REVIEW

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Adsorption of heavy metal onto biomass-derived activated carbon: review

Baoying Wang,[a] Jingming Lan,[a] Chunmiao Bo, [ID] [a] Bolin Gong [ID] *[a] and Junjie Ou [ID] *[abc]

Due to the rapid development of the social economy and the massive increase in population, human beings continue to undertake processing, and commercial manufacturing activities of heavy metals, which has caused serious damage to the environment and human health. Heavy metals lead to serious environmental problems such as soil contamination and water pollution. Human health and the living environment are closely affected by the handling of heavy metals. Researchers must find several simple, economical and practical methods to adsorb heavy metals. Adsorption technology has been recognized as an efficient and economic strategy, exhibiting the advantages of recovering and reusing adsorbents. Biomass-derived activated carbon adsorbents offer large adjustable specific surface area, hierarchically porous structure, strong adsorption capacity, and excellent high economic applicability. This paper focuses on reviewing the preparation methods of biomass-derived activated carbon in the past five years. The application of representative biomass-derived activated carbon in the adsorption of heavy metals preferentially was described to optimize the critical parameters of the activation type of samples and process conditions. The key factors of the adsorbent, the physicochemical properties of the heavy metals, and the adsorption conditions affecting the adsorption of heavy metals are highlighted. In addition, the challenges faced by biomass-derived activated carbon are also discussed.

1. Introduction

Heavy metals can cause serious harm to the environment and human health because most of them are toxic, mutagenic and carcinogenic.[1] Heavy metal pollution is one of the environmental pollution caused by heavy metals or heavy metal-derived compounds such as lead, cadmium, cobalt, and copper, which are produced by mining, waste gas discharge, sewage irrigation and industrial wastewater discharge.[2] These metals are also considered harmful at concentrations greater than or equal to 5 mg L^{-1}.[3] These metal ions enter the atmosphere, water and soil, resulting in the concentration of heavy metals in the natural environment seriously exceeding the standard.[4] Moreover, heavy metals in various chemical forms will accumulate, remain, and even migrate through the biological chain of the ecosystem after entering the environment, further leading to irreversible harm to the environment and the human body. The entry of heavy metals into human living environments is shown

in Fig. 1.[5] Great efforts have been made to develop efficient techniques for heavy metal removal in recent years, such as ion exchange,[6] chemical precipitation,[7] electrochemistry,[8] membrane filtration,[9] and adsorption.[10] The carbon-based adsorption technique is widely applied in environmental protection, and biomass-derived activated carbon is recognized as one of the most economical and promising adsorbents for heavy metal removal. Fig. 2 shows recent publications obtained searching for "Heavy metal pollution" and "Removal of heavy metal" in Topic *via Web of Science*. As can be seen, there were over 3500 publications related to heavy metal pollution and over 2500 publications associated with the removal of heavy metals in the period of 2018–2022.

The world produces a large amount of agricultural waste discarded indiscriminately every year, resulting in a huge waste of resources. The rational application of agricultural waste can not only reduce environmental pressure, but also create economic value, so it is necessary to develop new ways of recycling agricultural waste. Agricultural waste refers to the waste generated from agricultural production, livestock breeding, agricultural and sideline products processing, and life activities of rural residents, mainly including residues in farmland and orchard, livestock manure, and residues in agricultural and sideline products and domestic waste. These wastes not only contain 65% to 90% of carbon, hydrogen, and oxygen, but also are rich in nitrogen, phosphorus, potassium, calcium,

[a]*School of Chemistry and Chemical Engineering, Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs Commission, Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, PR China. E-mail: gongbl@nxu.edu.cn*

[b]*CAS Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: junjieou@dicp.ac.cn*

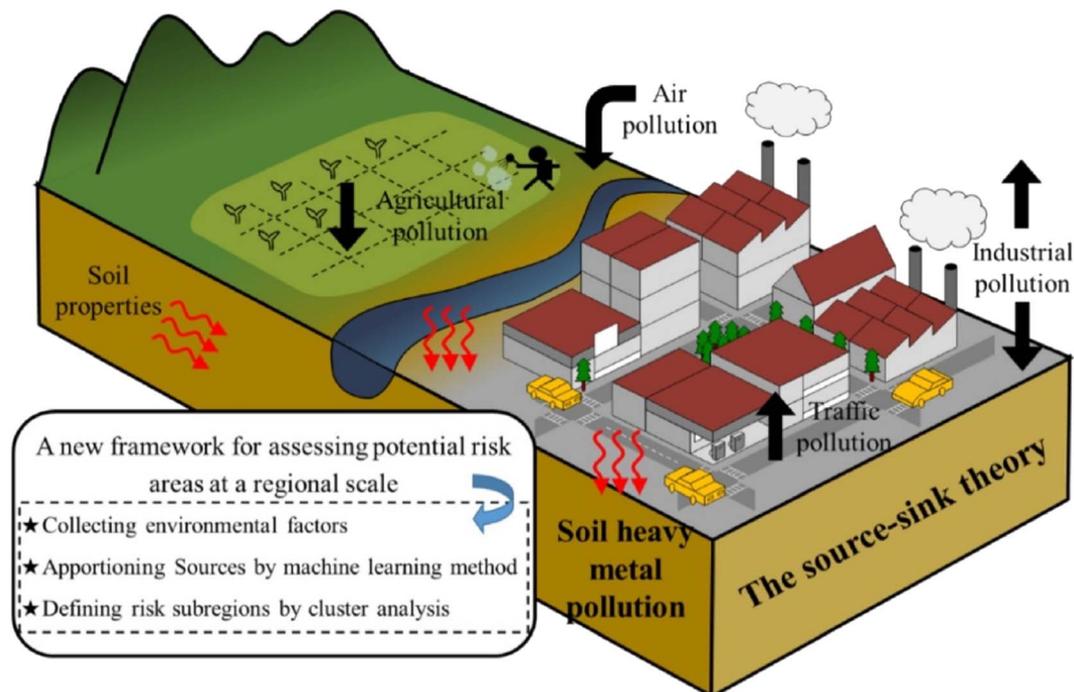[c]*University of Chinese Academy of Sciences, Beijing 100049, China*

Fig. 1 Environmental pollution map of heavy metals. This figure has been adapted/reproduced from ref. 11 with permission from *Journal of Hazardous Materials*, copyright 2023.
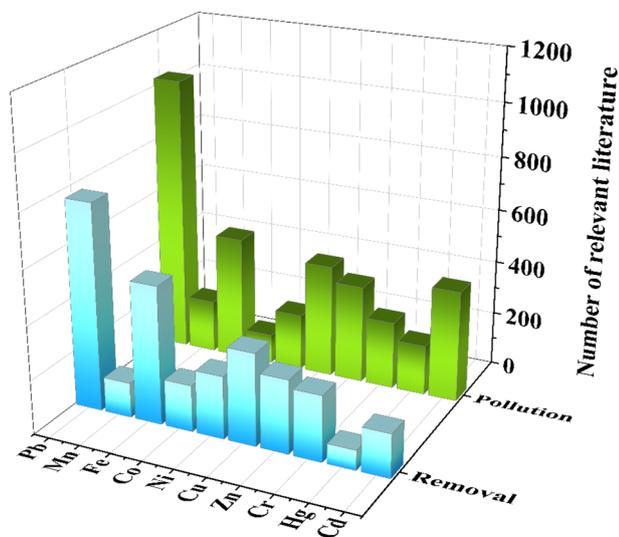

Fig. 2 Number of scientific publications related to the removal of various heavy metals with different techniques.

magnesium, sulfur, as well as trace elements. It is essential to pay attention to the extensive use of agricultural waste for sustainable development. Agricultural waste is usually the first choice to prepare biomass-derived activated carbon, attributing to its high specific surface area, high stability, excellent adsorption properties, simple production process and low price.[12]

This paper focuses on the advanced preparation progress of biomass-derived activated carbon and its application in the

adsorption of heavy metals from wastewater in the past five years. By collecting relevant information about heavy metals adsorbed by biomass and using appropriate language, the carbonization, activation and modification of biomass-derived activated carbon are reviewed. Furthermore, key factors controlling the adsorption process are summarized. The challenges of biomass-activated carbon facing in the adsorption of heavy metals are also discussed. The summary scheme of whole article is shown in Fig. 3.

2. Research status and control methods of heavy metals

2.1 Sources of heavy metals

Heavy metals are a large family with about 45 members in chemistry. Heavy metals have the commonness of irritation, target organ toxicity, carcinogenicity and immunotoxicity, and excessive discharge of them in nature will seriously endanger the health of water, soil and organism.[13–17] Heavy metals in the atmosphere mainly come from gases and dust produced by energy, transportation, metallurgy and building materials. The wastewater from industrial and mining enterprises is discharged into the sewer and mixed with domestic wastewater without diversion treatment, increasing the content of heavy metal in the soil of sewage irrigation area year by year.[18] During the stacking or treatment of both mining and industrial solid wastes, heavy metals are easy to move due to sunlight, rain and water washing and diffuse into the surrounding soil and water body in a radial and funnel shape. Pesticides, chemical fertilizers, and plastic film are necessary agricultural materials to
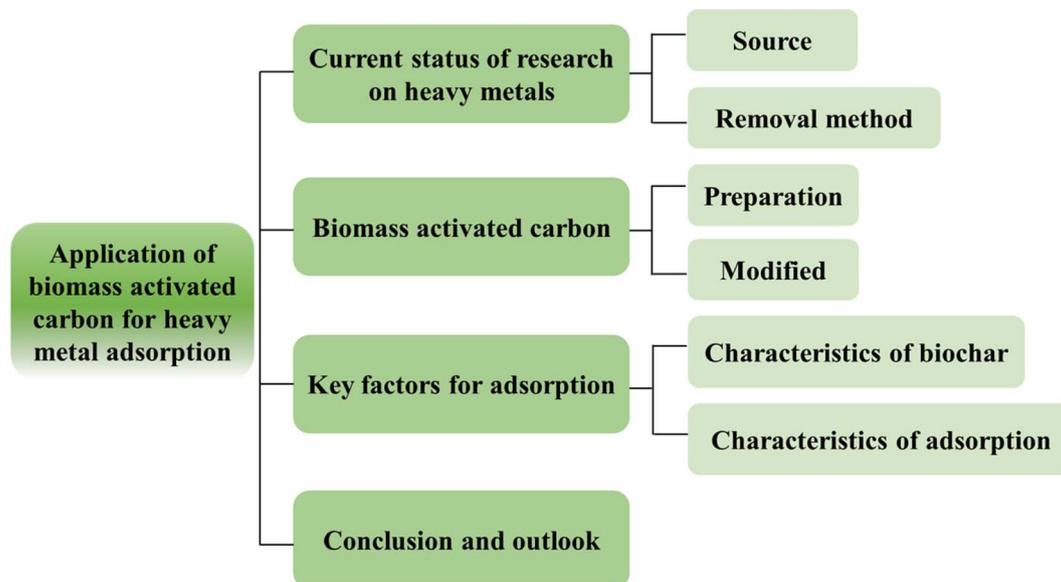
Fig. 3 Summary scheme for the whole article.

promote the development of agricultural production. However, the unreasonable long-term application can also lead to heavy metal pollution of soil.

Table 1 shows the sources and health effects of some harmful heavy metals such as lead, cadmium, mercury, chromium, and zinc ordinary in living. Any of these heavy metals can cause headache, dizziness, insomnia, forgetfulness, nervous disorder, joint pain, stones, cancer, etc[19]. For example, lead intake of human body is mainly through meat, fruits, fish, shrimp, eggs, etc, while lead in grains and vegetables comes from the soil, water. There are two primary sources of lead in the atmosphere, man-made emissions and natural sources. Natural source emissions are about one-tenth of man-made emissions. It is reported that the average proportion of zinc measured in the soil near the smelter in Korea is 45.8–83.3%. Zinc

concentration ranges higher than normal land. The average concentrations of lead, zinc and cadmium near the plant in northern Iran (302, 311 and 9.83 mg kg^{-1}, respectively) are also significantly higher than those in the control soil.[20,21] Lead has harmful effects on multiple organ systems through different mechanisms. Some heavy metals in water can be transformed into more toxic metal compounds under the action of microorganisms. Japan's pain is caused by cadmium entering the water body, painful disease is a strange disease that first occurred in the watershed of Toyama Prefecture, Japan, causing a large loss of calcium in human bones, osteoporosis, bone atrophy and joint pain. There was a patient who sneezed and broke many parts of his body. The other patient finally had 73 fractures in his whole body, and his length was shortened by 30 cm. His illness was very miserable. Painful disease has been

Table 1 Sources of heavy metals and their harm to human body and environment

Heavy metal	Main sources	Harm to human body	Ref.
Lead	Cosmetics, puffed food, water pipes, cast type, radioactive radiation, X-ray protective equipment, etc.	Anemia, neurological disorders, renal injury	24,25
Cadmium	Industrial wastewater, waste batteries, pigments, plastic stabilizers, coating corrosion prevention of steel parts, etc.	Severe bone softening and visceral dysfunction	26,27
Mercury	Precious metal smelting, cosmetics, lighting lamps, aquatic organisms, dental materials, etc.	Damage brain cells and kidneys, causing systemic poisoning	28
Chromium	Leather preparation, metal chromium plating, inferior cosmetic raw materials, etc.	Pharyngitis, bronchitis, rhinitis, dermatitis, tuberculosis	29–31
Zinc	Machinery manufacturing, and emissions from industries such as galvanizing, instrumentation, organic synthesis and papermaking	Metabolic disorder, anemia, zinc fever, etc.	32,33

prevalent in the local area for more than 20 years, causing more than 200 deaths.[22] After ingesting mercury, the human body will directly enter the liver and seriously damage the brain's optic nerve. Chromium poisoning can cause limb numbness and mental abnormalities. And the clinical manifestations of zinc poisoning are abdominal pain, vomiting, diarrhea, gastrointestinal bleeding, anorexia, fatigue and lethargy. Copper is an essential material for the development of industrialization and urbanization, and needed by more than 90% of modern industrial enterprises, copper smelters have caused severe pollution. For example, more than 130 hectares of farmland near the largest non-ferrous metal smelters in China have been polluted.[23] Heavy metal pollution is common and especially harmful. It is urgent to remove heavy metal pollution.

2.2 Removal methods of heavy metals

There are many treatment methods for heavy metal wastewater, including methods of ion exchange, chemical precipitation, electrochemical, membrane filtration, adsorption, *etc.* Table 2 shows a few methods commonly utilized to remove heavy metals and summarizes their advantages and disadvantages.

2.2.1 **Ion exchange method.** Ion exchange method is the exchange of metals in wastewater in the form of cations (anions) on certain anionic (cationic) exchangers,[39] which usually exist as a solid. In previous studies, the surface positive charges inhibit the usability of poly (*m*-phenylenediamine) as an adsorbent for removing heavy metal. To overcome these drawbacks, a magnetic $MnO_2@Fe_3O_4$/poly (*m*-phenylenediamine) core–shell adsorbent was designed. The surface negative charge of the prepared adsorbent increases, and the adsorption of metal ions is significant enhanced by ion exchange with maximum capacities of 438.6 mg g^{-1} for lead and 121.5 mg g^{-1} for cadmium.[40] Ion exchange is an important treatment method to remove heavy metals from wastewater, exhibiting the advantages of large treatment capacity, good effluent quality, and

recyclable heavy metal resources. However, these exchangers are easy to oxidize and difficult to preserve. Excessive waste liquid will be generated during operation, resulting in high operation cost.

2.2.2 **Chemical precipitation method.** Chemical precipitation method is that the precipitant reacts with heavy metal ions to produce metal salts with low solubility and then separates them from the aqueous solution through filtration or centrifugation, to achieve the purpose of removing heavy metal ions from wastewater.[41] Typical chemical precipitation methods using lime, soda ash and sodium sulfide for removals of heavy metals from aqueous solutions were compared. A removal of 99.9% from aqueous solutions with three precipitants was achieved for copper and zinc at an initial concentration of 100 mg L^{-1}, and lead was efficiently removed (99.8%) by sodium sulfide. These precipitants showed good removal efficiency for heavy metals.[42] The treatment effect of chemical precipitation method is negatively correlated with the solubility of metal salt. Lower solubility of metal salt causes better treatment effect. Due to the influence of metal salt solubility and environmental conditions, it is difficult to make the concentration of heavy metal ions reach the discharge standard by exploring the chemical precipitation method alone. A combination of chemical precipitation and other methods to control heavy metal pollution will be the focus of research in the future. Tang *et al.*[43] designed a novel combined biosorption precipitation process. Firstly, lead ions were selectively removed from wastewater by bagasse-fixed column modified with pyromellitic dianhydride, then desorbed into concentrated eluent and recycled by adding chemical precipitant. The maximum adsorption capacity reached 242 mg g^{-1}, which was much higher than that prior to modification (60.5 mg g^{-1}). Chemical precipitation method has the advantages of simple process, which can be completed at room temperature and in a wide pH range, and is not affected by the low concentration of heavy metal ions. However, large

Table 2 Advantages and disadvantages of various methods for metal ion removal

Methods	Advantages	Disadvantages	Ref.
Ion exchange	High removal rate, high concentration of useful substances, high recovery rate, simple equipment and convenient operation and control	High pre-treatment requirements, excessive regeneration waste, long experimental cycles, high salt consumption and poor general applicability	34
Chemical precipitation	Simple process, low equipment investment, convenient and safe operation	More chemical precipitation and high treatment cost	35
Electrochemical	No requirement of oxidant, flocculant and other chemicals, no secondary pollution, equipment with small volume, small floor area and convenient and flexible operation, low operation cost and remarkable pollutant removal effect	Low treatment efficiency of trace samples, large power consumption, and requirements of conductive salt for wastewater quality	36
Membrane filtration	Low energy consumption, high efficiency, simple process and low investment	Membrane fouling, frequent membrane replacement, high cost	37
Adsorption	Good selectivity, high stability, good treatment effect, convenient management, high adsorption efficiency, simple process, convenient installation, good reusability and simple material replacement	High usage and high cost	38

doses of chemicals need to be injected, and the treatment of sludge generated by chemical precipitation will increase the cost.

2.2.3 Electrochemical method. The electrochemical method is to utilize the external electric field to make the oxidation–reduction reaction of metal ions on the electrode, mainly including electrocoagulation and electrolysis.[44] For example, after extraction by citrate at initial pH of 8.3 and electrochemical adsorption at 0.9 V for 7 days, the concentration of copper in soil decreased from 1090 to 281 mg kg^{-1}, while the concentration of zinc decreased from 262 to 39 mg kg^{-1}.[45] The electrode-modifying material was prepared by chemical activation of rice husks with phosphoric acid and calcined at 450 °C. The results obtained at optimal conditions are as follows: 10% of activated carbon in the carbon paste, electrolysis potential of −0.9 V, accumulation time of 8 min, pH of 8 and the pH at zero load point of 3.45, the results showed that the modified electrode is more sensitive and stable.[22,46] But the concentration of heavy metal ions will not be greatly reduced by electrochemical method, it consumes a lot of energy.

2.2.4 Membrane filtration method. Membrane filtration method refers to the membrane separation technology driven by hydraulic pressure. As an advanced means of water treatment, membrane filtration method has the advantages of simple operation, small floor area, good selective permeability, no phase change in the separation process, and can be carried out at room temperature.[47–49] For example, Deng *et al.*[50] fabricated a novel nanocomposite films to treat 240 and 170 mL of copper ions and lead ions. The membrane separation method exhibits the advantages of high efficiency, energy saving and no secondary pollution, the long-term operation of membrane filtration will cause membrane pollution and gradual reduction of filtration capacity. The membrane pollution is a significant constraint in the wide application of membrane filtration.

2.2.5 Adsorption method. The adsorption method is to physically or chemically adsorb heavy metal ions in wastewater through the fluffy structure or special functional groups of adsorption materials with high specific surface area.[51,52] Adsorption materials can be divided into polymeric materials, inorganic materials, carbon-based materials and biological adsorption materials according to their chemical structure.[53] Table 3 summarizes the representative kinds of adsorbents classified by chemical structure, including polyacrylamide resins, alumina, zeolite, activated carbon peel and microalgae.[54] Their advantages, disadvantages and properties are introduced in detail.

Common polymer adsorption materials include polystyrene, polyacrylate, polyacrylamide resins with good plasticity. Their functional groups with specific properties can be easily introduced through chemical modification. Additionally, polymer materials can also be swelled, which will expand their three-dimensional structure and is conducive to the mass transfer rate of adsorption. Researcher studied the adsorption performance of lead and copper ions using macroporous polystyrenic chelating resin with a thiourea functional group. The ion-exchange recovery of Cu^{2+} exceeded 95% with resin dosage of 0.070 g mL^{-1} in the pH range of 2.5–4.5.[61] The resins have the advantages of fast adsorption speed, high adsorption capacity and wide application range. Furthermore, they can be utilized well at low temperature and normal pressure conditions and regenerated after simple treatment. However, the disadvantage of ion exchange resin is relatively low selectivity.[62] The ions of the resin itself are generally low valence ions, so when the resin contacts with water, the high valence ions in water will be adsorbed and the low valence ions will be released. For example, divalent ions are more easily adsorbed than monovalent ions.[63]

Common inorganic adsorbents include alumina and zeolite, which have the characteristics of rich reserves and low price. Alumina is made by heating and dehydration of aluminum hydrate, whose properties depend on the structural state of initial hydroxide.[64] It is divided into alkaline alumina, acidic alumina, and neutral alumina. Alkaline alumina is suitable for separating alkaline substances (such as amines and alkaloids) and acid-sensitive samples (such as acetals and glycosides) and neutral substances such as hydrocarbons and steroids. Acidic alumina is appropriate for separating acidic substances such as organic acids, amino acids, pigments and aldehydes. Neutral alumina is proper for separating aldehydes, ketones, quinones, glycosides, nitro compounds and unstable substances in an alkaline medium, such as esters and lactones.[65] The activated carbon was prepared using rice husk and reacted with it using caustic soda and alumina at 500 °C. The adsorption efficiency of uranium was 96.35% at an equilibrium time of 1 h, and an initial uranium concentration of 121 mg L^{-1}.[66] Activated alumina also shows good adsorption properties due to its high pore surface activity and affinity for water.[67] Zeolite also showed excellent adsorption properties. It has a uniform pore size. And it has been widely used in gas adsorption and separation, gas and liquid drying and separation of *n*-isoalkanes. Compared with other adsorbents, zeolite also has special adsorption performance. Under the condition of low partial pressure (or low concentration) and high temperature, the molecular sieve is significantly superior over other adsorbents. The pores of zeolite are easy to be blocked.[68]

Carbon-based adsorbent refers to the porous carbonaceous material with high specific surface made of coal or organic matter. Activated carbon is one of the most widely used carbonaceous materials. A new type of activated carbon was prepared, it takes straw as precursor because the carbon element content in the straw was about 40%. The removal efficiencies of heavy metals (Cu^{2+}, Cr^{4+} and Fe^{3+}) aren't less than 90%. And the adsorption–desorption experiments indicated that the adsorbent was sufficiently reusable.[69] Activated carbon contains many pores and has an excellent adsorption capacity it is applied in a wide range of applications such as waste water treatment, decolorization, catalysis and medical applications.[70]

Bio-adsorbent refers to biomaterials that can adsorb heavy metals and other pollutants. At present, fungi, bacteria, algae and agricultural wastes are widely studied and applied as biosorption materials. This material generally contains a large number of active groups such as hydroxyl, carboxyl and amino groups, which can have electrostatic adsorption, chelation, coordination and inorganic micro precipitation with heavy metal ions. In northern Chile, Chlorella and Echinococcus

Table 3 Different types of adsorbents

Adsorbent		BET surface area (m^2 g^{-1})	Aperture (nm)	Characteristic	Ref.
Polymer adsorbent	Polyacrylamide resin	≤1000	0.3–4	High adsorption rate, large adsorption capacity, good performance, stable to alkali, unstable to inorganic acids, good adsorption performance for organic wastewater. Poor antistatic property, poor selectivity after regeneration and heat resistance	55
Inorganic adsorbent	Aluminium oxide	200–500	2–50	Strong affinity, good purification performance of acid waste gas. Low service life	56
	Zeolite	500–1000	0.4–1	Regular microporous structure, good thermal stability, hydrothermal stability, strong selectivity, good adsorption performance. Poor anion adsorption, hole blockage	57
Carbon based adsorbent	Activated carbon	500–1000	2–50	Rich microporous and mesoporous structures, adsorption of organic compounds, heavy metals, heavy hydrocarbons and other organic substances	58
Biomass adsorption material	Microalgae	—	—	Fast growth and reproduction, strong tolerance, high removal rate. Poor system stability, prone to pollution and death, high requirements for training equipment, not conducive to practical application	59
	Agricultural waste	—	—	Wide source, low cost, adsorption of dyes and heavy metals. Not recyclable, easy to cause secondary pollution	60

scenarios were tested for metal mine tail water removal. The removal rates of copper and molybdenum by microalgae were 64.7% and 99.9%.[71] Although biomass materials are good, biomass such as microalgae is not easy to survive, and the adsorption capacity is not high. The adsorption capacity of pomelo peel to methylene blue and chromium ions in wastewater was explored. The maximum adsorption capacities for methylene blue and chromium ions were 219 mg g^{-1} and 11.3 mg g^{-1}, respectively. The main adsorption mechanism for methylene blue is electrostatic attraction and hydrogen bond formation, while the adsorption mechanism for chromium ion is electrostatic attraction.[72] Although biomass adsorbent has the advantages of low price, its adsorption capacity is lower than other adsorption materials.

In a word, the adsorption method is considered as one of the most favorable methods to deal with pollutant due to its advantages of good treatment effect, wide application range, easy recovery, comprehensive source of adsorbent, reusability and the treatment effect of adsorption method is less affected by the concentration of heavy metal ions.[73] The carbonaceous materials are considered as the efficient adsorbent because of high surface area and a variety of active surface sites.[74] However, the regeneration of industrial activated carbon is a high cost and complex process, which makes the application of this material economically infeasible. In addition, other types of carbon materials are not suitable to be adsorbents because of their high cost or poor adsorption performance. For example, the adsorbents were prepared by oxidation of multiwall carbon nanotube, then derivatizing the oxidized product with hydroxyl amine, hydrazine and amino acid. The adsorption capacity of the adsorbent for lead ion is 24.34 mg g^{-1}.[25] In order to reduce the overall cost and increase adsorption capacity in this adsorption process, using low-cost and due to the rich structure of biomass as the precursor of activated carbon has become a promising strategy.

3. Biomass-derived activated carbon

As one of the most miraculous materials in nature, carbon materials have excellent properties such as resistance to acids and bases, corrosion, high and low temperatures, and biocompatibility. Additionally, through its sp electron orbital hybridization, it can mutate into different forms and properties, including excellent electrical conductor, semiconductor material and insulator, opaque black material or explicit transparent material and so on. Fig. 4 shows the manifestations of carbon with different dimensions.[75] Carbon materials have played a significant role throughout history as human civilization has progressed. At each stage of history, carbon had a unique expression. Since the invention of fire, porous charcoal has
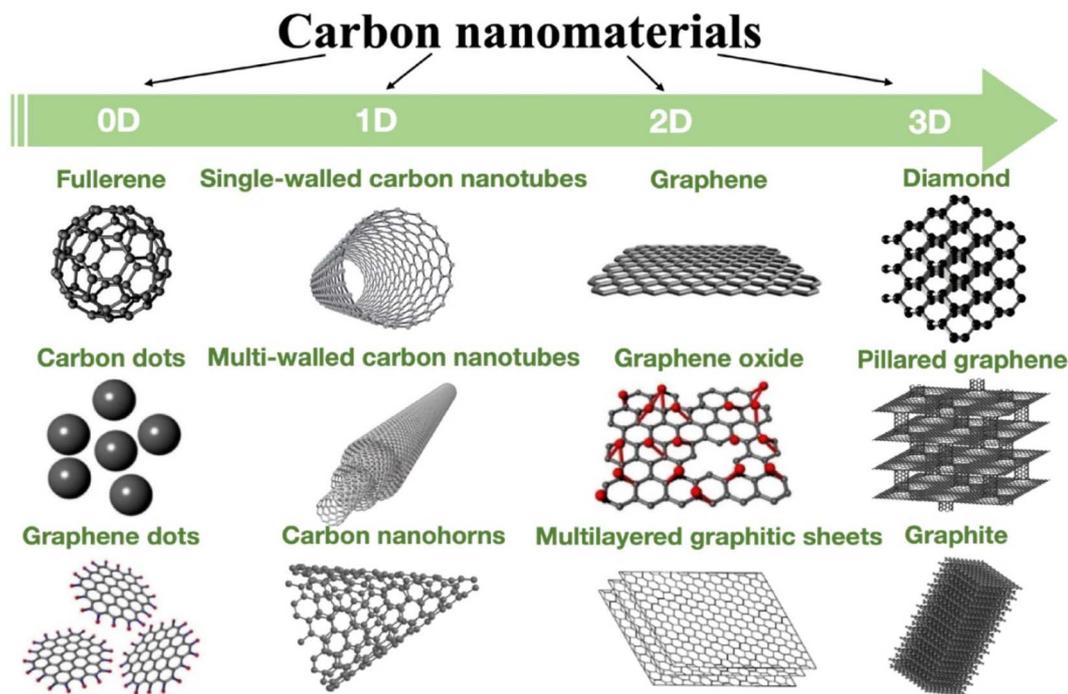
Carbon nanomaterials

Fig. 4 Carbon allotropes in different dimensions. Environmental pollution map of heavy metals. This figure has been adapted/reproduced from ref. 75 with permission from *Carbon*, copyright 2023.

been used consciously or unconsciously. For example, the use of charcoal to stop bleeding, the use of soot to heal wounds, the use of carbon sterile sheets. From the deodorization and disinfection of clothes, food and housing in daily life to the profound evolution of living places. From protective escape materials in personal space to environmental purification in public places.[76]

Different types of activated carbon have emerged following the advent of coal and oil and the rapid development of modern industry. Activated carbon is widely used, and the raw materials for manufacturing activated carbon are also various. There are many sources of raw materials for making activated carbon, including animals, plants, coal, petroleum by-products, and other raw materials such as synthetic resin and organic substances. In general, carbon materials can be divided into three categories, as summarized in Table 4. Mineral activated carbon can be widely used in many fields of liquid phase application and gas-phase application, it is difficult to make high-performance activated carbon in high-demand fields due to containing high impurities. Furthermore, with the increase of raw material cost in recent years, its advantages gradually receded. Activated carbon prepared from waste car tires has also been widely used. The waste car tires need high-temperature pyrolysis, which consumes a lot of energy and costs a lot. Among many raw materials, the advantages of biomass to prepare activated carbon are particularly prominent. Modern agriculture uses a large amount of chemical fertilizer to replace farmyard organic fertilizer and artificial feed to replace agricultural waste feed. In addition, the intensive and large-scale development of modern agriculture has broken the waste

recycling in traditional agriculture. As a result, much agricultural waste has been accumulated, resulting in serious environmental problems and resource waste. Therefore, the rational utilization of agricultural waste resources has become a great challenge faced by most countries. The preparation of activated carbon from biomass realizes the concept of waste utilization and resource utilization. The harmless treatment of agricultural waste is an effective way to control agricultural, environmental pollution, improve the rural environment and develop a circular and sustainable economy. As a result, activated carbon fabricated from biomass has made great contributions to energy conservation and environmental protection through waste reuse.

According to the definition of the International Energy Agency (IEA), "biomass" refers to various organisms formed through photosynthesis.[84] Its definition can be divided into broad and narrow sense.[85] The former includes all plants, microorganisms, and waste generated by them, while the latter refers to inedible crop by-products, agricultural and forestry wastes such as wheat straw, fruit shell, wood, and other lignocellulose, and livestock manure (Fig. 5).[86] Biomass materials are renewable, widely available, inexpensive, environmentally compatible, porous and environmentally friendly, and the adsorbents prepared after modification have the advantages of high selectivity and removal rates.[87,88]

Biomass activated carbon and activated carbon are both carbonaceous pyrolysis materials and important products of environmental technology. The main raw materials of activated carbon are divided into four categories, including coal activated carbon, wood activated carbon, synthetic activated carbon and

Table 4 Characteristics of activated carbon prepared from different raw materials

Activated carbon	Raw materials	Shape	Characteristics	Ref.
Biomass-activated carbon	Coconut husk, wood flour, coffee bean stalks, oil palm husk, sugarcane bagasse, manure, animal bones, *etc.*	Powdered, honeycomb, columnar, granular and powdered activated carbon, *etc.*	Wide aperture distribution, and most micropores. Adsorb substances of different sizes	77–79
Mineral raw materials activated carbon	Peat, bituminous coal, anthracite, bitumen and petroleum and their processing products, *etc.*	Columnar activated carbon, honeycomb activated carbon, spherical activated carbon, raw coal crushed carbon, *etc.*	Flat mesopores and micropores. Adsorb small molecules and macromolecules with large molecular diameter	80,81
Other raw materials activated carbon	Waste rubber, waste plastic, *etc.*	Columnar activated carbon, *etc.*	Adsorb organic matter and heavy metals	82,83

Fig. 5 Schematic diagram of using biological waste as adsorbent.

other types of activated carbon. The precursor material of biomass activated carbon is only biomass.

3.1 Preparation of biomass derived activated carbon

3.1.1 Carbonization of biomass. Fabrication of biomass-derived activated carbon has been developed. Fig. 6 is the flow chart of carbonization and activation of biological activated carbon.[89–91] The carbonization process is the carbonize of biomass in an anaerobic or anoxic environment at 400–600 °C, and the process of removing oxygen, hydrogen, nitrogen, sulfur, and other elements to manufacture materials with high carbon content.[92,93] Biomass is thermochemically transformed to produce carbon rich solid material, which is called biomass-derived activated carbon.[94] There are three stages of carbonization. First, the temperature is lower than 110 °C, the raw material gradually loses water, the internal molecules do not change. Second, the raw material is heated to 350 °C, the carboxyl and carbonyl functional group release carbonize gases such as H_2O, CO and CO_2.[95] The

temperature rises to 400 °C, a large number of chemical bonds, including C–C bond, O–H bond, C–H bond, benzene ring and ether bond are broken. Minor molecular gases and small molecular groups of hydroxyl, methyl, hydroxymethyl and methoxy are generated through chemical bond recombination, decarbonization, dehydration, and polycondensation. These small molecular groups gradually form water, methane, and methanol, meanwhile, a large number of benzene free radicals form polycyclic aromatic compounds. When the temperature is 450–500 °C, the volatile substances are removed so as to improve the relative content of fixed carbon in the carbonize products.[69,96]

3.1.2 Activation of biomass-derived activated carbon. Carbon materials are commonly activated *via* both chemical and physical activation approaches. Chemical activation methods can be divided into two types depending on the operation. The first method is to mix the activator with the biomass in a specific ratio (or soak the biomass raw material with the activator), the carbonization and activation are then
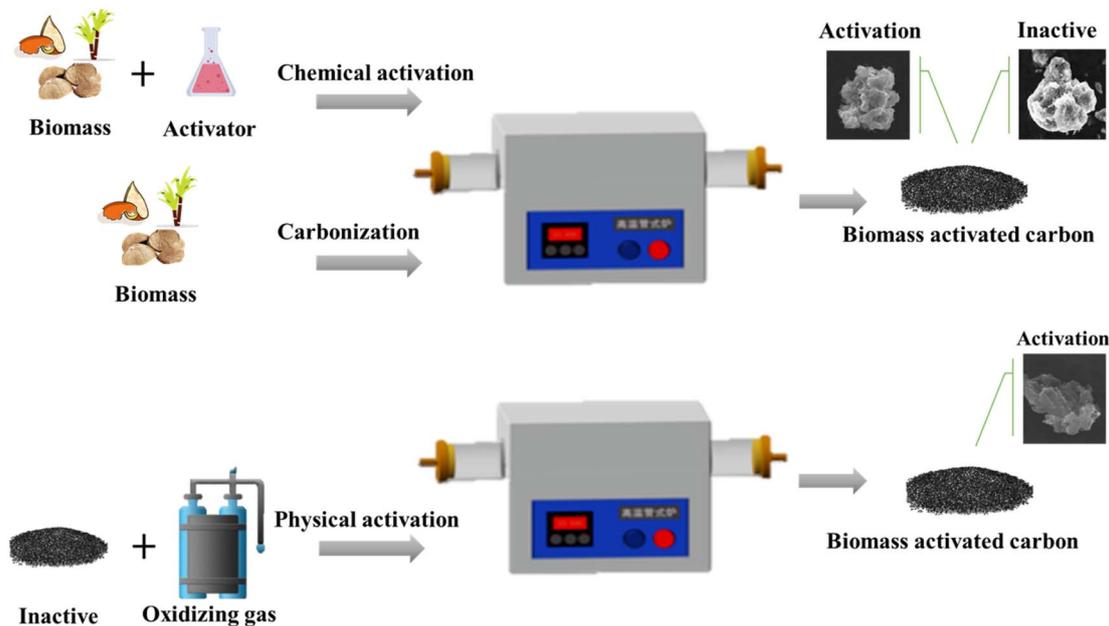
Fig. 6 Preparing biomass-derived activated carbon (including carbonization, chemical activation, and physical activation).

carried out simultaneously under high temperature conditions. Li *et al.*[97] prepared corncob activated carbon by one-step chemical activation method of phosphoric acid. The adsorption result showed that the optimum mass ratio of corncob to phosphoric acid was 1 : 2, and the carbonization temperature was 500 °C. Under these conditions, the removal rate of chromium was more than 98%, and the maximum adsorption capacity was 9.99 mg g^{-1}. The concentration of residual chromium in water was less than 0.05 mg L^{-1}. In another method, the carbonized carbon is activated with an activator in a certain ratio at high temperature.

Chemical activation is known to induce specific surface features of porosity and functionality which play a definite role in enhancing the adsorptive potential of the developed activated carbons. The physical and chemical properties of activated carbon are affected by the type of biological reagent and the impregnation time. The effect of zinc chloride and potassium hydroxide on the activation of lignocellulose activated carbon were investigated, respectively.[98] The carbon impregnated with zinc chloride produces micropores, while the carbon impregnated with potassium hydroxide forms a wide pore size distribution. The activated carbon obtained by both activation methods exhibited large specific surface area, and the pore size is mainly composed of mesopores and micropores. The chemical activation method possesses the advantages of good treatment efficiency of activated carbon, wide application range and easy recovery. In the process of chemical activation, many chemical reagents such as potassium hydroxide, phosphoric acid, zinc chloride, and potassium carbonate are the most commonly used as chemical activators (Fig. 7).

Table 5 shows in detail the effect of different raw materials and different proportions of activators on the specific surface area of activated carbon. Activators can be divided into alkaline, acidic, neutral, self-activator so on. Carbon materials with

different raw materials and activators have different specific surface area. Phosphoric acid is a common acidic activator. When phosphoric acid is used, the activation temperature is lower, and the activation time is shorter. Potassium and sodium hydroxide are the most effective activators for preparing biomass-derived activated carbon with a high specific surface area. The specific surface area of biomass-derived activated
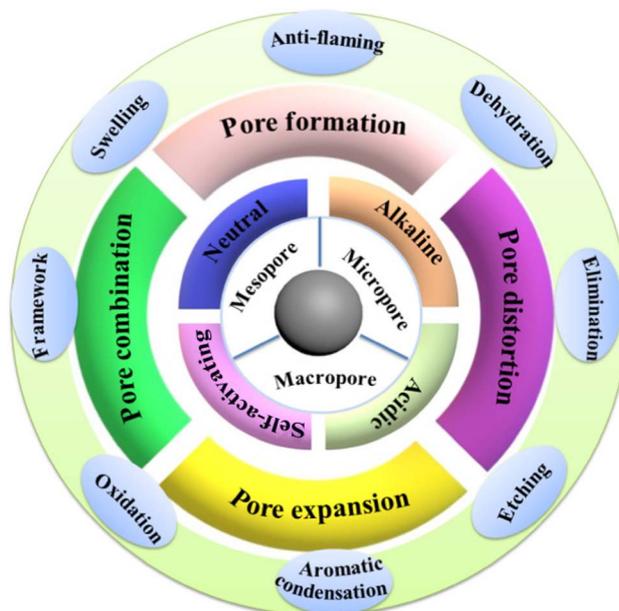

Fig. 7 Schematic diagram of activation mechanism by alkaline and acidic activating agent. Carbon allotropes in different dimensions. Environmental pollution map of heavy metals. This figure has been adapted/reproduced from ref. 99 with permission from *Science of the Total Environment*, copyright 2023.

Table 5 Process parameters and specific surface area of biomass-derived activated carbon prepared with different activators

Biomass source	Activator	Activating agent to biomass ratio	Activation conditions	BET surface, area $(m^2\ g^{-1})$	Ref.
Coconut shell	Phosphoric acid	1:1	800 °C, 2 h	2648	100
Orange peel	Phosphoric acid	2:1	700 °C, 1 h	2210	101
Coffee grounds	Phosphoric acid	1.8:1	450 °C, 1 h	925	102
Chinese fir bark	Potassium hydroxide	4:1	700 °C, 2 h	1242	103
Longan shell	Potassium hydroxide	2:1	800 °C, 2 h	3260	104
Guava seed	Sodium hydroxide	3:1	800 °C, 1 h	2574	105
Honeycomb	Sodium hydroxide	4:1	650 °C, 2 h	3291	106
Chestnut shell	Sodium amino	3:1	450 °C, 1 h	2615	107
Textile	Magnesium chloride	1:1	900 °C, 1.5 h	1307	108
Lignin	Potassium phosphate	1:1	900 °C, 2 h	477	109

carbon prepared from Chinese fir bark and longan shell with potassium hydroxide is higher than 1000 $m^2\ g^{-1}$. The specific surface area of activated carbon derived from guava seed and honeycomb biomass activated by sodium hydroxide is higher than 2000 $m^2\ g^{-1}$. It is generally believed that potassium hydroxide and sodium hydroxide can inhibit the formation of tar, reduce the activation reaction temperature, accelerate the removal of non-carbon components and improve the carbonize reaction rate. Sodium amino and magnesium chloride are neutral activators. The specific surface area of biomass-derived activated carbon prepared by them is higher than 1000 $m^2\ g^{-1}$, the activator for a neutral activator is used at higher temperature. The biomass-derived activated carbon activated by potassium phosphate as a self-activator has slightly lower specific surface area, it can simplify the procedure, reduce the cost and the risk of environmental consequences, and better adapt to scalable production.

Physical activation is also known as gas activation. The feedstock is carbonized in the absence of oxygen or inert gas at a certain temperature.[110–113] The commonly used activation gases include oxidizing gases such as steam, air, CO_2 and O_2.[114–118] In the process of activation, carbon reacts endothermically with H_2O and CO_2, and the reaction rate is moderate. The reaction between carbon and O_2 is exothermic, and the reaction rate is fast.[119–124] Therefore, the reaction time is shortened when O_2 is added to the mixture to burn the intermediate products H_2 and CO and release heat. And the reaction of carbon with CO_2 and water vapor makes the porous structure highly developed.[125] Physical activation also has little environmental pollution.[126] The physical activation method of CO_2 and steam agent to activate were investigated.[127] The activation under the condition of CO_2 and steam saturation correspondingly increases the specific surface area from 89 to 653 $m^2\ g^{-1}$ and from 89 to 1015 $m^2\ g^{-1}$, respectively. Steam also promotes the generation of mesoporous structures of carbon products, thus expanding their potential applications. Jiang *et al.*[128] also investigated the pore properties and structural characteristics of activated carbon prepared from coconut shells. According to the thermochemical properties of coconut shell, the process was characterized by carbonization at 500 °C with a constant heating rate of 10 °C min^{-1} under nitrogen flow and then switching to gasification with CO_2. The gas temperature in the same reactor was set to 700–900 °C for

activation. The pores of coconut shell-activated carbon increased with the increase of activation temperature and holding time. These findings are attributed to the severe reaction of lignocellulose-based carbon with CO_2. The surface area reached 1100 $m^2\ g^{-1}$, and the mesoporous rate exceeded 40%. Physical activation method shows excellent advantages. More different biomass precursors are activated by the different activation method, whose experimental conditions and biomass-derived activated carbon physical and chemical properties are presented in Table 6. It is easy to find that the type of activator, the time and temperature of carbonization, the ratio of raw materials to activator, and the raw materials have severe impacts on the specific surface area of activated carbon.

3.2 Modification of biomass-derived activated carbon

The adsorption performance of biomass-derived activated carbon is determined by its physical and chemical properties. The physical property of biomass-derived activated carbon refer to its specific surface area and pore structure, and the adsorption capacity of carbon is affected by these factors. The chemical property of biomass-derived activated carbon depends on the type and number of surface functional groups, which impact the interaction between the activated carbon and pollutants.[139–145] The existing biomass-derived activated carbon possesses certain limitations in the actual wastewater treatment due to large variety of pollutants and high standard requirements for wastewater discharge.[146–148] Modification techniques for biomass-derived activated carbon are very important. And the physicochemical properties of biomass-derived activated carbon are closely related to the raw materials, carbonization method, activation and modification techniques. The modification techniques of activated carbon include physical, chemical or microbiological methods by changing the physical structural properties or surface chemical functional groups of biomass-derived activated carbon.[149,150]

3.2.1 Chemical modification. The functional groups on the surface of activated carbon give activated carbon a certain degree of acidity, alkalinity and polarity, which largely determine the type of pollutants adsorbed and the adsorption capacity of activated carbon. Therefore, the content of these functional groups on the activated carbon can be changed, and the selective adsorption capacity to specific substances is also

Table 6 Process parameters and specific surface area of biomass-derived activated carbon prepared by different physical activation methods

Biomass source	Experimental condition		BET surface, area (m^2 g^{-1})	Ref.
	Carbonization	Activation		
Bean dregs	Nitrogen, 800 °C, 0.5 h	30 mL steam, 1000 °C, 0.5 h	1004	129
Bamboo	Nitrogen, 10 °C min^{-1} 950 °C	80 mL min^{-1} ammonia, 950 °C, 2 h	2032	130
Eucalyptus original wood chip	Oxygen, 2.5 °C min^{-1} 700 °C	700 °C, 2 h	870	131
Rice husk	200 mL min^{-1} nitrogen, 900 °C	0.4 mL min^{-1} steam, 900 °C, 0.5 h	1343	132
Mushroom substrate	200 cm^3 min^{-1} nitrogen, 900 °C	2.0 mL min^{-1} steam, 900 °C, 1 h	332	133
Jute	Nitrogen, 500 °C, 1 h	Carbon dioxide, 800 °C, 1.5 h	1120	134
Amazon Peshawar fiber	Oxygen, 100 °C h^{-1} 550 °C, 1 h	150 mL min^{-1} carbon dioxide, 800 °C, 2 h	804	135
Hops	170 mL min^{-1} nitrogen, 10 °C min^{-1} 550 °C, 1 h	250 mL min^{-1} carbon dioxide, 800 °C, 1 h	417	136
Apple branch	Oxygen, 500 °C	Nitrogen, carbon dioxide, 500 °C, 2 h	526	137
Large	100 cm^3 min^{-1} nitrogen, 5 °C min^{-1} 300 °C, 2 h	165 cm^3 min^{-1} carbon dioxide, 750 °C, 1 h	740	138

changed. Chemical modification of activated carbon is changing the inherent functional groups on the surface of activated carbon by physical or chemical means to prepare adsorbents with specific adsorption properties. Common chemical modification techniques include acid modification, alkali modification, load modification and plasma modification.

Acid modification technique is the oxidation treatment of activated carbon with oxidizing agents such as nitric acid, sulfuric acid, citric acid, and hypochlorous acid under appropriate conditions.[151–154] The functional groups on the surface of activated carbon are oxygen-containing functional groups, such as hydroxyl, carboxyl, carbonyl and lactone groups, which are introduced through the oxidation pathway.[155–157] The introduction of carboxyl groups on the surface of biomass-derived activated carbon will play an important role in the adsorption of metal ions. The hydrogen in the carboxyl group will be ion-exchanged by metal ions, and the carboxyl group will chelate with metal ions.[158,159] Li et al.[160] employed in situ modification of the activated carbon with phosphoric acid and disodium EDTA salts to increase the adsorption of nickel ions. The adsorption capacity was increased from 15.4 to 27.9 mg g^{-1}. Nickel ions were adsorbed by cation exchange, electrostatic interaction and surface complexation mechanism, and the adsorption amount was proportional to its surface functional groups under appropriate environments. A similar experiment is that the spent coffee grounds were used as a precursor to obtain activated carbons. The raw material was modified with phosphoric acid. The specific surface area of the carbon increased to 720 m^2 g^{-1}, and the pore volume increased to 0.334 cm^3 g^{-1}. And all the obtained carbons possessed acidic (mainly carboxyl) groups and exhibited an amorphous structure.[161] These results indicated that activated carbon-containing carboxyl groups have very promising adsorption prospects. The pyrolysis-driven eucalyptus carbon was treated with phosphoric acid.[162], whose surface area was increased almost fivefold from 253 to 1265 m^2 g^{-1}. The modified biomass-derived activated carbon was able to remove 99.76% of chromium, which was higher than the unmodified activated carbon (25.24%). Such high adsorption capacity was attributed to not only excellent specific surface area, but also the phosphoric acid modification which increases the oxygen-containing functional groups on the surface. Li et al.[163] investigated the metal removal efficiency of carbonized sewage sludge obtained at 500 °C, and nitric acid modification. The prepared biomass-derived activated carbons removed 98.9%, 42.6% and 34.6% of copper, zinc and aluminum ions, respectively, in less than 5 min. The complexation of functional groups to metal ions not only shortened the adsorption time, but also exhibited higher removal efficiency.

Alkali modification of activated carbon refers to the use of alkaline reagents such as sodium hydroxide, potassium hydroxide and ammonia to modify the activated carbon.[164,165] For example, the ZnO-activated carbon was successfully prepared from sugarcane bagasse with sodium hydroxide impregnation, followed by carbonization, and the ZnO-activated carbon nanocomposite was finally synthesized by the hydrothermal method.[166] The removal efficiency of

chromium reached 97% at pH = 2. Additionally, the adsorption capacity of activated carbon for chromium ions in wastewater was increased after the modification in a high-temperature environment. Biomass-derived activated carbon is modified in the temperature range of 950 °C, producing a surface area >2000 $m^2\ g^{-1}$.[118] The microporous structure, specific surface area, iodine adsorption value, and nitrogen-containing groups on the surface of modified activated carbon increased. Similarly, researchers synthesized biomass-derived activated carbon with Schiff base structure by ammonia-assisted hydrothermal treatment of industrial hemicellulose and applied to adsorb toxic hexavalent chromium, possessing a high adsorption capacity of 349.6 mg g^{-1}.[167] There were electrostatic gravitational, redox, and chelation interactions between the amino groups, Schiff base structure, heterocyclic nitrogen of biomass-derived activated carbon and chromium ions. Although alkali modification has great advantage of improving the adsorption capacity, the adsorption process is often complex.[168–170]

Loading modification of activated carbon means that activated carbon is treated by soaking in the solution of the loaded material, and surfactants such as polyethylene polyamine and polyethyleneimine are combined to the surface of activated carbon. Such activators do not significantly change the acidity and alkalinity of the activated carbon surface, can improve the adsorption capacity of the activated carbon for pollutants.[171,172] Jiang et al.[173] investigated the removal of lead ions from wastewater by polyethyleneimine loaded activated carbon, and the removal rate of lead ions increased from 32.6 to 214 mg g^{-1}. Through the study of polyethyleneimine modified activated carbon, it is not difficult to find that the adsorption capacity of modified activated carbon for formaldehyde also increased significantly.[174] The adsorption capacity of unmodified activated carbon was 190 mg g^{-1}, and the adsorption capacity of activated carbon after loading 2.50 g of polyethyleneimine was up to 650 mg g^{-1}, which was about 3.42 times that of unmodified activated carbon.

Plasma modification is an efficient, easy-to-operate, and environmentally friendly surface modification technique. In many recent researches, it plays an essential role as a new technology for the modification of activated carbon. The pore structure of activated carbon is changed, and the surface functional groups such as acidic hydroxyl, carbonyl and carboxyl are generated.[175–177] Activated carbon particles from peat soils were modified by a flying jet plasma torch. The samples were dried at 70 °C for two nights, carbonized at 800 °C for 4 h, and then sieved on a 2 mm sieve. The surface morphology and chemical composition changed significantly. The increase in mass oxygen percentage indicated an increase in the carbonyl C=O group, and higher polarity and solubility in polar liquids, an effective surface area increased from 1069 to 1270 $m^2\ g^{-1}$, which more conducive to adsorption.[178]

3.2.2 Physical modification.
Physical modification refers to the modification of activated carbon by heating. Under its action, the specific surface area, pore volume and pore space of activated carbon will change significantly.[179–181] Activated carbon with food waste as precursor was prepared by microwave modification. The thermal stability after physical modification is higher than that of the raw material. In addition, the specific surface area and total pore volume of modified activated carbon are increased.[182] Wang et al.[183] investigated the effect of three organic acid ammoniums (ammonium succinate, ammonium tartrate and ammonium citrate) on the activated carbon during microwave modification. Microwave modification refers to the modification of samples under specific microwave power. Microwave modification has little effect on the specific surface area of activated carbon, the functional groups have obvious changes. The nitrogen content and basic groups of all modified carbon increased, the surface area decreased. Despite the low surface area of the modified reed-based activated carbons, they have a higher adsorption capacity (115 mg g^{-1}) due to the higher amount of nitrogen-containing groups. The role of microwave in the synthesis of carbon adsorbent was explored. The adsorption capacity of modified carbon to lead ion was as high as 282 mg g^{-1}. Microwave heating modified activated carbon changed the surface structure of activated carbon and surface chemistry groups. Excessive heating treatment can destroy the unstable oxygen-containing functional groups on the surface of activated carbon, thus weakening the chelating ability of activated carbon with metal ions and reducing the adsorption performance of metal ions.[184]

3.2.3 Microbial modification.
In the past decades, researchers have found that the special structure of activated carbon surfaces provides a good living environment for the parasitization and reproduction of microorganisms.[185,186] Microbial modification of activated carbon means adsorbing microorganisms on the surface of activated carbon to change the adsorption performance of activated carbon.[187] Microbial modification of biomass-derived activated carbon exhibits many advantages in application, such as high activity, fast reaction speed, strong toxicity resistance, easy separation of products and continuous operation. Therefore, microbial modification technology has been rapidly developed and widely used in the field of water treatment in recent years. Microorganisms fixed on the surface of activated carbon can preoxidize some organic matter, reduce the contact between organic matter and activated carbon adsorption sites, and prolong the service life of activated carbon. However, microbial-modified activated carbon also has some disadvantages, such as the propagation of microorganisms on the surface of activated carbon and thickening of membrane will hinder the diffusion of adsorbed substances in the pores of activated carbon and reduce the adsorption efficiency.[188–190]

3.2.4 Other modifications.
With the continuous development of activated carbon, new activated carbon modification technologies have emerged for specific applications.[191] Gohr et al.[192] successfully modified the activated carbon by mechanical friction on the activated carbon in the presence of sodium hydroxide and chloroacetic acid. The maximum adsorption of activated carbons for methyl blue and crystalline violet was 124 and 120 mg g^{-1}, respectively. This result demonstrated the mechanical friction technique in the modification of activated carbons and the functional groups and active sites (phenol, alcohol, and carboxyl groups) on the activated carbon adsorbent have a significant effect on their use in considerable adsorption affinity for dye removal. Metal-modified carbon materials have been widely utilized for fluoride removal, the traditional

impregnation by soaking method suffers from low loading of metals and substantial use of chemicals. A new method for preparing zirconium modified activated carbon fiber by drop coating method is proposed. Using the same amount of chemicals, the drop-coating method yielded 5.5 times higher fluoride adsorption capacity than the soaking method due to more effective loading of zirconium onto activated carbon fibers. The advantages of drop coating are simple experimental process, mechanized process and high production efficiency. However, the drop coating method also possesses some disadvantages, such as uneven drop coating.[193]

In summary, acid modification is one of the most applied and technically mature methods so far, which is also one of the most beneficial methods to improve the adsorption capacity of activated carbon for metal ions in aqueous solution.[194–198] The adsorption capacity of metal ions after alkali modification is weaker than that after acid modification. The reason is that alkali modification reduces the amount of acidic oxygen-containing functional groups on the surface of activated carbon, resulting in the binding sites reduction of metal ions on the surface of activated carbon. Moreover, the increase of nitrogen-containing functional groups enhances the alkalinity, and the competition mechanism between OH^- and metal ions under an alkaline environment leads to the decrease of adsorption performance of activated carbon for metal ions. Heating modification and alkali modification are beneficial to improve the adsorption of organic matter in aqueous solutions by activated carbon.[199–204] Loading modification allows for targeted loading of chemical substances on the surface of the activated carbon to enhance its adsorption capacity for the target substance.[205] Microbial modification, which uses microorganisms adsorbed on the surface of activated carbon, can pre-degrade organic matter in an aqueous solution for the purpose of extending the service life of activated carbon.[206] The special properties of activated carbon have led to its wide application as an adsorbent in wastewater treatment.[207] With the development of activated carbon modification technology, special modification treatment can be applied to activated carbon according to the characteristics of pollutants in the water environment so as to realize the improvement of selective adsorption capacity of activated carbon in water treatment. Although many modification technologies have been proposed in recent years, many of them are not suitable for practical application because of their low efficiency, high energy consumption or serious toxic by-products. The research on the modification of activated carbon by combining existing modification methods is not yet in-depth. And the modification technology to improve the removal ability of two or more pollutants (such as metal ions and organic matter) has not yet been developed.

4. Key factors to control the adsorption of heavy metals by biomass derived activated carbon

4.1 Characteristics of biomass derived activated carbon

Three important factors including specific surface area, pore structure, and surface chemical functional group would affect the adsorption capacity of biomass-derived activated carbon.[208,209]

4.1.1 Specific surface area.
For any adsorbents, a large specific surface area usually means superior adsorption performance, because the surface area provides adsorption space in the adsorption process.[210] Researcher summarizes the N_2 adsorption desorption curves of four ultra-high specific surface areas. The specific surface areas of four samples were 1348, 2004, 1324 and 1974 $m^2\ g^{-1}$, respectively. The result shows that high specific surface area makes it have better contact wettability between electrode material and electrolyte and excellent adsorption ability in removing pollution.[211] Zhang et al.[212] carbonized rape straw powder at different temperatures and then magnetized the activated carbon by hydrothermal method to prepare magnetized activated carbon. The modified biomass-derived activated carbon exhibited a high specific surface area (553 $m^2\ g^{-1}$) and maximum adsorption capacities of lead ions of 253 $mg\ g^{-1}$ and cadmium ions of 73.3 $mg\ g^{-1}$. To increase the surface area of carbon adsorbent, modification of carbon adsorbent by heat, acid, alkali, microwave, ozone, plasma and impregnation are commonly applied to modify carbon adsorbent. For example, humic acid-coated nitrogen-doped magnetic porous carbon was successfully synthesized by lignin separated from black liquor as the main carbon source.[213] The porous carbon had a high adsorption capacity of 131 $mg\ g^{-1}$ for chromium ions, and the BET-specific surface area of the porous carbon was 748 $m^2\ g^{-1}$. Such a high surface is expected to provide a large number of adsorption sites for metal ions. The adsorption material obtained by impregnating zeolite with iron salt possessed a high specific surface of 1358 $m^2\ g^{-1}$, and also can effectively remove more than 99% of lead ions in 20 min. The maximum adsorption capacity reached 790 $mg\ g^{-1}$, which was much higher than those of most previously reported unmodified zeolite.[214]

The specific surface area of carbon materials can be increased by increasing the proper temperature and concentration of acid or alkali treatment, too high or too low temperature and pH will lead to the collapse of existing pores, thus reducing the specific surface area. Although most of the research has been conducted on activated carbons with large specific surface areas.[215,216] However, a high surface area of activated carbon does not necessarily mean that it has the best adsorption capacity for organic compounds. Kharrazi et al.[217] investigated the effect of pretreatment of elm sawdust with alkali metal on the adsorption of lead and chromium ions. The adsorption capacity of activated carbon for lead ions increased significantly from 233 to 1430 $mg\ g^{-1}$. However, the specific surface area of the magnesium chloride leached pretreated carbon (585 $m^2\ g^{-1}$) was found to be significantly reduced compared to the pristine carbon from the nitrogen adsorption/desorption isotherms and pore size distribution. In the preparation of oxidized mesoporous carbon with fluffy structure from petroleum asphalt, it can be found that the specific surface area decreased from 479 to 334 $m^2\ g^{-1}$. However, the prepared carbon exhibited excellent absorption performance for the removal of malachite green and led ions with maximum adsorption capacities of 963 and 198 $mg\ g^{-1}$, respectively.[218]
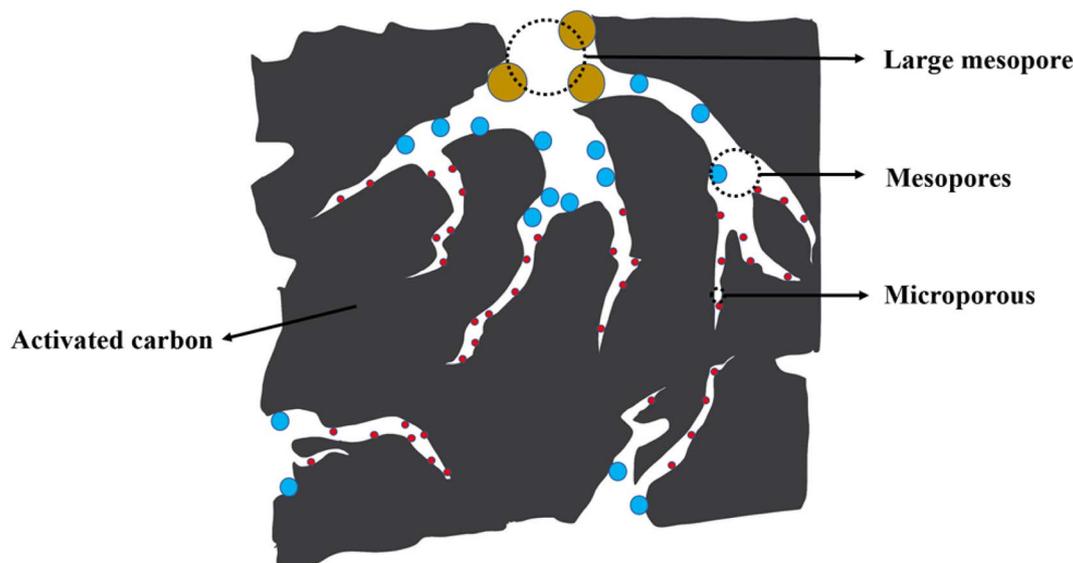
Fig. 8 Pore diagram of activated carbon.

4.1.2 Pore structure. Biomass-derived activated carbon is a porous adsorbent, and its morphological structure, especially the pore size distribution, determines its adsorption capacity for heavy metals.[219,220] Biomass-derived activated carbon contains a variety of pores, the largest of which can be observed by optical microscope and the smallest of which is the same size as the molecules being adsorbed. Fig. 8 shows a thumbnail sketch of the pores of the activated carbon. The IUPAC considers micropore of $r < 2$ nm, transition pore of 2 nm $< r <$ 50 nm, and macropore of $r > 50$ nm.[221–223] Micropores are the main sites of adsorption, while mesopores promote intra-particle diffusion and shorten the adsorption time. The adsorption of heavy metals by biomass-derived activated carbon can be affected by the pore size.[224–226] The macropore of biomass-derived activated carbon is also called transport pore, which usually plays the role of transport channel in the adsorption process. The adsorbed molecules first enter the mesopores through the macropores, then enter the micropores, and finally enter the interior of biomass-derived activated carbon particles for adsorption. Transition pores, also known as mesopores, are smaller than macropores but much larger than adsorbed molecules. The adsorption process starts with a single molecular layer, followed by a multi-molecular layer, which means that this forms a continuous adsorption layer. The smallest pores in carbon are called micropores, also known as capillaries or micropores, which have a smaller effective radius. Micropores are the most important contributors to the specific surface area and pore volume and play a very important role in adsorption, they usually determine the adsorption capacity of carbon. Xue *et al.*[227] pointed out that the adsorption of volatile organic compounds by carbon materials is mainly determined by the micropores. Obviously, the ultramicropores loaded with copper chloride ($d = 0.46$ nm) did not leave enough space for the accommodation of carbon monoxide molecules ($d = 0.38$ nm), resulting in low adsorption of carbon monoxide, and the large mesopores had a large enough pore size to load copper chloride, the surface area used to disperse the copper chloride was low, resulting in low adsorption of carbon monoxide as well. In contrast, ultramicroporous and small mesopores provide high surface area and suitable pore size to disperse ferric chloride well and provide enough space for carbon monoxide adsorption. Similar observations were reported for the preparation of a bioresource of porous carbon for waste-water treatment from tea pomace. The activated carbon was activated with zinc chloride and had the highest iodine value of 1519 mg g^{-1}. The optimized activated carbon possesses a well-developed microporous structure with a high specific surface area of 1029 m^2 g^{-1} and a small pore size of 0.65 nm. And the removal efficiency of the activated carbon was 99.9% for the heavy metal mercury and 74.7% for copper.[228]

Macropores and mesopores can be utilized as diffusion channels for adsorbate molecules to enter the interior of activated carbon particles quickly. Micropores can adsorb pollutants through pore size interception. At the same time, mesopores can produce capillary condensation and adsorb macromolecules that cannot enter micropores. The pore structure is one of the main factors determining activated carbon's adsorption properties.[229] Physical properties such as specific surface area and pore size heavily influence the adsorption capacity of activated carbon.

4.1.3 Functional groups. The oxygen-containing and nitrogen-containing functional groups are the adsorption sites of activated carbon, and the pollutants adhere to the surface of the activated carbon through electrostatic interaction, ion exchange, hydrogen bonding, acid–base interaction, and complexation with the adsorbent.[230–232] The adsorption of heavy metals by carbon adsorbents includes both physical and chemical adsorption. So, in addition to the morphological structure of carbon itself, the chemical functional groups on the surface of the carbon material may also be one of the main

factors in its adsorption of heavy metals. The surface functional groups of carbonaceous adsorbents are not only related to the nature of the biomass but also to the activation or modification method. The heteroatoms of carbon surface functional groups include oxygen, nitrogen, halogen and hydrogen, and determine their surface chemistry, among which oxygen and nitrogen groups on porous carbon are considered to be the most important adsorption groups. Fig. 9 shows the common functional groups on the surface of activated carbon.[233–235]

At activation temperature up to 100 °C, carbon adsorbs oxygen. The adsorbed oxygen molecules are decomposed into oxygen atoms, which are bonded to unsaturated bonds on the carbon surface, producing oxygen complexes. Due to their unstable nature, hydroxyl groups or other basic groups eventually form when they meet water. It also forms basic oxygen groups at 800 °C to 1000 °C in the presence of a little oxygen. The same phenomenon occurs when the activated carbon is cooled at low temperature in contact with oxygen. However, if the starting temperature of the activated carbon is 300 °C and the maximum temperature does not exceed 450 °C, some acidic oxygen groups will appear. Oxygen groups show three types of acidity, basicity, and neutrality, which are related to the oxidation phase.[236–238] In general, liquid oxidation favors the formation of carboxylic acids, while gas oxidation favors the formation of hydroxyl and carbonyl groups.

In addition to oxygen-containing functional groups, the surface of carbon may also contain nitrogen-containing functional groups. Its main source is the introduction of ammonium, nitric acid and nitrogen-containing compounds in the preparation of activated carbon. Nitrogen atoms take different forms due to different conditions in the preparation of activated carbon. The nitrogen group on the surface of carbon is very stable. When heated at 900 to 1200 °C, most of the nitrogen changes to the free state, and a small portion locates at the surface of carbon in the formation of hydrogen cyanide compound, *etc*.[239]

Sulfur containing groups are also common functional groups in carbon materials. And fixing an appropriate amount of sulfur-containing functional groups on the surface of activated carbon will significantly increase the adsorption capacity of metal ions such as mercury and cadmium. Carbon raw materials are treated with sulfur, hydrogen sulfide, sulfur dioxide, carbon disulfide, or sulfides such as sodium thiosulfate at high temperature to produce more surface sulfur-containing groups.[240] The sulfur group on the carbon surface is very stable in strong alkaline solutions and stabilizes after losing a few in strong acid solutions. The presence of surface sulfur groups tends to narrow the pore distribution of activated carbon.[241,242]

4.1.4 Others. Bulk density is an important factor affecting the adsorption capacity of biomass-derived carbon, especially when biomass-derived activated carbon is applied in medical adsorption columns or industrial filtration in adsorption columns. Higher density carbon can capture more heavy metals per unit volume.[243–245] Both physical and chemical properties of activated carbon will affect its adsorption performance. To improve the adsorption capacity of biomass-derived activated
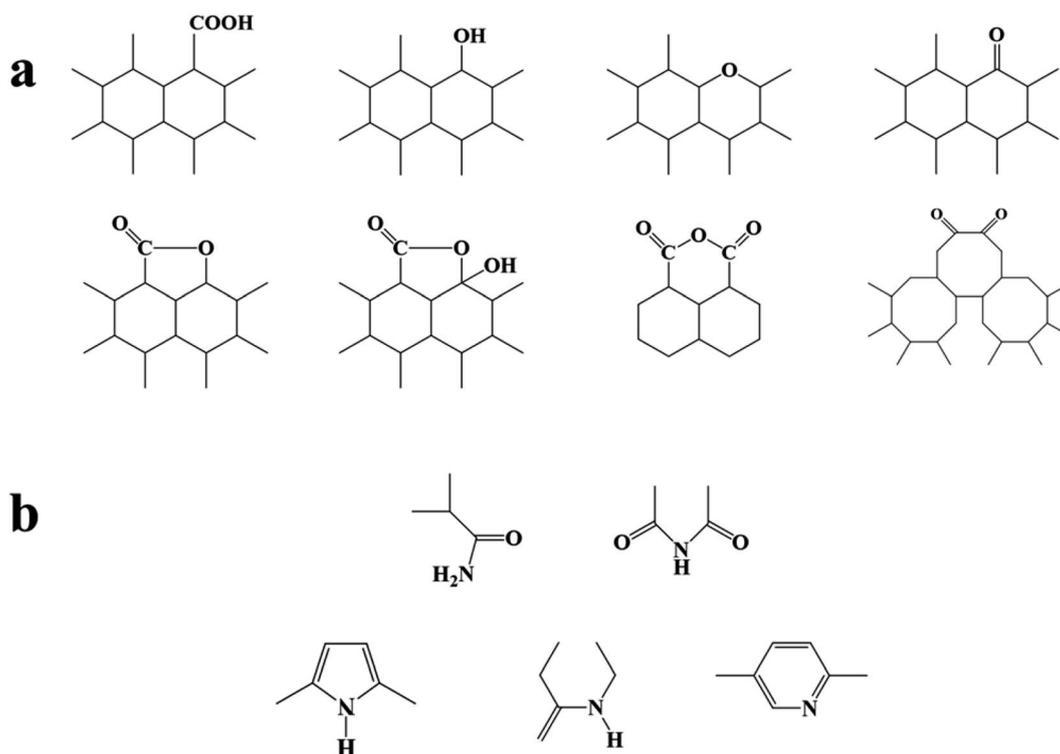

Fig. 9 (a) Common oxygen-containing groups on the surface of activated carbon, (b) common nitrogen-containing groups on the surface of activated carbon.

carbon, it is necessary to investigate the synergy of various properties of activated carbon.

4.2 Adsorption conditions

4.2.1 Temperature. In the adsorption process, the adsorption mechanism of the same activated carbon may be different for different pollutants. The temperature also has different effect on adsorption process. Firstly, the diffusion rate within the pores in activated carbon is a major factor affecting the adsorption rate. The diffusion process is a heat absorption process, so the increase of temperature is beneficial to the acceleration of adsorption rate. Second, the adsorption process is divided into physical adsorption and chemical adsorption. The former is mostly exothermic, so lowering the temperature can improve the adsorption performance, while the adsorption rate in the chemical adsorption process increases with an increase of temperature, and some of the chemical bonds will break with the increase of temperature, further increasing the adsorption sites and the saturation adsorption capacity of activated carbon.[246,247] Khalil *et al.*[248] prepared a biomass-derived activated carbon, named ACPH800, from orange peel obtained from navel oranges by a thermochemical activation method. The result confirmed that the adsorption of chromium ions on ACPH800 is spontaneous in nature ($\Delta G < 0$), and the

negative sign of ΔH indicated that the adsorption is an exothermic process favorable to adsorption at low temperatures. It is also clear from Fig. 10 that the adsorption capacity decreases with increasing temperature. A related class of experiments on the roots of summer grass plants was also reported. The maximum adsorption of lead ions by the prepared and treated adsorbent was 108 mg g^{-1} at 288 K, and the removal of lead ions was 85.7 mg g^{-1} at 308 K. The increase in temperature had a negative effect on the adsorption of metal ions, revealing that these processes are exothermic in nature. However, the adsorption capacity of chromium ions showed a positive effect of temperature on adsorption, with an increase in absorption from 77.2 to 102 mg g^{-1} when the temperature was increased from 288 to 308 K.[249] In conclusion, the effect of temperature on the adsorption of heavy metals by biomass-derived activated carbon is complex. Increasing the adsorption temperature can inhibit physical adsorption on the one hand and enhance molecular diffusion and chemisorption on the other.

4.2.2 pH value. The pH value of the solution is an important factor for adsorption, because it affects the existing form of heavy metal ions in the wastewater solution. The chemical state of the active groups on the adsorbent (degree of protonation) and the charge distribution on the adsorbent surface, which in turn affects the affinity of adsorbent for the target metal ions.[251,252] The effect of pH on cadmium ion removal in water is shown in Fig. 11.[253] The solute equilibrium concentration is decreased with enhancing the solution pH, which could be attributed to the rise of negative surface of adsorbent, consequently favoring the attraction of positive cadmium ions onto the surface of adsorbent. Kokab *et al.*[254] explored the effect of pH on chromium ion adsorption. At pH of 3.2, the adsorption capacity of chromium was 91 mg g^{-1}. Chromium adsorption decreased gradually from 94.5 to 89 mg g^{-1} at pH values between 5.5 and 6.2. This proves higher adsorption capacity at acidic pH and a lower adsorption capacity at alkaline pH. The final result also demonstrated the highest adsorption at pH of 5.5. The main reason for this highest value was the neutralization of the maximum adsorption. The hydroxyl ions (OH$^-$) were neutralized due to excess hydrogen (H$^+$) ions, which promoted the diffusion of dichromate ions and the absorption of biomass-derived activated carbon. At the acidic pH, the surface of biochar adsorbent is positively charged, while the chromate ions are negatively charged, so biochar and chromate ion can interact. However, when the pH increases above 5.5, the concentration of hydroxyl ions increases. The concentration of hydroxyl ions increases due to the excess OH$^-$ ions, and the surface solution of biochar and chromium ions in biochar repel each other. Therefore, determining pH value is necessary prerequisite for studying the adsorption performance, and the selection of suitable solution pH is of great significance for heavy metal adsorption.

4.2.3 Contact time. Generally, with the extension of adsorption time, the amount of chemisorption increases sharply at first, then slowly rises to the emergence platform, and the instantaneous adsorption rate decreases gradually. On the contrary, physical adsorption usually increases slowly with the
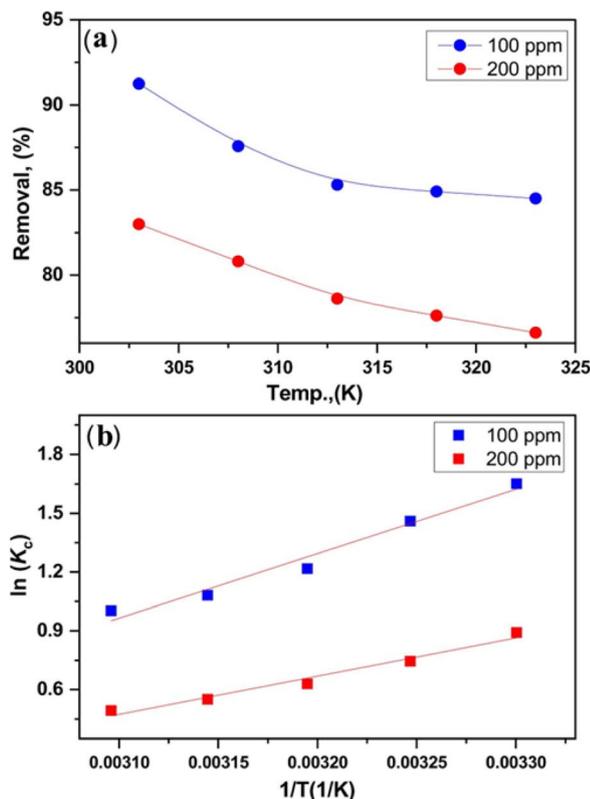

Fig. 10 (a) Effect of temperature on removal of chromium ion by ACPH800, (b) Van't Hoff plot for chromium ion adsorption on ACPH800. This figure has been adapted from ref. 250 with permission from *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, copyright 2023.
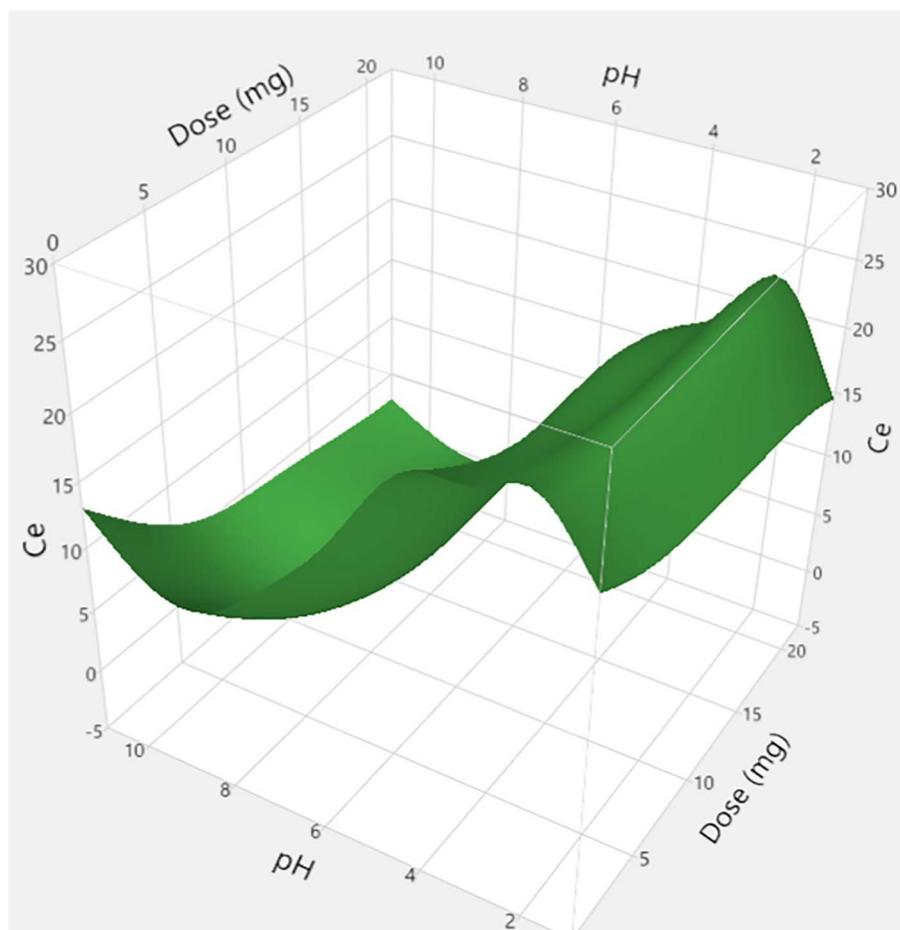
Fig. 11 Surface plot of predicted adsorption capacity. This figure has been adapted from ref. 255 with permission from *Journal of Molecular Liquids,* copyright 2023.

increase of adsorption time, and the adsorption time is longer than that of chemical adsorption.

4.2.4 Others. In addition to the experimental temperature and pH, other adsorption conditions such as the concentration of metal ions, the amount of activated carbon dosing, and the adsorption time also affect the adsorption of heavy metals on carbon materials. When the initial concentration of pollutants in the solution is small, the adsorption capacity of activated carbon will increase with an increase of initial concentration. After the initial concentration reaches a certain amount, the adsorption sites will be saturated, and the adsorption capacity will reach the saturation value at the same time. The adsorption rate will gradually decrease with the increase of initial concentration. Therefore, selecting an appropriate initial concentration is necessary for the practical industrial application of activated carbon adsorption.

The amount of activated carbon is one of the conditions affecting the adequacy of the adsorption process. If the adsorption sites per unit mass of activated carbon are certain, a large amount of activated carbon will increase the adsorption capacity, it will also increase the cost of wastewater treatment, so choosing the amount of activated carbon with high

adsorption capacity and relatively low cost is one of important factors to remove pollutants and reduce the cost of activated carbon adsorption treatment.

The length of adsorption time is a key factor affecting the adequacy of the removal effect. By increasing the adsorption time appropriately, the amount of activated carbon adsorption will effectively increase. However, the increase in adsorption time increases the stagnation time of wastewater, reduces the overall wastewater treatment efficiency, and increases the wastewater treatment cost. Therefore, selecting the appropriate adsorption time is beneficial to improve the adsorption efficiency of activated carbon.

5. Conclusions and prospects

To date, human activities have led to the accumulation of various heavy metals at a rate that exceeds the capacity to treat or manage them. In the last five years, public awareness of environmental protection and the selection of suitable sorbents are among the most challenging things in removing heavy metal pollution.

Although many methods for removing heavy metals have been proposed in recent years, many of these techniques are not

suitable for commercial application due to low efficiency, high energy consumption, or poor selectivity. Biomass-derived activated carbon has shown prospective potential due to its large specific surface area, rich pore structure, high stability and relatively low cost.

In this paper, the sources of heavy metals, removal methods and preparation methods of biomass activated carbon were reviewed. The key factors of adsorbents, physical and chemical properties of heavy metals and adsorption conditions affecting heavy metal adsorption were emphatically introduced. In addition, most of heavy metals adsorbed on biomass-derived activated carbon materials can be recovered by desorption processes under various conditions. Biomass is widely utilized as a precursor for the formation of activated carbon. The choice of biomass, type of carbonization, and activation can also affect the porosity and surface area of the carbon. Under suitable conditions or appropriate modifications, almost all of biomass-derived activated carbons exhibit high adsorption capacity of heavy metal—both the physical form and the chemical functional groups of the adsorbent influence the adsorption of heavy metals. In general, larger specific surface areas and smaller pore sizes favor adsorption, while the influence of functional groups is related to the pH of heavy metal-containing wastewater. Adsorption conditions such as temperature and pH content seriously affect the adsorption of heavy metals. Too high a temperature is not favorable for heavy metal adsorption. Too high or too low a pH level can also hurt adsorption.

Currently, "green" is the trend of today's society, there is no doubt that the application of biomass-activated carbon in wastewater is becoming more promising. However, some knowledge gaps still need to be filled to improve further the adsorption capacity of biomass-derived activated carbon for heavy metals in actual complex samples. Reducing the production cost of carbon adsorbents, the large-scale production of biomass-derived carbon is complex due to the limitation of harsh reaction conditions, high equipment requirements, and high dosage of modifier agents. Therefore, researchers must seek simple synthetic methods to meet the mass production of adsorbents from biomass-derived activated carbon. In addition, several challenges need to be overcome. For example, the aim is to improve the selectivity of carbon adsorbents for heavy metals. Furthermore, most of the current co-modifications of biomass-derived activated carbons are still based on laboratory studies, so the reproducibility of commercial biomass-derived activated carbons is an issue that we must consider. Shortly, the preparation of biomass-derived activated carbon will certainly be commercialized in a simple, fast and easy way.

Conflicts of interest

All authors disclosed no relevant relationships.

Acknowledgements

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