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Application of biomass adsorbents in the treatment of heavy metals in wastewater: a review

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ABSTRACT

In recent years, heavy metal pollution has become an increasingly serious problem, and various remediation technologies are progressing and breaking through. Biomass is the most widespread and most abundant substance on earth, and it has low cost and good environmental compatibility. The adsorption materials prepared from biomass as a raw material have high removal rates, green environmental protection, degradability, large specific surface area and high porosity. This article reviews the research progress of biomass adsorption materials in heavy metal wastewater treatment. First, we elucidate the basic types of biomass materials, the common preparation and modification methods, and the main mechanisms of biomass materials in adsorption. Second, the application of various biomass adsorption materials in heavy metal pollution treatment is highlighted, and we also summarize the main factors affecting the biomass adsorption process. Finally, there are still many problems with biomass adsorption materials, and biomass adsorption materials with high recovery rates, good selection performance and mass production are not yet available. More extensive and comprehensive research is urgently needed.

Keywords: Biomass material; Heavy metal; Water pollution; Adsorption

1. Introduction

In the aqueous environment, heavy metals exist in the form of ions or water-insoluble compounds. Volcanic eruptions, untreated mining wastewater, domestic sewage, and the input of atmospheric depositions rich in heavy metals will sharply increase the content of heavy metals in water [1,2]. A large number of studies have shown that the most toxic heavy metals to the human body are mainly lead, mercury, arsenic, cadmium, and chromium. Table 1 shows the sources, hazards, and vulnerable groups of heavy metals. Heavy metal pollution can pose a serious threat to human health. Therefore, strengthening the prevention and control of the natural environment, as well as repairing the damaged environment, have become urgent tasks and are important parts of today's environmental protection work.

Common heavy metal wastewater treatment technologies include ion exchange, membrane separation, bioremediation, chemical precipitation, and adsorption [3–5]. The membrane separation method and chemical precipitation

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have the potential to cause secondary pollution [6–9]. Azamat et al. [10] used a molybdenum sulfide membrane to separate mercury ions from wastewater, and the results showed that the molybdenum sulfide membrane could accurately separate mercury ions from wastewater, but the molybdenum sulfide membrane used was difficult to degrade by itself, which would cause membrane fouling. Zou et al. [11] reviewed the application of nanozero valent iron and its composite materials in the removal of heavy metal ions. After chemical precipitation, the heavy metal ions in the wastewater will be converted into insoluble compounds and enter the sludge. Therefore, we need to consider the recycling and harmless treatment of the reactants after treatment. Compared with other technologies, the adsorption method has the advantages of low cost, simple operation, good removal effect, and the adsorbent can be degraded or regenerated by itself. Therefore, it has good application prospects in the field of wastewater treatment and remediation.

The selection of suitable adsorbent materials is the key to effective wastewater treatment. In recent decades, the most commonly used adsorbent materials have been activated carbon, nanomaterials, etc. [12–16]. However, agriculture and industrial processing often produce a large amount of waste, which will cause solid waste accumulation problems if not treated in time. Therefore, biomass adsorption materials have become a major trend in the research and development of materials for removing heavy metal ions from wastewater [17,18]. The number of articles on the application and review of biomass adsorbents in wastewater is increasing, but most of the review articles only discuss a specific heavy metal or simply summarize the application of biomass materials in polluted wastewater. However, a comprehensive review of the preparation and modification methods of biomass adsorption materials and their adsorption mechanism for heavy metal removal is still lacking. For example, Fan et al. [19] reviewed the research status of biomass-based adsorption materials for uranium pollution removal, and the research content is relatively singular. Ani et al. [20] reviewed the application of biomass adsorption materials in dye wastewater, heavy metal pollution, and crude oil wastewater, but the summary of heavy metal pollution is very brief and insufficient for reference.

Therefore, considering the complexity of biomass adsorbents in the treatment of heavy metal pollution, this paper comprehensively summarizes the application of biomass adsorbents in the treatment of heavy metals in wastewater according to the following points. (1) The types, preparation and modification methods, and adsorption mechanism of biomass adsorption materials are summarized. (2) We focus on the theory and application of biomass adsorption materials in heavy metal pollution remediation. (3) We discuss the main factors affecting the adsorption of biomass materials. (4) We point out the current problems of biomass adsorption materials and prospect their future industrial-scale applications.

2. Preparation and mechanism of biomass adsorption materials

2.1. Preparation modification of biomass adsorbent

Biomass has a wide distribution, many types, and sufficient resources, including all living substances (animals, plants, microorganisms) and their excreta and metabolites [26]. The materials commonly referred to as biomass are mainly lignocellulose, agricultural and forestry waste, algae, fungi, and other substances (Fig. 1) [27]. However, natural biomass contains many impurities, which reduces the heavy metal absorption rates. In addition, natural biomass has a large amount of moisture and is an adsorbent material that is difficult to store. Therefore, in practical applications, this natural biomass is usually activated and modified first to improve the adsorption capacity of the adsorbent and to

Table 1
Sources, hazards, and vulnerable groups of heavy metals

Heavy metal	Source	Harm	Vulnerable population	References
Pb	Atmospheric deposition, sewage irrigation, pesticides, fertilizers, electronic waste, automobile exhaust, etc.	Anemia, cerebral hypoxia, cerebral edema, pregnancy abortion, fetal malformation, etc.	Children, elderly individuals, and the immunocompromised	[21]
Hg	Coal-burning, nonferrous metal smelting, cement industry, domestic waste incineration and landfill, volcanic eruptions, etc.	Slurred speech, facial dementia, paralysis of hands and feet, loss of senses, ataxia, heart failure, etc.	Pregnant women, seafood lovers	[22]
As	Mining, smelting, rock weathering, volcanic eruptions, use of arsenic pesticides, coal burning, etc.	Skin lesions, myocardial damage, polyneuritis, etc.	Farmers, housewives, special occupation workers groups	[23]
Cd	Mining, smelting, fuel, used batteries, etc.	Hypertension, cardiovascular and cerebrovascular diseases, renal dysfunction, etc.	Mining workers, immunocompromised people	[24]
Cr	Inferior cosmetic raw materials, leather preparations, industrial pigments, etc.	Numbness of limbs, mental abnormality, rhinitis, pharyngitis, laryngitis, bronchitis, etc.	Residents in areas with serious water pollution	[25]

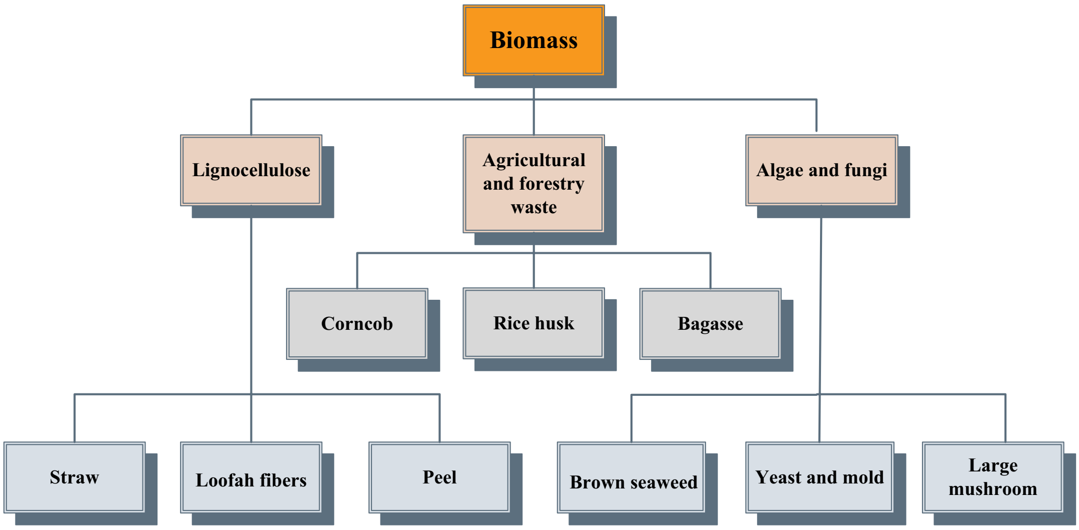

Fig. 1. Common biomass materials.

make it easier to store. At present, the commonly used modification methods include physical modification, chemical modification, and composite modification (Table 2).

2.1.1. Physical modification

Physical modification is used to change the surface structure of biomass employing pyrolysis and microwaves, thereby improving the adsorption and increasing the adsorption capacity [28,29]. Biomass that is more sensitive to heavy metals and has a high adsorption capacity can be considered for physical modification, and the basic preparation steps are shown in Fig. 2 [30,31]. First, biomass raw materials are collected from different sources and cleaned according to the parameters of the biomass adsorption material to be prepared, and waters of different purities (tap water, deionized water, distilled water, or ultrapure water) are used to remove the dirt and dust particles from the surface of the raw material. Then, the samples are dried to remove moisture. They can be dried naturally at room temperature and then placed in an oven for drying or directly placed in an oven for vacuum drying and finally ground and sieved. Wang et al. [32] prepared cork biomass carbon (CBC) by pyrolysis and studied its adsorption behavior on Cu(II). As seen in Fig. 3, compared with the unmodified cork, the cell wall of CBC modified by pyrolysis became thinner than that of the raw material, with a large number of open pores on the surface and an increase in the specific surface area. With the increase in temperature and time, the number of small pores gradually increases, and some small pores also collapse to form larger pores. The results showed that the biochar prepared at 750°C had the highest specific surface area (392.5 m^2/g), and the maximum adsorption capacity of Cu(II) was 18.5 mg/g. Das et al. [33] prepared maize stalk biochar (MSB), Lantana Camara biochar (LCB), pine needle biochar (PNB), and black gram biochar (BGB) by the microwave method. and their adsorption capacities were preliminarily evaluated. The characterization revealed that MSB had the largest porosity (65.90%), PNB had the smallest porosity (52.66%), the total pore volume of LCB was the largest (3.99 cm^3/g), and BGB had the smallest porosity (2.47 cm^3/g). The experimental results show that the heavy metal removal rates by the biomass carbon prepared are above 45%~50%, which are much higher than that of all the original biomass without modification (2%~5%).

2.1.2. Chemical modification

Chemical modification mainly involves chemical reactions such as cross-linking, grafting, and oxidation of biomass materials and their derivatives. On the one hand, by adding chemical reagents such as acids and bases and organic substances to change the functional groups on their molecular chains [34], while on the other hand, biomass can be compounded with other materials to introduce new functional groups, thus improving the adsorption performance. Compared with physical modification, chemical modification can change the molecular formulas and molecular structures of the biomass materials, improve the adsorption effect of adsorbents and increase the mechanical stability of adsorbents. Singha et al. [35] used an aqueous sodium hydroxide solution to modify agricultural and forestry waste okra and used it as an adsorbent to treat toxic metal ions in wastewater. Through characterization, it was found that when okra was treated with alkaline solution, lignin and polysaccharides underwent a hydrolysis reaction, introducing a large amount of –COOH, which increased the adsorption capacity. Adsorption experiments showed that the maximum adsorption capacities of alkali-modified okra reached 72.72, 57.11, 121.51, and 273.97 mg/g for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}, respectively, which were 3–11 times higher than those of untreated okra. Okoli et al. [36] treated pristine mosses with sodium tripolyphosphate and ethylene glycol while using pristine and modified mosses to remove Pb(II) and Cd(II) from aqueous solutions. The adsorption data showed that the mosses treated with tripolyphosphate and ethylene glycol adsorbed more Pb(II) (74.9%) than the original mosses (14.4%) and more Cd(II) (33.6%) than the original

Table 2
Commonly used biomass adsorbent modification methods

Modification method		Mechanism	Advantages	Disadvantages	References
Physical modification	Pyrolysis	In an inert gas atmosphere, the pore structure of the material is changed by high temperature.	Ease of operation; increased specific surface area and the total number of pores	The pore structure collapses easily	[45]
	Microwave method	Exposing biomass materials to microwave radiation causes the material to absorb the number of microwaves, thereby changing its surface groups.	Fast heating; no pollution; easy to control	The surface of the prepared material is rough and the carbon skeleton shrinks easily	[46]
	Graft cross-linking method	After pretreatment, a specific grafting and cross-linking process is used to attach small specified organic molecule groups to the biomass adsorbent material.	It can link a variety of functional groups and polymeric small molecules to enhance adsorption performance	The operation is cumbersome, the experimental conditions are harsh, and it is difficult to achieve industrial applications	[47]
Chemical modification	Acid modified	Introduction of acidic functional groups to promote the formation of mesoporous structures in materials.	Increased polarity and specific surface area	Fewer nonpolar groups on the surface and reduced nonpolarity	[48]
	Alkali modified	Similar to acid modification, commonly used alkaline reagents include NaOH, $(NH_4)^+$ reagents, etc.	Effectively increases the specific surface area of the material and the content of oxygen-containing functional groups	Fewer polar groups, surface polarity to be improved	[49]
Compound modification		Composite of two different biomass materials, or composite modification and blending of a biomass material with a certain polymer material.	Enhanced thermal stability	Severe experimental conditions make it difficult to achieve industrial applications	[50]

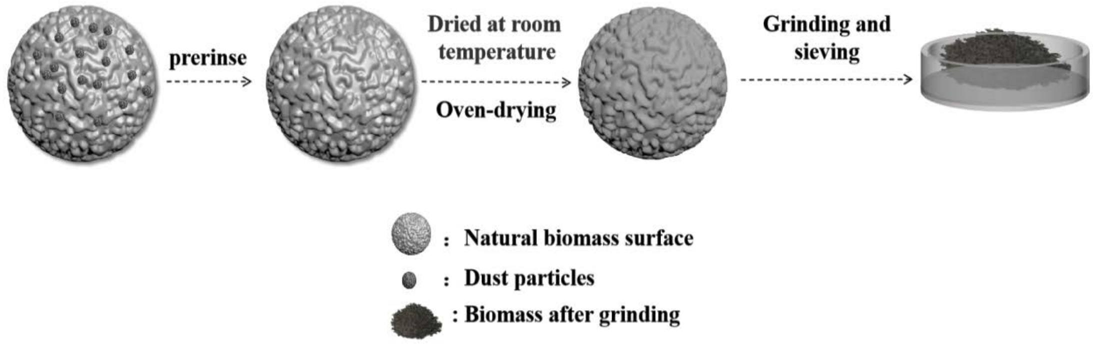

Fig. 2. The basic steps of physical modification.

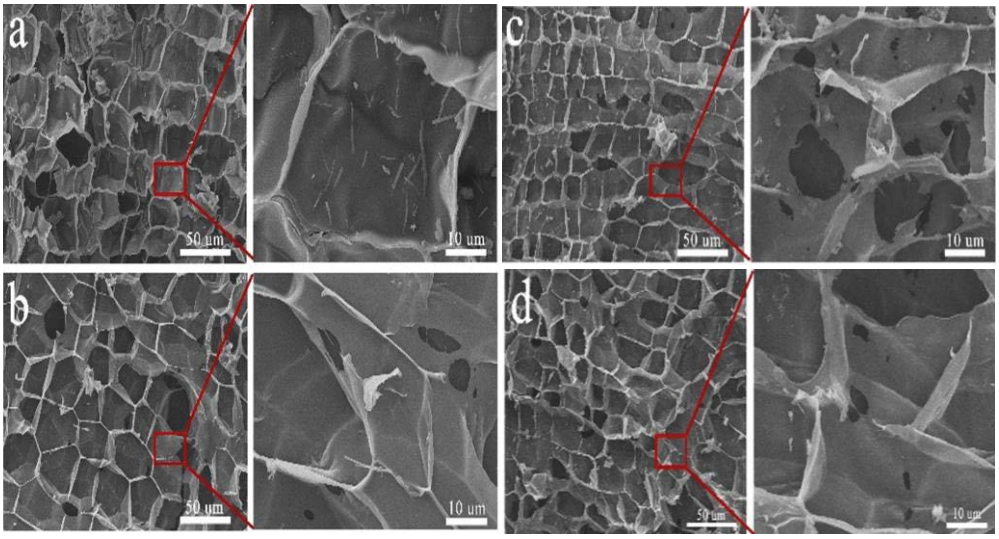

Fig. 3. SEM images of the cork adsorbents (a), CBC-450°C (b), CBC-750°C (c), and CBC-550°C (d).

mosses (26.2%). This is because tripolyphosphoric acid and ethylene glycol effectively remove Gram bacteria in moss, and in addition, the specific surface area and active functional groups of the modified moss are effectively increased. Ibrahim et al. [37] prepared an adsorbent by cross-linking a crown ether onto corn starch and using it to adsorb heavy metals. Their results show that the adsorbent removal rates were still as high as 75%~99.8% during the fourth adsorption. It can be seen that chemical modification can effectively improve the heavy metal adsorption performance of biomass adsorption materials and exert its maximum effect.

2.1.3. Composite modification

In addition to physicochemical modification, two different biomass materials can be compounded, or a biomass material can be modified or blended with a polymer material to a prepare composite material with better adsorption properties [38]. Sargın et al. [39] added bleached algae to a chitosan matrix to investigate the adsorption capacity of new chitosan algal beads for Cd(II), Cr(III), Cu(II), Ni(II), and Zn(II). As shown in Fig. 4, the surface of the chitosan beads is smooth, the surface of the chitosan-algae composite is rough, algae particles almost cover the surface of chitosan, and the addition of algae enhances the thermal stability of the composite. The results show that the adsorption capacities of chitosan algae beads for Cd(II) and Zn(II) ions were higher than those of ordinary chitosan beads, and the concentrations of Cd(II) and Zn(II) in the treated aqueous solutions were lower than 0.500 mmol/g. In addition, to improve the recycling rate of biomass adsorbents, magnetic composite adsorbents can be prepared by combining biomass with magnetic materials [40,41]. Son et al. [42] used marine macroalgae as a raw material to prepare magnetic biochar by doping the microalgae with iron oxide particles such as magnetite, which was then used to remove Cu^{2+}. The results show that although the magnetic biomass carbon has a low surface area (63.33 m^2/g), the removal rate of Cu^{2+} can reach 75%, and the recovery rate of the magnetic biomass carbon after use is as high as 96.3%.

2.2. Adsorption mechanism

The adsorption mechanisms of heavy metal ions by biomass adsorbents have been the object of interest for researchers. In recent years, many researchers have conducted

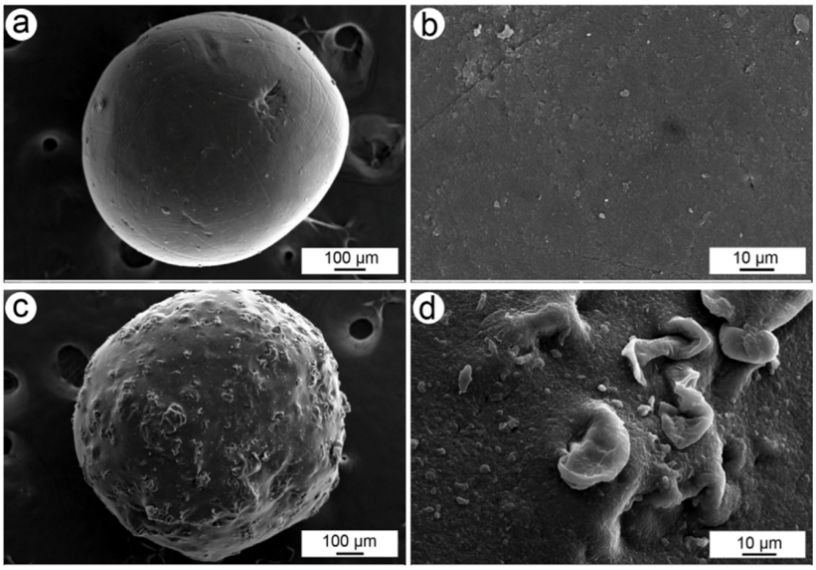

Fig. 4. SEM images of the plain chitosan microbeads (magnification: a: 100×, b: 10×) and chitosan–algal biomass composite microbeads (c: 100×, d: 10×).

numerous studies on biomass adsorbents and proposed various adsorption mechanisms. However, due to the wide variety of biomass adsorbents and the different heavy metal ions to be adsorbed, a unified and complete theoretical system has not been formed until today. However, as far as the current study shows that of the adsorption mechanisms of heavy metal ions by biomass adsorbents, there are two main types [43,44]: physical adsorption and chemisorption (Table 3). Depending on the type of adsorbent used and the conditions under which it is applied, these mechanisms may act synergistically (Fig. 5).

3. Applications of biomass adsorption materials in the removal of heavy metals from wastewater

In the process of heavy metal adsorption and removal, we often use various raw or modified biomass adsorbent materials. This section summarizes the application of lignin fibers, agricultural and forestry wastes, and algae and fungi in the adsorption and removal of heavy metals from water.

3.1. Applications of lignocellulose materials in the removal of heavy metals from wastewater

Lignocellulose refers to by-products of agriculture, forestry, and other cultivation industries and their processed waste, such as vines, straw, fruit residues, corn stalks, rice stalks, tree branches, and fruit peels [56,57]. At present, the most widely studied are corn stalk, loofah, peel, and other lignin fibers. The main components of lignocellulose are cellulose (30%–50%), hemicellulose (10%–30%) and lignin (20%–30%), which have a certain ion exchange and adsorption capacity [58], and the mechanisms of their adsorption of heavy metal ions are mainly surface complexation and ion exchange [59]. Cellulose, which is the backbone of lignocellulose, is a linear polymer consisting of dehydrated glucose groups linked by β-1,4-glycosidic bonds. Cellulose is an alkaline soluble substance of amorphous polymers that use hydrogen bonds (with ion exchange) to form a hard network structure of cell walls. Hemicellulose is a complex phenolic macromolecule composed of monomers of the phenylpropane structure linked by C–O or C–C bonds (functional groups for adsorption), and lignin plays a role in filling and reinforcing cell walls.

Corn stover has a rough surface and high porosity and contains surface functional groups such as carboxyl, hydroxyl, phosphorus-containing, sulfur-containing, and nitrogen-containing groups, which are very favorable for the physical–chemical adsorption of pollutants by corn stover [60]. Second, the direct accumulation of corn stover is very easy, the cost of purchasing corn stover is low, and the use of corn stover for the adsorption of hazardous substances is simple and free of secondary contamination. It has been shown that unactivated corn stover exhibits good adsorption properties for certain heavy metal ions [61]. Jia et al. [62] used untreated corn stover as an material to adsorb Pb(II) from wastewater, and the results showed that the maximum adsorption capacity of corn stover for Pb(II) (15.0269 mg/g) was achieved after 3 h of contact at pH = 6 and T = 298 K, and the removal efficiency reached 90.75%. Meng et al. [63] physicochemically modified corn stover with $ZnCl_2$ and adsorbed vanadium (V) from contaminated groundwater with the modified material, and their results show that the removal efficiency of the modified corn stover reached 100% for vanadium (V). Therefore, corn stover has broad development prospects as an adsorbent for the efficient removal of the heavy metals in water.

Loofah fibers are vascular bundles in the mature fruits of loofah, and their system is a mesh of interwoven multilayered filamentous fibers, each of which in turn consists of many parallel-arranged bundles of micron-sized ducts, resulting in a unique porous structure and excellent mechanical strength [64]. Tang et al. [65] used loofah activated by NaOH to adsorb Cu(II) ions and found experimentally

Table 3
Biomass adsorption mechanisms

Adsorption method		Mechanism	Mechanism	References
Physical adsorption		The adsorbent adsorbs the adsorbate to the surface and immobilizes it without changing the physicochemical properties of the adsorbent.	Adsorption of Pb^{2+} by algae	[51]
Chemical adsorption	Ion exchange mechanism	The heavy metal ions are exchanged with another cation on the cell wall of the adsorbent, the heavy metal ions are adsorbed and the cations are released by the process.	Pb^{2+} adsorption by rapeseed	[52]
	Surface complexation mechanism	Nitrogen, oxygen, and sulfur in the main functional groups on the surface of biomass adsorbent can act as ligand atoms, providing lone pair electrons to form complexes with heavy metal ions in ligand complexes.	Solid nitrogen source doped biomass activated carbon complexed with heavy metal ions	[53]
	Enzymatic mechanism	It occurs during the adsorption of heavy metals by active biological cells, and during active adsorption, the activities of certain cellular heavy enzymes have an important influence on the adsorption of metal ions.	Heavy metal adsorption from wastewater by filamentous fungal biomass	[54]
	Inorganic microprecipitation mechanism	The process by which heavy metal ions form an inorganic precipitate on the cell wall or within the cell.	Yeast biomass adsorbent on Pb^{2+} in adsorption solution	[55]

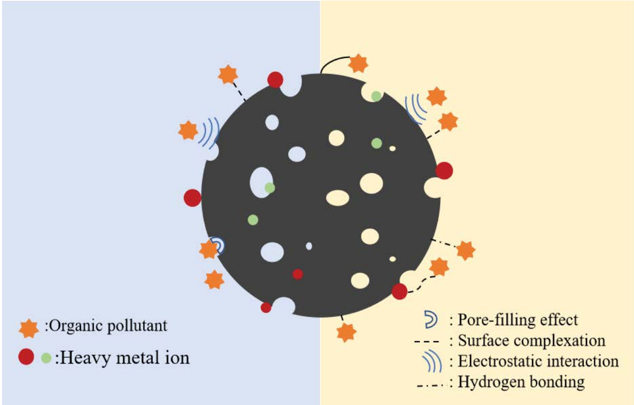

Fig. 5. Physical–chemical collaboration.

that the highest removal of Cu(II) ions by the modified loofah was achieved when the pH of the aqueous solution was 8.0. Zhao et al. [66] successfully synthesized magnetic loofah biochar for the removal of copper ions from water. Their results show that the adsorption process was dominated by chemisorption, and the highest removal rate was achieved when the adsorbent dose was 20 mg and pH = 5.5. The adsorption performance of the magnetic loofah biochar could still be maintained at more than 75% after four cycles.

Fruits are an indispensable part of daily life and provide essential nutrients for human health. Both in the fruit processing industry and in the daily consumption of fruits, a large amount of waste peel is produced. The outer surface of the peel is usually honeycomb or irregularly folded, with a rich pore structure inside and a large specific surface area, thus allowing sufficient contact with dye particles and heavy metal ions in wastewater [67,68]. In addition, the main components of fruit peels are cellulose, hemicellulose, and pectin, which are rich in functional groups such as –COOH, –OH, and $–NH_2$, allowing the peels to adsorb pollutants from wastewater [69,70]. Abdić et al. [71] investigated the adsorption performance of eight heavy metal ions (Cd, Co, Cr, Cu, Cu, Mn, Ni, Pb, and Zn) with untreated and chemically modified orange peels. Their results show that the adsorption capacities of the natural adsorbent materials were lower than those of the modified adsorbents, and the adsorption capacities of these eight heavy metal ions by the modified orange peels were increased by approximately 40% on average, with removal rates of 97.90%. Rashed et al. [72] used physically modified pomegranate peel for the removal of Cu^{2+}, Cd^{2+}, and Zn^{2+} from wastewater. The experimental results show that the adsorption and removal rates of these three heavy metal ions by pomegranate peel were Cu^{2+} (80%) > Cd^{2+} (50.5%) > Zn^{2+} (32.5%). All the above results indicate that fruit peels can be used as a good adsorbent for the removal of heavy metals from wastewater.

3.2. Application of agroforestry wastes in the removal of heavy metals from wastewater

Agroforestry wastes are by-products of the production and processing carried out in agricultural and forestry plants, and common agroforestry wastes include corn cobs, peanut shells, bagasse, and rice husks [73,74]. Agroforestry wastes have the advantages of a wide source, low price, well-developed pore structure, large specific surface area, and regeneration [75]. Agroforestry wastes contain special structures, such as cellulose, lignin, pectin, and tannin, which contain a variety of functional groups, such as hydroxyl, carboxyl, and amino groups that have a strong ability to bind to heavy metal ions [76].

The corn cob is the corn shaft after threshing, and the corn cob contains a special structural and chemical composition that can provide a large number of active groups, such as hydroxyl, carboxyl, and amino groups [77], which are conducive to chemisorption reactions, such as surface complexation and ion exchange with heavy metal ions (Fig. 6) [78]. Additionally, after modification, the internal porosity and specific surface area of corn cob will be increased, and the content of active groups with adsorption capacity for heavy metals will be increased; thus, the adsorption capacity of corn cob will be substantially increased [79]. Luo et al. [80] modified corn cobs with acrylonitrile at different pyrolysis temperatures to improve the adsorption capacity of corn cobs and investigated the adsorption capacity of modified corn cobs for cadmium in solution. The results showed that at 350°C, the corn cob modified with acrylonitrile was successfully activated and modified, and the modified corn cob had enhanced thermal stability and more pore channels, so the adsorption effect was significantly improved.

In daily life, most peanut shells, rice husks and bagasse will be directly discarded, and only a little will be used as fuel, which causes some pollution to the environment. To make full use of its high specific surface area and abundant functional groups, peanut shells [81,82], rice husks [83,84], and sugarcane bagasse [85,86] were physically and chemically modified to enhance their adsorption capacities for wastewater treatment. Wisniewska et al. [87] removed highly toxic Pb(II) and acrylic acid with activated carbon made from waste materials such as peanut shells and corn cobs. It was found that Pb(II) could penetrate the porous structure of activated carbon. Zhan et al. [88] prepared highly charged carboxy cellulose nanofibers from rice husks by a chemical oxidation method and investigated their adsorption performance for the removal of Pb(II) and La(III) from polluted water. The adsorption amounts of Pb(II) and La(III) were found to be 193.2 mg/g and 100.7 mg/g, respectively. Razi et al. [89] prepared adsorbents by modifying sugarcane bagasse activated carbon with phosphoric acid and subsequently removed zinc and iron from textile wastewater. They found that sugarcane bagasse activated carbon could achieve 80% removal of both Fe and Zn.

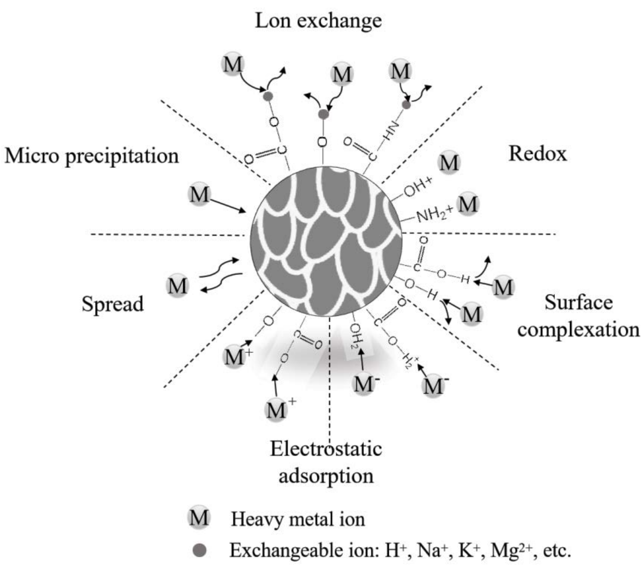

Fig. 6. Adsorption mechanisms of corncob for heavy metal ions.

3.3. Applications of other biomass adsorbent materials in the removal of heavy metals from wastewater

Other biomass adsorption materials include substances such as algae and fungi. The cell walls of algae are mainly composed of polysaccharides, lipids, and proteins [90]. The cells on the surface of algae are covered with folds, so they have a large specific surface area, and there are many negative charges on the surface of algae cells, which can provide functional groups, such as hydroxyl, amino, carboxyl and carbonyl groups, which can bind to heavy metal ions. Poo et al. [91] compared the adsorption capacity of marine macroalgae with that of pine wood for heavy metal ions. Their results show that the maximum removal of Cu, Cd, and Zn by pinewood was 81%, 46%, and 47%, respectively, while the removal rates of all three heavy metals by marine macroalgae were higher than 86%, which indicates that the adsorption performance of marine macroalgae on heavy metal ions was better than that of pine wood. Foroutan et al. [92] investigated the adsorption of copper and cobalt from synthetic wastewater by modified brown algal biomass. They found experimentally that the adsorption capacities for Cu(II) and Co(III) by the adsorbent were 13.73 and 13.966 (mg/g), respectively, and that the process was spontaneous and increased with increasing temperature.

Fungi, such as yeasts, molds, and large mushrooms, are eukaryotic microorganisms without chloroplasts that are widely distributed in nature. The cell walls of natural fungi contain large amounts of proteins, lipids, organic acids, and other metabolites [93]. Common fungi include yeasts, molds, and large mushroom species. Alothman et al. [94] synthesized fungal biomass sorbents using Penicillium and Aspergillus and used them to remove heavy metals. The experimental results showed that the adsorption performance characteristics of the synthesized novel biomass adsorbents were enhanced. Yan et al. [95] used NaOH pretreated fungi to prepare adsorbents as a means to adsorb heavy metal pollutants in an aqueous solution. The adsorption capacities of the adsorbents increased rather than decreased with five adsorption–elution–regeneration cycles, showing good adsorption performance. This shows that fungi are a promising adsorbent material.

4. Main factors affecting the adsorption process

The factors affecting the adsorption process are diverse and various factors produce different effects on the adsorption process, which are related to the physicochemical properties of the adsorbent and the target heavy metal ions as well as the specific mechanism of adsorption.

Numerous studies have shown that the pH, temperature, adsorbent dosage, and contact time during the adsorption treatment process can have an impact on the final removal effect [96–98].

4.1. pH

There are three main effects of the solution pH on adsorption as follows [99]. (1) It affects the degree of dissociation of different compounds. When the solution is too acidic or too alkaline, dissolution of some adsorbents may result. Naseem et al. [100] investigated the adsorption of Cu(II), Co(II), and Ni(II) by Vigna radiata husk in wastewater. They found that when the pH was too high, heavy metal ions would form hydroxides and precipitate due to the presence of a high concentration of –OH in the aqueous solution, hindering the adsorption of heavy metal ions by quinoa hulls. (2) The pH value will change the chemical state of the active site of the adsorbent and the existing form of heavy metal ions in water, thereby affecting the electrostatic interaction and adsorption free energy between the adsorbent and the adsorbate and changing the performance of the adsorbent. Yang et al. [101] prepared a porous double network hydrogel adsorbent from peanut shells and investigated the optimal parameters for the adsorption of Cd(II) and Pb(II) by this adsorbent. Their final results show that when pH was < 2.5, it was difficult to adsorb metal cations onto the hydrogel surface due to electrostatic repulsion. When the pH was > 2.5, the electrostatic repulsion was weakened, the functional group of the adsorbent could be complexed with metal cations, and the removal efficiency of the adsorbent for Pb(II) and Cd(II) increased to nearly 100% and 85%, respectively. (3) The solution pH also affects the solubility of the adsorbent as well as the charge and other chemical properties of the adsorbent surface, promoting its molecularization and the formation of complexes to increase the adsorption amount. Noli et al. [102] investigated the effect of pH on the adsorption of uranium and cadmium by aloe vera. The results show that when the pH is 4, the maximum absorption of uranium by aloe vera can reach 370.4 mg/g. This is because under acidic conditions, the surface of aloe vera is negatively charged, and its surface complexes will dissociate and easily interact with the uranium complex. With increasing pH, aloe vera more easily adsorbs cadmium, and the maximum adsorption amount was 104.2 mg/g.

4.2. Temperature

The adsorption process involves endothermic and exothermic reactions, which correspond to chemical adsorption and physical adsorption. When physical adsorption is the main method, the adsorption process is exothermic, and the lower the temperature is, the better the adsorption. However, physical adsorption between biomass adsorbents and heavy metal ions is a reversible process; in the case of metal ion adsorption, this mechanism does not play much of a role because biomass adsorbents usually require significant warming to desorb the adsorbent molecules [103]. When chemisorption is predominant, the adsorption process is a heat absorption process, and the higher the temperature is, the better the adsorption because the surface activity of the adsorbent increases with increasing temperature [104]. Lee et al. [105] used the waste biomass adsorbent persimmon leaf in an aqueous solution to remove heavy metals, and their thermodynamic experimental analysis yielded negative values for $\Delta G°$, positive values for $\Delta H°$ and $\Delta S°$, and adsorption rates of up to 22.59 mg/g of persimmon leaf with increasing temperature. Thus, the process of heavy metal adsorption using persimmon leaves is essentially spontaneous, a heat absorption process, with chemisorption being the mainstay.

4.3. Amount of adsorbent

The adsorbent dosage is also referred to as the adsorbent concentration. Increasing the amount of adsorbent can introduce more active sites and thus improve the removal of heavy metal ions. However, in a large number of studies, it has been found that as the number of adsorbents increases, the adsorbent particles will agglomerate, and the active sites will overlap each other, leading to an overall decrease in removal efficiency [106,107]. Therefore, the cost of the adsorbent, the utilization rate of active sites and whether too much adsorbent will cause an agglomeration phenomenon need to be considered in practical studies. Imran et al. [108] used *Moringa oleifera* leaves to remove Pb(II) from aqueous solution and explored the optimal dose of adsorbent. They found that the lowest removal rate (45%) was achieved when the adsorbent dose was 1.5 g/L, and the removal rate of Pb(II) increased with increasing dose. When the adsorbent dose was 70 g/L, the removal rate reached 98.6%, and when the adsorbent dose was greater than 10.0 g/L, the removal of Pb(II) by Moringa oleifera leaves did not improve further and even tended to decrease slightly.

4.4. Contact time

The adsorbate and adsorbent must have enough contact time to reach adsorption equilibrium, and the adsorption capacity of the adsorbent can be fully utilized [109]. The time required for adsorption equilibrium depends on the adsorption rate; the faster the absorption rate is, the shorter the time required to reach equilibrium. Li et al. [110] prepared a new adsorbent by physically activating banana peel for the efficient removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{6+} in water. They found that the surface area of the modified adsorbent was substantially increased with abundant binding sites and functional groups, which enabled the adsorption reaction to reach equilibrium in 5–10 min, and the removal rates of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{6+} were 92.05%, 89.35%, 91.89%, and 82.88%, respectively. The removal rates of the four metals by the adsorbent could be increased to 98% with 1 h of contact time.

5. Summary and future perspectives

In conclusion, we have tried to summarize the applications of biomass adsorbent materials in the treatment of heavy metals in wastewater in a more comprehensive manner. This review covers the adsorption mechanism of biomass adsorbent materials, types, preparation and modification methods, the basic role of biomass adsorbent materials in the treatment of heavy metals in wastewater, and the main factors affecting the adsorption performed by biomass adsorbent materials. However, at present, there are still problems regarding the applications of biomass adsorbent materials in the treatment of heavy metals in wastewater, such as the difficulty of recovery, the impossibility of mass production, the poor selectivity, and the possible atmospheric pollution during the preparation process, which need to be further explored.

To this end, several prospects are proposed in conjunction with the development trend of biomass adsorbents from theoretical promotion to practical engineering applications. (1) Widely screen natural biomass adsorbent materials to identify those with excellent adsorption properties and continuing to broaden the research scope of biomass adsorbents. (2) Improve the research on the desorption regeneration of biomass adsorbent after treating wastewater based on the previous desorption regeneration by acid–base activation modification treatment, or improve the research on the compounding with other adsorbent materials (magnetic adsorbent materials) to reduce the production and recovery costs of modified biomass. (3) Adsorbents can be synergistically treated with traditional wastewater treatment processes (such as chemical precipitation), which can expand the biomass adsorbent working pH range and overcome the disadvantage that it is difficult to adapt to strong acid and alkali reaction conditions, and thereby reduce the secondary pollution caused by using traditional treatment processes alone. (4) Realize the large-scale standardized production of biomass adsorbent, optimize the test methods of modification, and explore the engineering application tests of biomass alternatives to traditional adsorbents. It is hoped that this review will help to advance the realization of these goals and ultimately show great advantages in the field of heavy metal pollution treatment and remediation in water bodies. It is believed that with the deepening of the research, biomass-based adsorbents can 1 d overcome the obstacles and be produced in large volumes for the benefit of nature and human life.

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