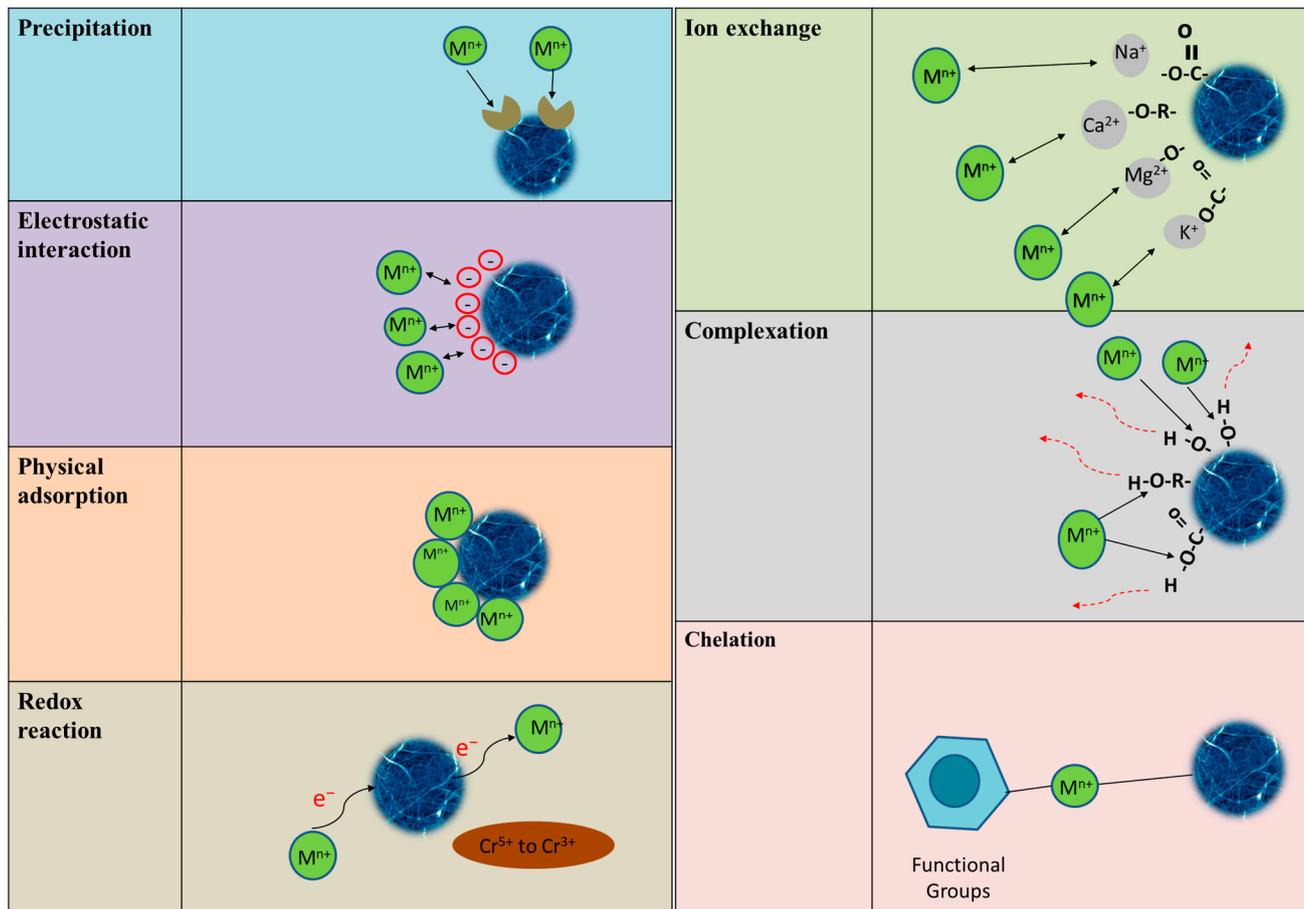
## 2. Adsorption Processes of Heavy Metals

### 2.1. Adsorption Mechanisms

The adsorption process forms a layer of adsorbate (metal ions) on the surface of adsorbents. Adsorption can be reproduced for multiple applications via a desorption method (reverse adsorption in which adsorbate ions are transported from the adsorbent surface) because adsorption is a reversible process in certain circumstances [23]. Adsorption onto a solid adsorbent includes three major steps: transportation of the pollutant to the adsorbent surface from aqueous solution, adsorption onto the solid surface, and transport within the adsorbent particle. Generally, electrostatic attraction causes charged pollutants to adsorb on differently charged adsorbents because heavy metals have a vigorous affinity for hydroxyl ( $\text{OH}^-$ ) or other functional group surfaces [24].

Adsorption is mainly classified into two types: physical adsorption and chemisorption (described as activated adsorption as well). Physical adsorption is the adhesion of an adsorbent to the surface of an adsorbate because of the nonspecific (i.e., independent of the nature of the material) van der Waals force, whereas chemisorption occurs while chemical bonding creates strong attractive forces, i.e., chemical adsorption constructs ionic or covalent bonds through chemical reactions. Nevertheless, physical adsorption is a reversible process but less specific, whereas chemisorption is irreversible but more specific [25]. When adsorption occurs over biological systems, the process is referred to as biosorption. Biosorption is a process that combines metal removal and recovery. Biosorption is effective due to the adsorbents' low cost and ease of regeneration. Bacteria, fungi, algae, industrial waste, agricultural waste, natural residues, and other biological materials have all been widely

used to adsorb heavy metals from wastewater [26]. Physical adsorption, chemisorption, electrostatic interactions, simple diffusion, intra-particle diffusion, hydrogen bonding, redox interactions, complexation, ion exchange, precipitation, and pore adsorption are all possible mechanisms to adsorb heavy metal ions onto bioadsorbents [27,28]. Figure 2 illustrates several possible mechanisms of metal adsorption onto the biosorbents.



**Figure 2.** Different mechanisms of cationic heavy metals adsorption by several types of biosorbents. Adapted from [29,30].

Biowaste materials contain a variety of functional groups, the majority of which are negatively charged, such as hydroxyl, carboxyl, carbonyl, and amino groups. Bioadsorbents, such as plant fibers or other biomass-based materials, often have a porous structure with various cavities and surface sites where metal ions can bind. The presence of these pores and cavities increases the surface area available for adsorption, providing more opportunities for metal ions to interact with and be retained by the biosorbent [31]. As a result, the porous nature of bioadsorbents contributes to their high metal ion adsorption capacity and efficiency in wastewater treatment applications. Adsorption of contaminants from effluents is a process that involves the diffusion of pollutant molecules and their electrostatic attractions to the surface. The adsorption of potentially toxic elements onto wood biochar, for example, can be described by a variety of mechanisms [32]. Possibly, the electrostatic attractions between positively charged metal ions and negatively charged functional groups of bioadsorbents successfully promote the adsorption capacity. Additionally, attractive forces such as hydrophobic interactions, van der Waal forces, and hydrogen bonding could be involved in the process of metal adsorption on the surface of biosorbents [33]. Additionally, complexation and chelation are other known mechanisms in the adsorption process. Generally, complexation is a process that occurs when multiple species combine, whereas chelation is a specific case of complexation that results in the development of

rings [34]. A metal surrounded by ligands takes the central position in the complexation process and forms mononuclear complexes. Polynuclear complexes are created when two or more metals are bound together by ligands in the central position. Likewise, polydentate ligands could be used in the chelation to aid a stable structure formation via multiple bonding [31].

## 2.2. Equilibrium Models

Adsorption at a given temperature can be quantified using mathematical equations in the form of an adsorption isotherm that relates the amount of adsorbate retained by the adsorbent ( $q_e$ ) to the concentration in solution at equilibrium ( $C_e$ ) (Table 1). The two empirical models that are most frequently used for describing the heavy metal adsorption process at a certain temperature and on different bioadsorbent materials are the Freundlich and Langmuir isotherms [35–37]. In addition, Temkin, Dubinin–Radushkevich, Redlich–Peterson, Koble–Corrigan, and Toth isotherms are used to describe how toxic pollutants interact with adsorbent materials [38–41]. Adsorption isotherms play a vital role in interpreting the mechanism of metal ion adsorption onto different adsorbents [42]. These models shed light on the surface properties of adsorbents and the intermolecular interactions between adsorbed molecules and the adsorbent matrix [43]. Isotherm and kinetic models contribute to understanding the adsorption process, relying on various factors, including the adsorbent’s structure and the physical and chemical characteristics of the solute [42]. The Langmuir model finds application in solid–liquid systems, elucidating that all sites on the surface of the adsorbent have equal opportunities to be occupied by heavy metals. On the contrary, the Freundlich model characterizes a non-ideal process occurring on heterogeneous surfaces, often involving multilayer formation [44].

**Table 1.** Commonly used isotherm models for heavy metal adsorption.

Models	Adsorbents	Heavy Metals	Main Findings	References
<b>Langmuir</b> $q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ $q_e$ : amount of adsorbed metal ions per unit mass of adsorbent at equilibrium (mg/g) $C_e$ : metal ion concentration in solution at equilibrium (mg/L) $K_L$ : Langmuir binding constant (L/mg) $q_{max}$ : maximum amount of metal adsorbed per unit weight of adsorbent (mg/g)	Orange peel, Pomegranate peel, Banana peel	Cd <sup>2+</sup> ,		[45,46]
	Peanut Husk	Cu <sup>2+</sup> , Pb <sup>2+</sup>	• Homogeneous surface of bioadsorbents.	[47]
	Rice straw	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>6+</sup>	• Mono layer adsorption.	[48]
	Olive stones	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	• Adsorbate amount has no influence on the adsorption kinetic.	[49]
	Modified rice bran	Pb <sup>2+</sup>	• No interaction between the adsorbed molecules.	[50]
	Oil tea shell	Cu <sup>2+</sup> , Cd <sup>2+</sup>	• A dimensionless model.	[51]
	Cotton fiber	Cu <sup>2+</sup> , Cr <sup>3+</sup> , Pb <sup>2+</sup>		[52]
	Green Alga ( <i>Ulva lactuca</i> ) and its activated carbon	Cr <sup>3+</sup> , Cr <sup>6+</sup>		[53]
<b>Freundlich</b> $q_e = K_F C_e^{1/n}$ $q_e$ : amount of adsorbed metal ions per unit mass of adsorbent at equilibrium (mg/g) $C_e$ : metal ion concentration in solution at equilibrium (mg/L) $K_F$ : Freundlich isotherm constant (mg/g) related to adsorption capacity $n$ : constant related to adsorption intensity	Palm kernel shell,	Cd <sup>2+</sup>	• Heterogeneous surface of biosorbent.	[54]
	Orange peel, Pomegranate peel	Cu <sup>2+</sup>	• Multilayer adsorption with interaction between adsorbed molecules.	[55]
	Chickpea husk	Pb <sup>2+</sup>	• Used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents.	[56]
	Activated carbon	AsFIGURE <sup>3+</sup>	• Amount of adsorbate increases infinitely with an increase in concentration.	[57]
	Moringa oleifera leaves	Pb <sup>2+</sup>		[58]
	Oil tea shell	Pb <sup>2+</sup>	• Used for lower concentration of metals.	[51]
	Rice husk, Bamboo biochar	Zn <sup>2+</sup>	• A dimensionless model.	[59]

Table 1. Cont.

Models	Adsorbents	Heavy Metals	Main Findings	References
<b>Temkin</b> $q_e = \frac{RT}{b_T} \ln(K_T C_e)$ $q_e$ : amount of adsorbed metal ions per unit weight of adsorbent at equilibrium (mg/g) $C_e$ : metal ion concentration in solution at equilibrium (mg/L) $K_T$ : Temkin isotherm equilibrium binding constant (L/mg) corresponding to the maximum binding energy $b_T$ : Temkin isotherm constant $R$ : universal gas constant (8.314 J/mol K) $T$ : absolute temperature (°K)	Olive stones	$\text{Cr}^{6+}$	<ul style="list-style-type: none"> <li>Describes adsorbate-adsorbent interaction.</li> <li>Measuring binding energy.</li> <li>Used to assess the relationship between the bioadsorbent surface and the adsorption heat of all molecules.</li> <li>Estimate adsorption energy of all molecules in a layer.</li> <li>Shows a linear decrease in heat of adsorption of all molecules with an increase in bioadsorbent surface coverage.</li> </ul>	[49]
<b>Dubinin–Radushkevich</b> $q_e = q_m \exp(-\beta \epsilon^2)$ $q_e$ : the amount of adsorbed metal ions per unit mass of adsorbent at equilibrium (mg/g) $q_m$ : theoretical adsorption capacity/the maximum amount of ion that can be adsorbed by unit weight of adsorbent (mg/g) $\beta$ : Dubinin–Radushkevich constant related to the mean free energy of adsorption ( $\text{mol}^2/\text{J}^2$ ) $\epsilon$ : Polanyi potential = $RT \ln(1 + \frac{1}{C_e})$ $R$ : universal gas constant (8.314 J/mol K) $T$ : absolute temperature (°K) $C_e$ : metal ion concentration in solution at equilibrium (mg/L)	<i>F. Carica</i> leaves  Coconut husk	$\text{Co}^{2+}$  $\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+}$	<ul style="list-style-type: none"> <li>Used to distinguish between physical and chemical adsorption by measuring E value.</li> <li>Describes the nature of the biosorption of the sorbate on the biosorbent.</li> <li>Used to calculate the mean free energy of biosorption.</li> <li>Temperature independent.</li> <li>Adsorbent size is comparable to micropore size.</li> <li>Characteristic curve is a Gaussian-type distribution.</li> <li>Follows pore-filling mechanism.</li> <li>Heterogenous surface.</li> </ul>	[50,60]  [61,62]
<b>Redlich–Peterson</b> $q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$ $q_e$ : amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg/g) $K_R$ $K$ $K_R$ (L/g), $a_R$ (L/mg) and $\beta$ (between 0 and 1) are empirical parameters of the R-P isotherm without physical meaning. When $\beta = 1$ , the equation is reduced to the Langmuir isotherm. $C_e$ : metal ion concentration in solution at equilibrium (mg/L)	Mistletoe leaves	$\text{Pb}^{2+}, \text{Cd}^{2+}$	<ul style="list-style-type: none"> <li>The first three-parameter isotherm model.</li> <li>Used to represent adsorption equilibrium over a wide concentration range.</li> <li>Three-parameter model which contains properties of the Freundlich and the Langmuir isotherm.</li> </ul>	[63]
<b>Koble–Corrigan model</b> $q_e = \frac{a C_e^n}{1 + b C_e^n}$ $q_e$ : amount of adsorbed metal ions per unit weight of adsorbent (mg/g) $C_e$ : metal ion concentration in solution at equilibrium (mg/L) $a$ , $b$ , and $n$ are Koble–Corrigan model constant	Activated carbon	$\text{Cr}^{6+}$	<ul style="list-style-type: none"> <li>A three-parameter empirical model.</li> <li>A combination of the Langmuir and Freundlich isotherm.</li> </ul>	[53]

Table 1. Cont.

Models	Adsorbents	Heavy Metals	Main Findings	References
<b>Tóth</b> $q_e = \frac{aC_e}{(b+C_e^d)^{1/d}}$ $q_e$ : amount of adsorbed metal ions per unit weight of adsorbent (mg/g) $C_e$ : metal ion concentration in solution at equilibrium (mg/L) $a$ : Tóth maximum adsorption capacity (mg/g) $b$ : Tóth equilibrium constant $d$ : Tóth model exponent	Rice husk ash	Ni <sup>2+</sup> , Cd <sup>2+</sup>	<ul style="list-style-type: none"> <li>Modification of the Langmuir isotherm to reduce the error between experimental data and predicted values of equilibrium adsorption data.</li> <li>Describes heterogeneous adsorption.</li> </ul>	[64,65]

In a study on Pb<sup>2+</sup> adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo), Lalhruaitluanga et al. utilized a combined Langmuir–Freundlich equation (L–F) to describe the equilibrium relationships between sorbent and Pb<sup>2+</sup> ions in solution [66]. Reddy, Seshaiyah, Reddy, Rao, and Wang evaluated the experimental equilibrium adsorption data using four widely employed two-parameter equations: the Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherms [38]. The findings indicated that the Freundlich model provided the best fit for the Pb<sup>2+</sup> adsorption data on *Moringa oleifera* bark. Chen, Li, Li, Chen, Chen, Yang, Zhang, and Liu [36] observed that the chitosan fibers had better adsorption of Cu<sup>2+</sup> ions than Cr<sup>4+</sup>. This might be due to the amino groups in chitosan fibers, which may have good chelation with Cu<sup>2+</sup> ions. The Cu<sup>2+</sup> ion adsorption process followed the quasi-second-order kinetic equation, and was compatible with the Langmuir isotherm.

### 2.3. Kinetic Models

Kinetic adsorption models describe the mechanism of adsorption of heavy metal ions by biosorbents and particularly determine the rate of biosorption during the removal of heavy metals from wastewater on an industrial scale to optimize the design parameters, including the adsorbate residence time and reactor dimension [67]. In experimental works, the kinetic description of adsorption processes and the removal efficiency of heavy metals by various adsorbents have frequently been evaluated by several mathematical models [68–70], most of which are empirical equations [71–73]. The common kinetics models (pseudo-first order, pseudo-second order, intra-particle diffusion kinetic, and Elovich), which were used to fit experimental data, are expressed in Table 2. The choice between these equations is frequently based on the goodness-of-fit, as judged by the coefficient of determination (R<sup>2</sup>) [73,74]. The use and misuse of adsorption kinetic data and linear forms of pseudo-first-order and pseudo-second-order equations were discussed in [75,76]. Recently, Bullen et al. revised the pseudo-order models and proposed the following equation (Equation (1)), called the ‘revised rate equation’ (rPSO) [77]:

$$\frac{dq_t}{dt} = K' C_t \left[ 1 - \frac{q_t}{q_e} \right]^2 \quad (1)$$

where  $k'$  is the revised pseudo-order rate constant ( $k' = k_2 q^2 / C_0$ ),  $C_0$  is the initial adsorbate concentration in the solution, and  $C_t$  is the adsorbate concentration at time  $t$ . They stipulated that this rPSO provides the first-order and zero-order dependencies upon  $C_0$  and  $C_t$  (amount of adsorbate adsorbed onto adsorbent).

**Table 2.** The kinetic models used for heavy metal adsorption.

Models	Adsorbents	Heavy Metals	Main Findings	References
<b>Pseudo-first order</b> Nonlinear form: $q_t = q_e (1 - e^{-k_1 t})$ Linear form: $\ln(q_e - q_t) = \ln q_e - k_1 t$ $q_e$ (mg/g): amount of adsorbed metal ions per unit mass of adsorbent at equilibrium $q_t$ (mg/g): amount of adsorbed metal ions per unit mass of adsorbent at time $t$ (min) $k_1$ (min <sup>-1</sup> ): pseudo-first-order rate constant	Palm kernel shell	Cd <sup>2+</sup>		[54,69,71,78]
	Chickpea Husk	Pb <sup>2+</sup>	<ul style="list-style-type: none"> <li>Known also as the Lagergren model.</li> <li>Indicates physisorption.</li> <li>Assumes one metal ion is adsorbed onto one adsorption site.</li> <li>Considers the rate of adsorption site occupation is proportional to the number of unoccupied sites.</li> </ul>	[56]
	Black tea leaves	Pb <sup>2+</sup>		[79]
Cherry leaves	Cr <sup>6+</sup>	[80]		
<b>Pseudo-second order</b> Nonlinear form: $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t}$ Linear form: $\frac{t}{q_t} = (\frac{1}{k_2 q_e^2}) + (\frac{t}{q_e})$ $q_e$ (mg/g): adsorption capacity at equilibrium $q_t$ (mg/g): adsorption capacity at time $t$ (min) $k_2$ (g/mg min): pseudo-second-order rate constant	Rice straw	Cu <sup>2+</sup> , Ni <sup>2+</sup>	<ul style="list-style-type: none"> <li>Ho's second-order rate equation</li> <li>Detected as the best suitable. Model with highest R<sup>2</sup> value.</li> <li>Express chemical adsorption of ions, which involve valence forces.</li> <li>Chemical coordination through sharing or exchange electrons between adsorbent and heavy metals (ion exchange).</li> <li>The rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites.</li> </ul>	[48,69,71,78,81,82]
	Oil tea shell	Pb <sup>2+</sup>		[51,83]
	Cotton fiber	Cu <sup>2+</sup> , Cr <sup>3+</sup> , Pb <sup>2+</sup>		[52]
	Rice husk, Bamboo biochar	Zn <sup>2+</sup>		[59]
	Bamboo charcoal	Cd <sup>2+</sup>		[46]
	Mango	As <sup>3+</sup>		[84]
<b>Intra-particle diffusion kinetics models</b> $q_t = k_{id} t^{0.5} + C_i$ $q_t$ (mg/g): amount of adsorbed metal ions at time $t$ (min) $k_{id}$ (mg/g min <sup>0.5</sup> ): intra-particle diffusion constant $C_i$ : thickness of the boundary layer	Raw maize cob	Cu <sup>2+</sup> , Pb <sup>2+</sup>	<ul style="list-style-type: none"> <li>Studies diffusion and rate-controlling steps in the adsorption of adsorbate.</li> </ul>	[69,71,78]
	Rice husk	Cd <sup>2+</sup>		[86]
	Mistletoe leaves	Cd <sup>2+</sup> , Pb <sup>2+</sup>		[63]
<b>Elovich</b> $q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta}$ $q_t$ (mg/g): adsorption capacity at time $t$ (min) $\alpha$ (mg/g min): initial adsorption rate $\beta$ (g/mg): desorption constant $\alpha$ and $\beta$ are related to the fraction of the surface covered and chemisorption activation energy	Peanut husk	Cu <sup>2+</sup> , Pb <sup>2+</sup>	<ul style="list-style-type: none"> <li>Describes chemisorption that controls the rate of adsorption.</li> </ul>	[87]

Wattanakornsiri et al. investigated the removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from waste aqueous solutions using naturally modified biosorbents derived from three local fruit peels: dragon fruit peel, rambutan peel, and passion fruit peel [88]. The study found that adsorption followed the pseudo-second-order kinetic model, and the adsorption data fit well with both the Freundlich and Langmuir isotherm models. However, the Langmuir model demonstrated the best fit.

#### 2.4. Thermodynamic Parameters

A thermodynamic study offers insights into the minimum kinetic energy necessary for the adsorbate to become bound to the adsorption site [89]. The nature of the adsorption process (spontaneity, randomness, endothermicity, or exothermicity) can be evaluated by estimating thermodynamic parameters [72,90] such as the Gibbs free energy change ( $\Delta G^\circ$ , kJ/mol), the standard enthalpy change ( $\Delta H^\circ$ , kJ/mol), and the standard entropy

change ( $\Delta S^\circ$ , J/mol K<sup>-1</sup>) [91]. These parameters can be calculated by the following equations [72,78,92,93] stated as (Equations (2)–(5)):

$$\Delta G^\circ = -RT \ln K_c \quad (2)$$

$$\ln K_c = \frac{C_{ad,e}}{C_e} \quad (3)$$

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

where R represents the universal (ideal) gas constant (8.314 J/mol K), T is the temperature in Kelvin (K);  $K_c$  is the apparent equilibrium adsorption [72] or the Langmuir isothermal constant [92];  $C_{ad,e}$  and  $C_e$  are the concentration (mg/L) of heavy metal in adsorbent and in solution, respectively [78].  $\Delta H^0$  and  $\Delta S^0$  values can be calculated at different temperatures, assuming these parameters to be independent of temperature [90]. A negative or positive value  $\Delta G^\circ$  at a known temperature confirms the spontaneity (or non-spontaneity) of the adsorption process, a positive value of  $\Delta H^\circ$  suggests the endothermic nature of the adsorption of a pollutant by the sorbent, and a positive value of  $\Delta S^\circ$  illustrates an increase in the randomness of the adsorption process [92,93].

The thermodynamic properties associated with the removal of metal ions exhibit variation due to the adsorbent's composition, structure, and surface characteristics, leading to differing affinities for metal ion removal. Enhanced surface area and a porous structure can promote interactions and subsequent adsorption [91]. Factors like the presence of competing ions and shifts in pH can modify the charge distribution on both the metal ion and adsorbent surfaces, thereby influencing thermodynamic equilibrium. Additionally, distinct metal ions possess varying thermodynamic affinities due to their unique electronic configurations and charge densities [22,94].

### 3. Different Adsorbents for Heavy Metal Removal from Wastewater

Numerous adsorbents were used in their native or modified forms to remove metallic trace elements (e.g., heavy metals and metalloids) from wastewater (Table 3). Activated carbons (AC), zeolites, clay minerals, nanosized metal oxides, animal-based wastes, agricultural and food wastes, industrial waste materials, and various advanced adsorbents have been tested for multi-metal removal from wastewaters and aqueous solutions [23].

**Table 3.** Commonly used adsorbents and their performance.

Adsorbents	Heavy Metals Removed	Comments	References
Agricultural wastes (such as rice husk and wheat bran)	As <sup>3+</sup> , Au <sup>2+</sup> , Cr <sup>3+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , Fe <sup>2+</sup>	On the adsorbents surface, functional groups (such as –OH, –COOH, –O–, and –CO–NH–) react with heavy metal ions to remove them from aqueous solution.	[95]
Carbon-based materials (biochar/activated carbon)	Hg <sup>2+</sup> , Cr <sup>6+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup>	Chemical and physical modification can improve heavy metals removal rate. High operating cost. Low selectivity. Regeneration issues could cause secondary pollution.	[29]
Chitosan	Hg <sup>2+</sup> , Cr <sup>3+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup>	Chitosan has a molecular structure similar to cellulose and able to bind ions. The presence of EDTA can decrease heavy metals removal by chitosan (EDTA makes a stronger chelating agent than chitosan).	[96–98]

Table 3. Cont.

Adsorbents	Heavy Metals Removed	Comments	References
Clay minerals	Zn <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>6+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Sr <sup>2+</sup>	Clay is 20 times cheaper than activated carbon. Temperature and pH had a positive effect on heavy metals removal.	[99,100]
Coal	Cd <sup>2+</sup> , Cr <sup>6+</sup> , Hg <sup>2+</sup>	Pre-treatment with nitric acid was necessary. Removal efficiency decreased with increasing temperature.	[101]
Fly ash	Cu <sup>2+</sup> , Cr <sup>6+</sup> , Hg <sup>2+</sup>	It is one of the cheapest adsorbents with high heavy metals removal ability.	[102,103]
Industrial wastes such as slurry and sawdust	Hg <sup>2+</sup> , Cr <sup>6+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup>	Inexpensive abundant materials. Temperature had a positive impact on heavy metal adsorption.	[104,105]
Natural oxide (iron oxide, aluminum oxide, zinc oxide)	Cd <sup>2+</sup> , Cr <sup>6+</sup> , Pb <sup>2+</sup> , As <sup>3+</sup> , As <sup>5+</sup>	Good chemical and physical stability. Low cost. Large specific surface area. High porosity.	[106,107]
Peat moss	Zn <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>6+</sup>	A complex soil material contains lignin and cellulose. The adsorption is higher at lower pH.	[29]
Zeolites	Pb <sup>2+</sup> : 1.6 > Cd <sup>2+</sup> : 1.2 > Cu <sup>2+</sup> : 0.82 > Co <sup>2+</sup> : 0.71 > Cr <sup>3+</sup> : 0.32 > Zn <sup>2+</sup> : 0.25 > Ni <sup>2+</sup> : 0.24 > Hg <sup>2+</sup> : 0	Less costly than activated carbon and 15 times cheaper than chitosan.	[100,108]

EDTA: Ethylenediamine tetra-acetic acid.

### 3.1. Industrial Solid Wastes

Industrial waste can encompass a wide range of materials, including leftover raw materials, production residues, processed by-products, and pollutants generated during manufacturing, processing, or other industrial activities. Various industrial solid wastes showed a significant capacity for adsorption, which could be used to remove metal ions from wastewater. Due to their by-product status, they are readily available and particularly cost-effective. Traditionally, the byproducts like fly ash [109,110], blast furnace sludge [111], waste slurry [112], lignin [113], Fe(OH)<sub>3</sub> [114], and red mud [115] have been utilized as effective adsorbents due to their technological viability to remove heavy metal ions from polluted water [116]. Among the industrial by-products, red mud is considered inexpensive and readily available, as well as highly efficient in metal adsorption. However, the difficulty of disposing of wastewater that is generated during its activation prior to application and its recovery after application has limited its practicability [117]. Several other industrial wastes, including sawdust [118], areca waste [119], tea factory waste [120], battery industry waste [121], waste biogas residual slurry [122], sea nodule residue [123], and grape stalk waste [124] have been used as low-cost adsorbents to remove heavy metals from contaminated water.

Recently, micro- and nano-plastics such as polyamide (nylon), polyester, polypropylene, polyethylene, and polyvinyl chloride were reported to have the ability of heavy metal adsorption. Polypropylene, among the other polymers, showed a higher capacity for adsorption [125]. Godoy et al. studied the adsorption of several heavy metals (Cd, Co, Cu, Cr, Ni, Pb, and Zn) on different types of microplastics [126]. They found that the polyethylene and polyvinyl chloride showed a higher ability to adsorb Pb, Cr, and Zn, while the low adsorption capacity was related to polyethylene terephthalate. Fu et al. described that microplastics have the ability to adsorb heavy metals, and the adsorption process can be influenced by many factors, such as particle size, type of microplastics, and the type and concentration of metal ions [127]. Zon et al. studied the adsorption of Cr by polyethylene micro-beads in seawater [128]. The process was influenced by surface area, reactivity of metals, particle size, and pH. Dong et al. reported the adsorption mechanism

of  $As^{3+}$  by polystyrene microplastic particles [129]. They described that electrostatic forces and non-covalent interactions might be the key mechanisms for  $As^{3+}$  adsorption.

### 3.2. Biomaterials as Metal Biosorbents

Biosorbents, where the biological matrix acts as an active binding site [130,131], are typically obtained from three sources: (i) non-living biomass such as bark, crab shells, shrimp shells, fish scales, krill, lignin, and squid, (ii) algal biomass including micro- and macro-algae, and algal-derived biochar [41], and (iii) living or dead microbial biomass like bacteria, fungi, and yeast [23,132].

Numerous cheap and non-living plant-based materials [133], including potato peels [134], seed shells [135], coffee husks [136], crude olive stones [137], apple peel bead [138], citrus peels [139], shells of hazelnut and almond [140], chemically modified orange peel [141], banana peels and chemically modified banana peels [142], peels from banana, orange, and potato immobilized on sodium alginate beads [143], physic seed hull [144], rice husk [145], millet and *Sorghum vulgare* (Guinea corn) husks [146], rice and corn husk biochar [147], peanut husk [35], coconut husk [148], palm fruit fiber [149], neem bark [150], sugarcane bagasse [151], *Rosa damascena* leaf powder [152], and ajwa date pits [92], watermelon rind [130], etc., have been extensively investigated as prospective heavy metal adsorbents (Table 4).

**Table 4.** Commonly used agricultural wastes for heavy metal removal from wastewater.

Adsorbents	Heavy Metal Removed	Adsorption Conditions	Modification Method	Adsorption Capacity (mg/g)	References
Apple pomace	$Pb^{2+}$ , $Ni^{2+}$ , $Cd^{2+}$	pH 5 IC: 100 mg/L SD: 80 mg to 0.04 g	Chemically modified by nanoparticles such as hydroxyapatite	$Pb^{2+}$ : 303 $Ni^{2+}$ : 250 $Cd^{2+}$ : 100	[153]
Apple pomace	$Pb^{2+}$	pH 4 SD 0.8 g 80 min IC: 100 mg/L	Xanthate	$Pb^{2+}$ : 165	[153]
Carrot	$Fe^{3+}$	pH 1–5 20–260 min IC: 50–200 mg/L	None	$Fe^{3+}$ : 24.33	[154]
Carrot	$Cr^{3+}$ , $Zn^{2+}$ , $Cu^{2+}$	pH 2–5 24 h IC: 20–500 mg/L for $Zn^{2+}$ , $Cu^{2+}$ IC: 20–1350 mg/L for $Cr^{3+}$	None	$Cr^{3+}$ : 1.66 $Zn^{2+}$ : 1.65 $Cu^{2+}$ : 1.82	[155]
Coconut Shaft	$Pb^{2+}$	pH: 1–10 AD: 0.1–1.5 g 20–120 min IC: 25–150 mg/L	KOH	$Pb^{2+}$ : 22.1	[156]
Chickpea (activated carbon)	$Pb^{2+}$ , $Cr^{6+}$ , $Cu^{2+}$	pH 2–10 AC 2–6 g/L 360 min 20–40 °C IC: 100–400 mg/L	KOH and $K_2CO_3$	$Pb^{2+}$ : 135.8 $Cr^{6+}$ : 59.6 $Cu^{2+}$ : 56.2	[56]
Dragon fruit peel	$Pb^{2+}$ , $Cd^{2+}$	pH 3–7 30 °C 15–180 min IC: 100–500 mg/L	$H_2SO_4$	$Pb^{2+}$ : 37.16 $Cd^{2+}$ : 38.04	[88]
Orange peel	$Pb^{2+}$ , $Ni^{2+}$ , $Cd^{2+}$	pH: 2–7 3 h 30 °C IC: 5–1200 mg/L	Methyl acrylate	$Pb^{2+}$ : 476.1 $Ni^{2+}$ : 162.6 $Cd^{2+}$ : 293.3	[141]
Soybean residue	$Pb^{2+}$	pH 2–7 60 min 37 °C 80 MPa	DHPM	$Pb^{2+}$ : 261.4	[157]

Table 4. Cont.

Adsorbents	Heavy Metal Removed	Adsorption Conditions	Modification Method	Adsorption Capacity (mg/g)	References
Soybean residue	Pb <sup>2+</sup>	24 h 30 °C IC: 10–200 mg/L	Microwave-assisted hydrothermal treatment	Pb <sup>2+</sup> : 65	[158]
Rambutan peel	Pb <sup>2+</sup> , Cd <sup>2+</sup>	pH 3–7 30 °C 15–180 min IC: 100–500 mg/L	H <sub>2</sub> SO <sub>4</sub>	Pb <sup>2+</sup> : 39.16 Cd <sup>2+</sup> : 37.60	[88]
Passion fruit peel	Pb <sup>2+</sup> , Cd <sup>2+</sup>	pH 3–7 30 °C 15–180 min IC: 100–500 mg/L	H <sub>2</sub> SO <sub>4</sub>	Pb <sup>2+</sup> : 37.80 Cd <sup>2+</sup> : 34.72	[88]
Date palm fiber	Cd <sup>2+</sup>	pH: 2–8 12–35 °C 250 min IC 10–100mg/L	Pulverization	Cd <sup>2+</sup> : 51.1 Cd <sup>2+</sup> : 3.71	[159]
Plant leaves ( <i>Syzygium cumini</i> and <i>Populus deltoides</i> )	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>6+</sup>	pH: 1–7 AD: 0.5, 1.0, 1.5, 2.0 g/L) 12 h 10–35 °C IC: 50–200 mg/L	HCl	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>6+</sup> (80–100%)	[160]
Sugarcane bagasse	Pb <sup>2+</sup> , Cu <sup>2+</sup> Cd <sup>2+</sup>	pH: 5–7 10–90 min IC: 200 mg/L	Sodium bicarbonate	Pb <sup>2+</sup> : 194 Cu <sup>2+</sup> : 189 Cd <sup>2+</sup> : 114	[161]
Rice husk	Zn <sup>2+</sup> , Hg <sup>2+</sup>	pH: 1.5–6 25–45 °C IC: for Zn: 25–300 mg/L IC: for Hg: 100–1500 mg/L	H <sub>2</sub> SO <sub>4</sub>	Zn <sup>2+</sup> : 19.3 Hg <sup>2+</sup> : 384.6	[162]
Watermelon	As <sup>3+</sup>	pH 2–7 NaOH 0.1 M 20–720 min IC: 5–100 mg/L AD: 5–25 g/L	None	As <sup>2+</sup> : 18.43	[163]

AD: adsorbent dose, IC: ion concentration, DHPM: dynamic high-pressure micro fluidization.

In a study, *Strychnos potatorum* seeds with chemically modified surfaces (SMSP) were examined for their ability to remove Pb<sup>2+</sup> ions from aqueous solutions [164]. The experimental adsorption isotherm data were analyzed, and it was determined that the Freundlich adsorption isotherm model provided a better fit. SMSP exhibited a maximal adsorption capacity of 166.67 mg/g for Pb<sup>2+</sup> ions under optimal conditions comprising a pH of 5.0, a contact time of 30 min, a dosage of 2 g/L, and a temperature of 30 °C. In addition, the adsorption kinetics of SMSP for the removal of Pb<sup>2+</sup> ions was consistent with the pseudo-second-order kinetic model. In a separate study, Shukla et al. assessed the ability of coir, a low-cost lignocellulosic fiber, to remove heavy metal ions such as Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>2+</sup> from aqueous solutions [165]. Langmuir-type adsorption was accomplished using coir fibers. The modified coir fibers (oxidized with hydrogen peroxide) adsorbed 4.33, 7.88, and 7.49 mg/g of Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>2+</sup>, respectively, whereas the unmodified coir fibers adsorbed 2.51, 1.83, and 2.84 mg/g [165].

Algae, a renewable biomass that grows universally and amply in the world's littoral zones, have piqued the interest of numerous researchers as potential new adsorbents for metal ion removal. Several advantages of algae involve their widespread accessibility, low cost, and relatively consistent features [23]. Bioadsorption of Cu<sup>2+</sup> and Zn<sup>2+</sup> using dried marine green macroalgae, *Chaetomorpha linum* [166]; Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> by *Caulerpa lentillifera* [167] are examples demonstrating the effectiveness of algae as heavy metal adsorbents (Table 5). Nowadays, metal ion removal by microorganisms has been considered extremely efficient. For instance, *Bacillus cereus* [168], *Escherichia coli* [169], *Pseudomonas aeruginosa* [170], etc., have all been studied for their ability to bind heavy

metals in aqueous solutions. Additionally, several species of bacteria, including *Bacillus* sp., *Micrococcus luteus*, *Pseudomonas cepacia*, *Bacillus subtilis*, and *Streptomyces coelicolor* have been successfully employed to remove  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  from an effluent [171–173].

**Table 5.** Biosorption of heavy metal ions using microorganisms.

Types of Microorganisms	Strains	Heavy Metal Adsorption Capacity (mg/g)	Main Findings	References
Algae/Macroalgae/Microalgae	<i>Chlorella Sorokiniana</i>	$\text{Cu}^{2+}$ : 8.59 $\text{Pb}^{2+}$ : 18.35	The presence of functional groups in the composition of the adsorption material ( $-\text{C}-\text{O}$ ; $-\text{NH}$ ; $-\text{C}=\text{O}$ ; $-\text{OH}$ ; $-\text{CH}_2$ ) suggests a chemisorption mechanism for heavy metal removal from wastewater.	[174]
	<i>Chlorella vulgaris</i>	$\text{Cd}^{2+}$ : 12.45 $\text{Zn}^{2+}$ : 6.42 $\text{Cu}^{2+}$ : 10.90 $\text{Pb}^{2+}$ : 17.13	Viable and non-viable microalgae biomass were used. Heavy metals adsorption increased significantly with rising initial ion concentration.	[175]
	<i>Spirulina platensis</i>	$\text{Cd}^{2+}$ : 12.08 $\text{Zn}^{2+}$ : 7.36 $\text{Cu}^{2+}$ : 10.33 $\text{Pb}^{2+}$ : 16.97		
	<i>Cystosiera compressa</i>	$\text{Pb}^{2+}$ : 98.8 * $\text{Cu}^{2+}$ : 99.6 *		
	<i>Sargassum vulgare</i>	$\text{Pb}^{2+}$ : 98.3 * $\text{Cu}^{2+}$ : 99.1 *	Brown algae have the highest removal tendency. The adsorption increased by increasing the pH.	[176]
	<i>Turbinaria</i>	$\text{Pb}^{2+}$ : 97 * $\text{Cu}^{2+}$ : 99 *		
	<i>Laminaria hyperborea</i> and <i>Fucus spiralis</i>	$\text{Zn}^{2+}$ : 0.15–0.24 ** $\text{Cd}^{2+}$ : 0.28–0.48 ** $\text{Pb}^{2+}$ : 0.23–0.35 **	Fast adsorption (75% removal of the total amount occurred in the first 10 min for all algal species).	[177]
	<i>Mycelial pellets, Aspergillus fumigatus, and Synechocystis</i> sp. PCC6803	$\text{Cd}^{2+}$ : 37.3	The fungi–microalgae symbiosis can significantly enhance the resistance of microalgae to $\text{Cd}^{2+}$ and increase the adsorption efficiency.	[178]
	<i>Sphaeroplea algae</i>	$\text{Ni}^{2+}$ : 4.15 ** $\text{Cu}^{2+}$ : 3.41 **	The metal ion uptake increased with increasing of initial metal ion concentration at pH 4–6.	[179]
	<i>Synechocystis</i> sp. PCC6803 + $\text{Fe}_2\text{O}_3$	$\text{Cr}^{5+}$ : 69.77 $\text{Pb}^{2+}$ : 62.63 $\text{Cd}^{2+}$ : 42.12 $\text{Cu}^{2+}$ : 38.68	Microalgae and $\text{Fe}_2\text{O}_3$ had a higher adsorption capacity for all four ions than that of $\text{Fe}_2\text{O}_3$ or microalgae alone.	[180]
Bacteria	<i>Bacillus</i> sp.	$\text{Cr}^{5+}$ : 32–83.30 * $\text{Zn}^{2+}$ : 30–78.15 * $\text{Ni}^{2+}$ : 55.06–99.20 * $\text{Cd}^{2+}$ : 66–98.34 * $\text{Hg}^{2+}$ : 40–96.40 *	Biosorption mechanism through the cell wall, as it is comprised of organic macromolecules (polypeptides, polysaccharides, and proteins), which can adsorb heavy metals via electrostatic forces, including van der Waal's forces, covalent or ionic bonds.	[181]
	<i>Desulfovibrio desulfuricans</i>	$\text{Cu}^{2+}$ : 200 $\text{Zn}^{2+}$ : 1700 $\text{Cd}^{2+}$ : 800	Metal biosorption by bacteria involves physicochemical interactions between the metal and the functional groups on the cell surface.	[182]
	<i>Escherichia coli</i>	$\text{Ni}^{2+}$ : 55.31 $\text{Cd}^{2+}$ : 45.37	The biosorption of $\text{Cd}^{2+}$ and $\text{Ni}^{2+}$ was dependent on the concentrations of metal ions. Adsorption efficiency followed the Freundlich adsorption isotherm.	[183]
	<i>Gluconoacetobacter hansenii</i>	$\text{Pb}^{2+}$ : 82 * $\text{Cd}^{2+}$ : 41 * $\text{Ni}^{2+}$ : 33 *	Bio-filtration: utilized heavy metals rapidly due to their small size and high surface-to-volume ratio. Biosorption: included covalent bonding, electrostatic interaction, redox interaction, van der Waals forces.	[184]

Table 5. Cont.

Types of Microorganisms	Strains	Heavy Metal Adsorption Capacity (mg/g)	Main Findings	References
Fungi	<i>Agaricus bisporus</i> (white button mushroom)	Cu <sup>2+</sup> : 43.4	Fungal chitin nanofibers as a film exhibited dynamic Cu <sup>2+</sup> adsorption capacities, with membrane separation mechanism because of its naturally porous structure.	[185]
	<i>Agaricus campestris</i>	Pb <sup>2+</sup> : 99.7 * Cu <sup>2+</sup> : 98.9 *	Biosorbent amounts, immersion time, initial metal ions concentration, and pH had a great effect on heavy metal adsorption.	[176]
	<i>Cunninghamella elegans</i>	Pb <sup>2+</sup> : 278.24 Cu <sup>2+</sup> : 264.88	Chitosan nanoparticles were more effective than bulk fungal chitosan for the remediation and biosorption of contaminant metals.	[186]
	<i>Penicillium chrysogenum</i>	Cd <sup>2+</sup> : 180 Cu <sup>2+</sup> : 190 Pb <sup>2+</sup> : 180	Biosorption capacity of the biomass increased with increasing initial metal ion concentration.	[187]
	<i>Aspergillus ustus</i>	Cd <sup>2+</sup> : 185 Cu <sup>2+</sup> : 185 Pb <sup>2+</sup> : 190	Temperature, pH, and contact time had a great impact on heavy metal adsorption.	
	<i>Penicillium janthinellum</i>	Cr <sup>6+</sup> : 1.77	Langmuir and Freundlich models were used to correlate the experimental data. Removal of Cr <sup>6+</sup> from electroplating wastewater observed was less than from synthetic solution.	[188]
	<i>Phanerochaete chrysosporium</i>	Pb <sup>2+</sup> : 81.93 Cu <sup>2+</sup> : 48.23	Biosorption was a mixture mode with physisorption and chemisorption.	[189]

\* Adsorption efficiency in %, \*\* mmol/g.

Fungi are another frequently used biosorbent, which is easy to grow to produce a high yield of biomass in a short time and can be simply manipulated genetically and morphologically [190,191]. Among the fungi used as biosorbents, *Aspergillus niger* [192], *Saccharomyces cerevisiae* [193], *Lentinus edodes* [193], etc., are the most common species. Bhainsa and D'souza [194] studied Cu<sup>2+</sup> ion removal using *Rhizopus oryzae* biomass modified with NaOH and achieved a maximum adsorption of 43.7 mg Cu<sup>2+</sup>/g. Although fungal biosorbents have a wide range of sources, are inexpensive, and exhibit rapid adsorption, their separation following the process can be difficult [23]. Yeast is also used as an adsorbent, which is a fungus larger than bacteria. Like other eukaryotic organisms, it contains a nucleus and related cytoplasmic organelles [190,195]. For living cells, the cytoplasm is critical because it interacts with metal ions and separates into compartments to remove them once they enter the cells [23]. Han et al. described that waste beer yeast from the brewing industry could be a promising adsorbent to remove Cu<sup>2+</sup> (1.45 mg/g) within 30 min [196].

Apart from the aforementioned biosorbents, biochar prepared from lignocellulosic materials and microalgae can prevent pollutants from reaching organisms via soil or water and reduce bioavailability through adsorption because of its graphene-like carbon matrix, large surface area, high porosity, and increased cation and anion exchange capacity [24]. Biochar has been widely used in anaerobic digestion and in wastewater treatment processes for eliminating pathogens, trace metals, and suspended matter [197]. The adsorption mechanism of biochar depends on the chemical properties of the biochar surface and the nature of pollutants. Generally, three major types of adsorption for biochar are: (i) physical passage, in which pollutants settle on the adsorbent surface; (ii) pore filling, in which adsorbate condenses into the pores of biochar; and (iii) precipitation, in which adsorbate forms layers on the adsorbent surfaces [198]. In fact, the dissociation of O<sub>2</sub>-containing functional groups creates a negatively charged biochar surface, which facilitates electrostatic attraction between cations and biochar. Removal of Cu<sup>2+</sup> from aqueous media was studied using rice straw biochar, which indicated that the ion exchange of native cations with Cu<sup>2+</sup> might be the dominant mechanism for heavy metal adsorption [199]. Microalgae-derived

biochar possesses an irregular porosity of 1 mm, which enables it to act as an adsorbent; however, it has a lower cation exchange capacity (CEC) compared to lignocellulose-derived biochar [200]. Van Hien, Valsami-Jones, Vinh, Phu, Tam, and Lynch applied biochar from biomass residue for remediating Zn-contaminated water and observed that the biomass dose, contact time, and metal concentration had a great effect on heavy metal uptake [59].

### 3.3. Activated Carbon

In recent times, the wastewater treatment industry has shown significant interest in activated carbon (AC) due to its remarkably high adsorption capacity for heavy metals. AC's porous structure, small particle size, high surface area, active free valences, appropriate surface functional groups, and affinity for adsorbing various substances make it a valuable resource with significant adsorption potential in diverse applications [201]. AC is derived from various naturally produced waste materials, including rubber wood sawdust [202], rice husk [203], coconut shell [204], hazelnut shell [205], palm shell [206], apricot stone [207], eucalyptus bark [208], soybean hulls [209], bamboo [210], etc., and has been investigated to extract metal ions from wastewater. Additionally, AC that is altered with alginate [211], tannic acid [212], magnesium nitrate [213], and surfactants [214] might be a viable alternative to remove heavy metals from wastewaters and aqueous solutions.

The mechanism of heavy metal adsorption by AC involves a combination of multiple mechanisms, including physical adsorption, electrostatic adsorption, ion exchange, reduction, complexation, and precipitation [215]. Ongoing advancements have focused on augmenting the adsorption efficacy of AC through modifications employing physical, chemical, organic, and inorganic loading techniques. Physical modification techniques, including microwave heating, ultrasound irradiation, steam activation, and non-thermal plasma technology, have been explored to enhance active sites [215]. Furthermore, chemical modification methods involving acidic and alkaline treatments have also been used [215,216]. While AC is primarily utilized to eliminate unpleasant color, odor, taste, and other organic impurities from water/wastewater, the adsorption capacity of AC is limited by several factors, including loss of adsorption efficacy upon regeneration, the need for regeneration following exhaustion, and the possibility of secondary contamination due to pollutants being separated from the AC but not eliminated [24]. Therefore, research and the use of alternative adsorbents are imperative.

### 3.4. Plant Fiber Components

The use of plant fiber-based food wastes, particularly agro-waste materials, as biosorbents for the removal of heavy metals from aqueous solutions is gaining momentum. Numerous studies have examined the potential use of plant fiber components such as hemicelluloses, cellulose, pectin, and lignin in heavy metal adsorption from an effluent (Table 6). Cellulose is the most prevalent organic compound on Earth, and its high surface area, hydroxyl groups, and porous structure allow for efficient adsorption of heavy metals [217]. Heavy metal removal has been studied using cellulose-based materials such as cellulose nanofibers, cellulose derivatives, and cellulose-based composites. Through surface complexation, ion exchange, and electrostatic interactions, they can absorb heavy metals [218].

**Table 6.** Plant fiber components used for removing heavy metals from wastewater.

Plant Fiber Components	Heavy Metals	Adsorption Condition	Adsorption Capacity (mg/g)	Modifications	References
Cellulose	Cd <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> and Cu <sup>2+</sup>	60 min 2–4 mg/L SLR*: 0.1:10	32–40	Chemically modified by di benzo-18-crown-6 in 5 mL chloroform.	[219]
	Pb <sup>2+</sup> and Cd <sup>2+</sup>	300 mg/L for Pb <sup>2+</sup> 200 mg/L for Cd <sup>2+</sup> pH: 5.5–6.5	Pb <sup>2+</sup> : 465.1 Cd <sup>2+</sup> : 344.8	Chemically modified with succinic anhydride.	[220]

Table 6. Cont.

Plant Fiber Components	Heavy Metals	Adsorption Condition	Adsorption Capacity (mg/g)	Modifications	References
Hemicellulose	Pb <sup>2+</sup> , Cd <sup>2+</sup> and Zn <sup>2+</sup>	120 min Room temperature 50–800 mg/L pH: 3.5–6.5 SLR: 10:50	Pb <sup>2+</sup> : 859 Cd <sup>2+</sup> : 495 Zn <sup>2+</sup> : 274	Chemically modified by microporous xylan-rich hemicelluloses-based hydrogel.	[221]
	Pb <sup>2+</sup>	Time: 6 h Temp: 30–50 °C Initial concentration: 1–20 mg/L SLR: 0.01:20	Pb <sup>2+</sup> : 5.88	Modified by acrylamide to make hydrogel-based hemicellulose.	[222]
Inulin	Pb <sup>2+</sup>	20–80 °C 100 mg/L pH: 7.8	Pb <sup>2+</sup> : 89.38 *	Novel treatment inulin-chitosan.	[223]
Lignin from rice straw	Pb <sup>2+</sup>	8 h 20–80 °C 50–2000 mg/L pH: 2–7 SLR: 0.1:100	Pb <sup>2+</sup> : 95 *	Chemical modified by SO <sub>3</sub> gas (micro-thermal-explosion process).	[224]
Lignin	Pb <sup>2+</sup>	1–8 h 25 °C 50–350 mg/L pH: 2–6.5 SLR: 0.02:35	Pb <sup>2+</sup> : 323.6	Chemical modified: microwave-assisted carboxymethyl lignin.	[225]
Lignin	Cu <sup>2+</sup>	20–60 °C 120 min 100 mg/L pH: 3–5.5 SLR: 0.1:50	Cu <sup>2+</sup> : 37.14	Chemically modified as Aminated lignin by Mannich reaction.	[226]
Pectin (commercial)	Cu <sup>2+</sup>	0–540 min 25 to 55 °C 50 mg/L SLR: 0.03:10	Cu <sup>2+</sup> : 12.38	Hydrogels prepared from pectin lead to increase heavy metal adsorption efficiency.	[227]
Pectin from sweet potato residue	Pb <sup>2+</sup>	25–100 °C 10–180 min 100 mg/L pH: 2–9	Pb <sup>2+</sup> : 263.15	Modified by high hydrostatic pressure-assisted pectinase.	[228]
Pectin from sisal waste	Pb <sup>2+</sup>	30 min Ultrasound 60 °C Cellulase 88 U/g SLR: 1:15	Pb <sup>2+</sup> : 184	Modified with enzymatic and ultrasound.	[229]

SLR: solvent liquid ratio (g/mL) \* adsorption efficiency in %.

Several agro-waste materials (agave bagasse, sorghum straw, oats straw) and their fractions to identify functional groups with hydroxyl, carboxyl, and nitrogen-containing compounds were observed [230,231]. They observed that the lignin exhibited a higher contribution than hemicelluloses regarding the adsorption capacity of Cr<sup>3+</sup> in sorghum straw and oats straw. In the case of agave bagasse, lignin was found to be the primary fraction responsible for Cr<sup>3+</sup> adsorption. In their study, the primary contributors to Cr<sup>3+</sup> removal from an aqueous solution were identified as hemicelluloses and lignin, whereas cellulose present in the studied agro-waste adsorbents did not appear to play a significant role in this process, although cellulose constitutes the largest proportion (greater than 46%) of the agro-waste materials compared to hemicelluloses (12–26%), lignin (3–10%), and other compounds (22–30%). In contrast, Pejic et al. investigated the sorption capacity of waste short hemp fibers for Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> ions in aqueous mediums [232]. They demonstrated that by gradually reducing the amount of lignin or hemicelluloses in hemp fibers via chemical treatment, the sorption characteristics of hemp fibers improved. Short hemp fibers can sorb metal ions (Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup>) from both individual and combined metal solutions. The maximum total adsorption capacities for Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> ions were the same in single solutions, which was 0.078 mmol/g. However, in ternary mixtures, their adsorption capabilities differed, with values of 0.074 mmol/g for Pb<sup>2+</sup> and 0.035 mmol/g for both Cd<sup>2+</sup> and Zn<sup>2+</sup> [232]. Hu et al. reported that the amount of metal

ions attached to rice bran fibers varies [233]. The maximum metal ion ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$ ) binding capacity was demonstrated by soluble hemicellulose: 76.3 mg/g for Pb, 68.5 mg/g for Cu, and 59.1 mg/g for Cd. In contrast, insoluble fiber removed 32.5 mg/g of Pb, 10.6 mg/g of Cu, and 18.3 mg/g of Cd. Rice bran cellulose exhibited low binding capacities: 20.5 mg/g for Pb, 13.6 mg/g for Cu, and 9.9 mg/g for Cd. Al-Ghouti et al. discovered that raw date pits (RDP) could be used as a solid adsorbent to remove copper ions, cadmium ions, and methylene blue (MB) [234]. They discovered two methods for MB adsorption: hydrogen bonding and electrostatic attraction. They observed that the most common method for  $\text{Cd}^{2+}$  to bind in the cellulose/lignin unit was via two OH-groups. In another study, the ability of spruce, coconut coir, sugarcane bagasse, kenaf bast, kenaf core, and cotton to remove  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  ions from aqueous solutions was investigated [235]. The purpose of the study was to determine the relationship between the lignin content of these substances and their capacity to absorb these metal ions. Kartel et al. observed that beet pectin had a high affinity for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , citrus pectin had a high affinity for  $\text{Ni}^{2+}$ , and apple pectin had a high affinity for  $\text{Co}^{2+}$  [236]. This could be due to the substantial structural differences between pectin sources. According to Khotimchenko et al., pectin with an esterification level close to “0” binds the most  $\text{Zn}^{2+}$ . The degree of methylation, which varies between 1 and 60%, is the primary factor influencing heavy metal adsorption [237].

It has been well-established that plant fiber components exhibit effective heavy metal removal from wastewater. The adsorption capacities are influenced by various factors, such as contact time, pH, concentration of heavy metals, adsorbent dosage, and temperature [13,22,238]. To better understand the adsorption behavior of these components, models of adsorption isotherms, kinetics, and thermodynamics have been utilized. Furthermore, numerous modification techniques, including chemical modification, surface functionalization, and composite formation, have been investigated to enhance the adsorption efficiency of these plant fiber materials.

### 3.5. Nanomaterials

Conventional adsorbents, some of which are depicted above, typically have an insufficient capacity for metal adsorption and thus cannot efficiently remove the majority of heavy metals in wastewater treatment [23]. In this concern, researchers investigated how to develop novel adsorbents with enhanced properties and functionalities. These days, there is a high demand for highly porous nanostructures such as graphene [239], fullerene [240], nanosized metal oxides and MXene [24], graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) and metal-organic frameworks [23], halloysite particles [216] and especially, carbon nanotubes [241] have been reported as substitute adsorbents to remove metal ions from wastewater considering the advantages of nanotechnology (Table 7). They are usually strong, resistant, electrically conductive, non-corrosive, and thermally stable. Additionally, high surface areas and large pore volumes of these nanomaterials, when associated with different types of intermolecular interactions, enable effective adsorption in a variety of systems [24]. By and large, these nanomaterials outperform conventional adsorbents such as titanium dioxide, activated carbon, and iron oxide. Nevertheless, novel materials also have shortcomings, and therefore, scientific and technological research must address issues of durability and functionalities, which are critical in environmental applications [24].

**Table 7.** Some commonly used nano-adsorbents for heavy metal removal.

Nano-Adsorbents	Heavy Metals Removed	Main Findings	References
Aluminum oxide ( $\text{Al}_2\text{O}_3$ )	$\text{As}^{3+}$ , $\text{As}^{5+}$ , $\text{Cd}^{2+}$ , $\text{Cr}^{6+}$ , $\text{Pb}^{2+}$	The highest adsorption of $\text{Cr}^{6+}$ was at pH 4. Adsorption of $\text{As}^{3+}$ , $\text{As}^{5+}$ was observed at a pH range of 2–8. Initial ion concentration showed a positive correlation with metal adsorption efficiency.	[106]

Table 7. Cont.

Nano-Adsorbents	Heavy Metals Removed	Main Findings	References
Carbon nanotube (multi-walled carbon nanotube functionalized and sulfonated)	$\text{Co}^{2+}$ , $\text{Zn}^{2+}$	Using nanofiltration. 98% removal of $\text{Zn}^{2+}$ due to the reduction of membranes' pore size. Functionalization was critical. Removal efficiency was dependent on zeta potential, hydrophilicity of the fillers, and oxygen functional groups on the surface of this membrane.	[242]
Cellulose (micellar-enhanced ultrafiltration)	$\text{As}^{3+}$ , $\text{Cd}^{2+}$	Using nanofiltration. >90% removal of $\text{As}^{3+}$ at pH > 7. Competing anions decreased removal rate.	[243]
Copper oxide (CuO)	$\text{Pb}^{2+}$ , $\text{Co}^{2+}$	High specific surface area. Uniform size distribution. High purity. pH affected the distribution of metal ions and surface activity.	[107]
Ferric oxide ( $\text{Fe}_3\text{O}_4$ )	$\text{Cu}^{2+}$	Using cyclodextrin as host substance. Very fast adsorption. $\beta$ -cyclodextrin polymer crosslinked with utilized aromatic groups.	[244,245]
Graphene oxide (GO)	$\text{Cd}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$	High cost Reusable High selectivity	[246]
Graphene oxide (GO: modified magnetic graphene oxide filled polyethersulfone)	$\text{Co}^{2+}$ , $\text{Cu}^{2+}$	Using nanofiltration. Led to a significant increase in the pure water flux due to changes in surface roughness and hydrophilicity of polyethersulfone 92% removal.	[242]
Graphitic carbon nitride (g- $\text{C}_3\text{N}_4$ )	$\text{Cd}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$	Challenges for cheap raw material Requirement of a specific reactor. High selectivity Limited reusability	[246]
Iron oxide ( $\text{Fe}_3\text{O}_4$ )	$\text{As}^{3+}$ , $\text{As}^{5+}$ , $\text{Cd}^{2+}$ , $\text{Cr}^{6+}$ , $\text{Pb}^{2+}$	The removal of $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ by this adsorbent is greater than aluminum oxide. The highest adsorption of $\text{Cr}^{6+}$ was at pH 4. Adsorption of $\text{As}^{3+}$ and $\text{As}^{5+}$ were observed at pH 2–8.	[106]
Iron oxide (magnetic $\text{Fe}_3\text{O}_4$ )	$\text{Al}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$	pH-dependent Nitrogen dependent Adsorption mechanism includes surface binding and molecular diffusion.	[247]
Manganese oxide ( $\text{MnO}_2$ )	$\text{Cd}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pb}^{2+}$	High redox potential, possible layer structures, and negatively charged surface in neutral pH. An efficient adsorbent for toxic metal ions, including $\text{Cd}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pb}^{2+}$ , etc. Adsorption of ions was not only on its surface but also intercalated the interlayers of $\text{MnO}_2$ .	[24,248]
Metal-organic framework-based nanocomposite	$\text{Cd}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$	Poor stability in water. Lack of information about regeneration. No competitive adsorption between coexisting heavy metals was unknown.	[26,249,250]
Nickel–ferrite (magnetic $\text{NiFe}_2\text{O}_4$ )	$\text{Cr}^{6+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$	Adsorbent dosage and contact time had a positive correlation with removal efficiency. pH showed a negative effect on heavy metals removal.	[251]
Nickle oxide (NiO)	$\text{Pb}^{2+}$ , $\text{Co}^{2+}$	Increase porosity. Increase hydrophilicity of membrane. Higher negative zeta potential. Higher $\text{Pb}^{2+}$ removal than the precipitation method.	[107]
Titanium Carbide ( $\text{Ti}_3\text{C}_2\text{T}_x$ )	$\text{Cu}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$	Limited reusability Lower durability High selectivity	[24]
Halloysite	$\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	Sulfuric acid pretreatment Low energy consumption Higher efficiency at higher pH levels	[216]
Alumina nanofibers	$\text{Hg}^{2+}$ , $\text{Pb}^{2+}$	The effects of initial concentration, contact time, and selectivity of the nanofibers were assessed. The removal efficiency was 98% for $\text{Hg}^{2+}$ ions and 90% for $\text{Pb}^{2+}$ ions. Most ion contaminants were eliminated within the first hour. The data best fit a pseudo-second-order model.	[252]

Nanosheets composed of two-dimensional nanomaterials, comprised of  $\text{Ca}^{2+}$  (Ca) and  $\text{Y}^{3+}$  (Y) cations along with carbonate  $[\text{CO}_3^{2-}]$  anions, referred to as  $\text{CaY-CO}_3^{2-}$  layered double-hydroxide (LDH) materials, exhibit exceptional affinity and selectivity for toxic transition metal ions such as  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , as well as metalloid  $\text{As}^{3+}$  [10]. Furthermore, there is an emerging focus on the use of nanoparticles derived from food wastes, particularly nano-cellulose, as potential adsorbents for heavy metal removal [253,254]. A review by Fayaz et al. explored the utilization of nano-cellulose obtained from food waste through various treatment processes [255]. When subjected to specific treatments, nano-cellulose can be modified to enhance its adsorption capacity for metal ions in wastewater treatment [256]. These modified nano-cellulose materials show promise as they possess inherent advantages like renewability, biodegradability, and low cost, given their origin from food waste. However, to fully harness their potential, further research and development efforts are required to optimize their durability and functionalities in environmental applications. The exploration of nano-cellulose and its derivatives from food waste as adsorbents represents a sustainable and innovative approach toward mitigating heavy metal pollution in water resources.

#### 4. Conclusions and Outlook

The use of various non-toxic adsorbents has proven to be a successful approach for the simultaneous removal of multiple heavy metals, metalloids, and other pollutants from polluted water and wastewater. This method is highly effective, practical, economical, and environmentally friendly [39,257]. To achieve optimal results, mathematical tools [258], such as machine learning algorithms [259], can be employed to assess and optimize the adsorption processes' isotherms, thermodynamics, kinetics, and operational parameters. In this regard, low-cost and locally available agro-biowastes have emerged as promising candidates for heavy metal and metalloid removal on an industrial scale. These biowastes, such as plant fibers, fruit and vegetable peels, and byproducts from food processing industries, possess large multi-chemical functional groups, surface area, cation-exchange capacity, and controllable pore structures [30,88]. Their physical preparation as adsorbents adheres to the principles of green chemistry. Additionally, these bioadsorbents can be reused for multiple cycles, further enhancing their cost-effectiveness and sustainability [39,260,261]. Despite these advancements, further research is necessary to optimize the performance of adsorbents, explore new materials, gain deeper insights into the underlying mechanisms, and develop more cost-effective and sustainable methods for heavy metal removal from wastewater. An outline diagram for the challenges and potential opportunities associated with the present topic is presented in Figure 3 and described as follows:

1. Biological adsorbents, including microbial biomass, algae, and fungi, utilize living or nonliving biomass to bind heavy metals. These bioadsorbents are eco-friendly, easily accessible, and can be regenerated through biomass regeneration or metal recovery procedures. However, their adsorption capacities and selectivity may vary depending on the biomass source and pretreatment techniques. In contrast, nanomaterials, such as nanoparticles and nanocomposites, offer distinct advantages for heavy metal adsorption due to their small dimension, large surface area, and enhanced reactivity. Through magnetic or functionalized modifications, their recyclability and reusability can be improved. Nevertheless, concerns about potential environmental impacts and long-term stability must be addressed;

2. Inexpensive adsorbents like agricultural waste materials, such as vegetable and fruit peels, have gained popularity due to their abundant surface functional groups, leading to high metal adsorption capacities. These readily accessible plant-based materials, including plant fibers and other detritus, offer cost-effective and efficient sorbents for metal ions. Utilizing plant-based byproducts as metal sorbents aligns with circular bioeconomy and green chemistry principles, offering economically viable and eco-friendly solutions. However, their application may require pretreatment to enhance adsorption efficiency and stability. A practical application involves using plant fibers as low-cost biowaste for adsorbing heavy metals from polluted water or acid mine drainage generated by mining industries. In this method, fibers can act as adsorbents in a bioreactor, attracting and retaining heavy metal ions (Figure 4);
3. Current research in the field of heavy metal adsorption and removal from water primarily focuses on the adsorption of heavy metal cations. However, there is a noticeable lack of specific studies on the adsorption of hydroxy compound ions or other complex ions. In most documents, the adsorption of complex ions is only briefly mentioned or addressed in a limited manner;
4. Modeling the biosorption process is challenging due to the diverse physical and chemical processes involved. The nature of active sites in bioadsorbents varies significantly based on their source, making characterization difficult. While successful in validating experimental data for single-component biosorption, real-life scenarios often involve multiple components adsorbing simultaneously on a heterogeneous biosorbent surface. This complexity leads to dynamic interactions between metal ions and functional groups, making the modeling of such systems more intricate;
5. Plant-based adsorbents require surface modifications to enhance their surface functionalities and develop suitable pores for effective adsorption. Surface oxidation, sulfonation, amination, and adjustments to pore structures are crucial processes in achieving improved adsorption performance. Various modification procedures, such as chemical, mechanical, thermal, gasification, and combinations of these techniques, are available to tailor the adsorbent properties according to specific contaminant removal needs. By exploring and optimizing these modification methods, plant-based adsorbents can be fine-tuned to be efficient and versatile tools for water and wastewater treatment, contributing to sustainable and eco-friendly solutions;
6. Modified carbonaceous materials have shown great promise in achieving high adsorption capacity and efficient removal of heavy metals. However, the process of modification, especially through chemical means, can be quite intricate. This complexity, along with considerations of cost, yield, and operational practicality, poses challenges for their application on an industrial scale. Additionally, the use of some novel modifiers might introduce new sources of pollution, making it essential to carefully assess their environmental impact;
7. Further study of selective adsorption and competitive adsorption behavior among heavy metal ions is highly valuable. Understanding the mechanisms that govern the preferential adsorption of specific metal ions and how different ions interact and compete for adsorption sites can significantly enhance the development of efficient and targeted remediation strategies for contaminated water and wastewater;
8. In future research, the regeneration of carbon-based materials, particularly plant fibers, holds significant practical importance. Exploring the properties of these materials and understanding the optimal operational conditions for the regeneration process are essential steps. Additionally, the development of effective desorption solutions is crucial for ensuring the full utilization and reusability of carbon-based adsorbents.

## Challenges and opportunities in heavy metal adsorption

**Diverse adsorbents and their characteristics**  
**Biological adsorbents**

- Possibility of regeneration and metal recovery
- Varying adsorption capacities and selectivity

**Nanomaterials**

- Enhanced reactivity and surface area
- Concerns of addressing potential environmental impacts and long-term stability

**Utilizing agricultural waste materials**

- Abundant surface functional groups
- Cost-effective and efficient sorbents
- Circular bioeconomy and green chemistry
- Practical applications (e.g., plant fibers for acid mine drainage)
- Require pretreatment for enhanced efficiency and stability

**Selective and competitive adsorption behavior**

- Understanding preferential adsorption and ion interactions

**Surface modifications of plant-based adsorbents**

- Tailoring surface functionalities and pore structures
- Modification techniques

**Complexities of modeling biosorption**

- Heterogeneous surface and dynamic interactions

**Expanding research scope**

- Focus on only heavy metal cations in current literature
- Lack of studies on hydroxy compound ions and complex ions

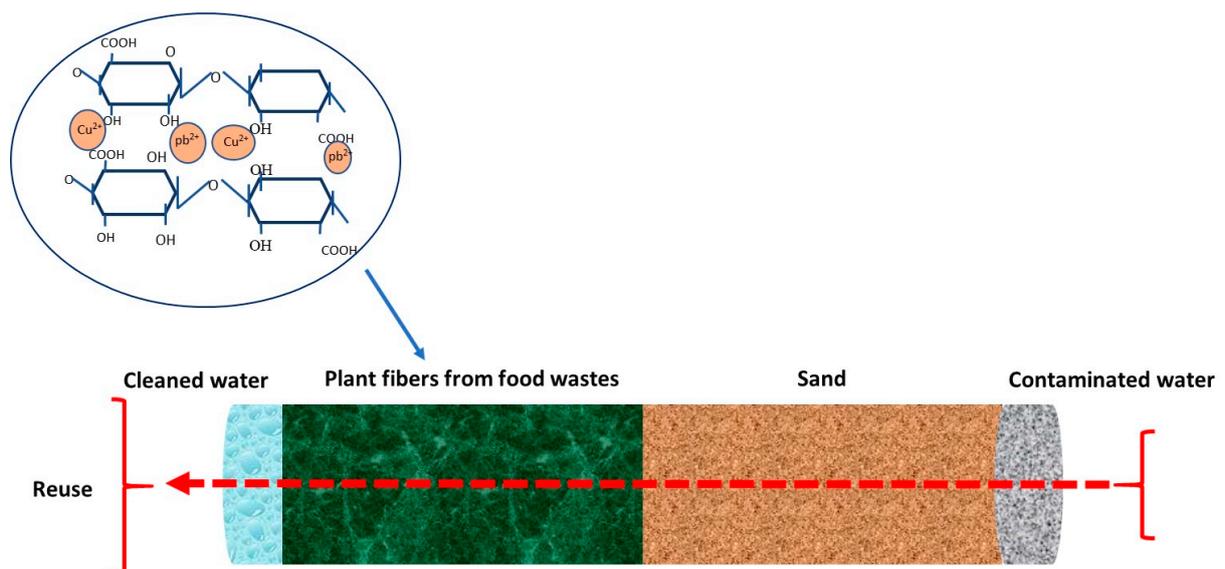
**Challenges in modified carbonaceous materials**

- Balancing high adsorption capacity and complexity of modification
- Cost, yield, and industrial practicality
- Evaluating environmental impact of novel modifiers

**Regeneration of carbon-based materials**

- Practical importance of regeneration
- Exploring properties and optimal conditions
- Developing effective desorption solutions

**Figure 3.** Outline diagram for the challenges and potential opportunities of heavy metal removal from wastewater.



**Figure 4.** Biofilter for removing heavy metals from contaminated water.

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