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REVIEW ARTICLE

The Application of Biochar as Heavy Metals Adsorbent: The Preparation, Mechanism, and Perspectives

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Abstract

With the increased activity from humans in agriculture and industry, a growing amount of waste containing heavy metals is discharged into the environment, which brings great risk to human health. Biochar, as a great absorbent for heavy metals remediation, has been extensively studied. The adsorption capability of biochar is affected by many factors, such as the species and properties of raw materials, the preparation methods (temperature, heating rate, and residence time), and functional sites introduced by the modification agent. However, how these factors determine the adsorption of heavy metals on biochar is not clear. The present work thoroughly reviewed the traditionally used methods for biochar preparation such as pyrolysis, hydrothermal carbonization and gasification, meanwhile, the emerging biochar preparation techniques (retort carbonization and torrefaction) are also explored. Accordingly, the commonly used modification methods (alkali modification, acid modification, ferromagnetic modification, microbial modification, etc.) are comprehensively investigated. The adsorption kinetics and isotherms are also discussed to demonstrate the adsorption mechanism from a theoretical basis. Notably, to facilitate the large-scale biochar application in practice, a discussion focusing on the factors associated with practical utilization is provided. Consequently, the review of environmental risk and the challenge regarding biochar disposal safety, a thorough economic analysis, detailed exploration of industrial-scale implementation challenges, enhanced life cycle assessment and sustainability analysis are included, aiming to contribute a better understanding of the practical implications of engineering biochar for application in heavy metals remediation.

Article Highlights

- **Biochar is a promising material in the remediation of heavy metal pollution.**
- **Modification of biochar dramatically improved the adsorption capacity.**
- **Easy and safe recycling of used biochar is of great interest and challenge.**

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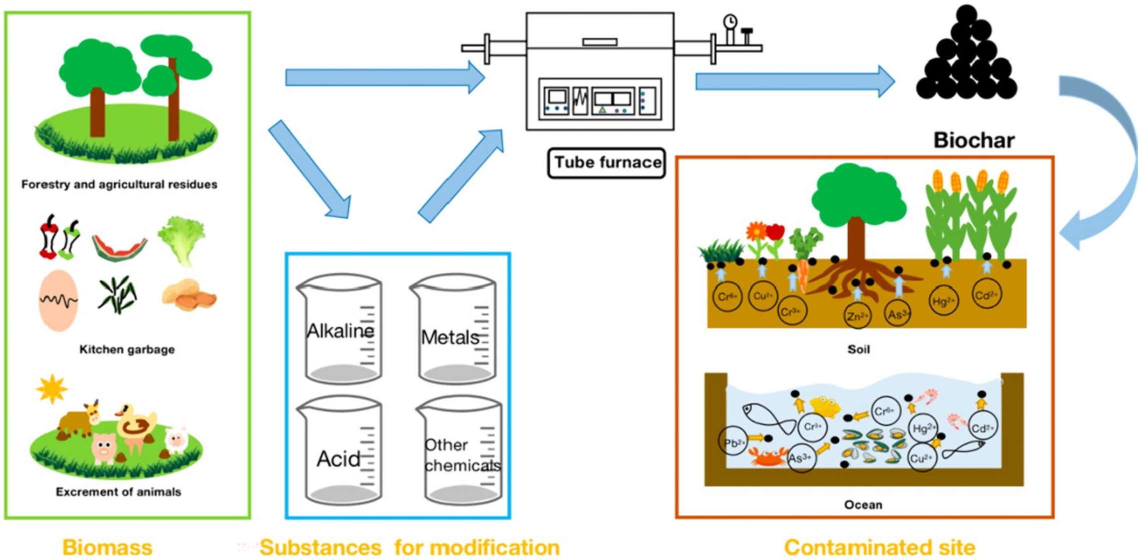
Graphical Abstract



Keywords Biochar · Heavy metals · Adsorption · Pyrolysis · Modification

Introduction

With the increased activity from humans in agriculture and industry, a growing amount of waste containing heavy metals is discharged into the soil and oceans, thus causing great pollution to the environment. Therefore, removing the heavy metals deposited in the soil and water is critical to establishing a safe and healthy environment for the lives on earth. Among the current methods of removing pollutants, adsorption is promising because of its simplicity, low energy requirement, and adaptability to various pollutants (Abdel Maksoud et al. 2022; Abdelfatah et al. 2021; Osman et al. 2022a).

There are many types of adsorbents, such as biosorbents, magnetic adsorbents, and industrial adsorbents (Osman et al. 2023). In the case of biosorbents, one of the basic factors to be considered in the selection of biosorbents is the cost and source of the biomass (Osman et al. 2023). Despite their current widespread use, biosorbents face a number of challenges and limitations. In agriculture, biochar has an inhibitory effect on soil aging and it needs to be added intermittently to optimize the soil environment (Kavitha et al. 2018). Secondly, the recovery of biochar from the site is not economically and technically feasible. Magnetic adsorbents are of interest due to their unique properties and low costs (Abdel Maksoud et al. 2020). They are easily recyclable, biocompatible, and reusable, making them a promising class of materials (Zhang et al. 2022b). A number of methods have been used to prepare magnetic adsorbents, and their limitations vary depending on the method of preparation. For example, co-precipitation is in a way that the particles are not homogeneous, thermal decomposition affects the safety of the reactants, and chemical reduction affects the probability of oxidation of the magnetic metal adsorbent (Osman et al. 2023). Therefore, the future research direction can be more inclined to explore more novel, safe, efficient, and functional group-rich magnetic adsorbent preparation. Thirdly, industrial adsorbents (Rangappa et al. 2024), low-cost adsorbents prepared from industrial wastes, are of interest due to their abundance. However, these industrial wastes have poor adsorption capacity and can only be converted into effective absorbents by modifying them, which resulted in an increase of the cost. Therefore, in future research, the reduction of production costs as well as the increase in the resistance to desorption should be investigated.

Biochar adsorbents come from a wide range of sources, mostly renewable resources, such as plant-based materials, animal wastes, and marine biomass, which can be easily modified to increase their adsorption capacity (Crini et al. 2019; Osman et al. 2020a). In particular, agricultural waste biomass can be used as functional materials or converted into many valuable products after various treatments (Rajamani et al. 2023). The biomass is mainly composed of cellulose, hemicellulose, and lignin (Tan et al. 2021). Lignocellulosic biomass contains 33–51% cellulose, 19–34% hemicellulose, and 11–25% lignin. Thermochemical conversion is one of the effective methods to deal with waste biomass, that is, biomass is burned into biochar at high temperatures with limited oxygen. Different temperatures and different oxygen content lead to variations in biochar properties. According to different pyrolysis process conditions, biomass pyrolysis can be divided into slow pyrolysis, conventional pyrolysis, fast pyrolysis, and flash pyrolysis. At high temperatures, the substrate undergoes complex chemical reaction processes, including chemical bond breaking, polymerization, isomerization, etc. The properties of biochar, such as the surface area, the types and quantities of surface functional groups, pore distribution, and mineral concentration, vary at different temperatures, thus affecting the adsorption characteristics of biochar (Li et al. 2020a). Therefore, the adsorption should be carried out under the most suitable temperature conditions to ensure a high contaminate removal rate. Biochar prepared at high temperatures usually contains more carbon elements that can be fixed in the biochar structure (i.e. a higher carbon content) (Pan et al. 2021). Increasing the pyrolysis temperature will also increase the aromatics of biochar, reduce the polarity of biochar, and reduce the hydrophilicity of the biochar surface (Pan et al. 2021).

With a large specific surface area, high porosity, and rich surface functional groups, biochar has demonstrated great contributions in the aspect of environmental protection, such as the application in soil pollution control, carbon fixation, polluted water treatment, greenhouse gas reduction, etc. However, in some cases, the application of unmodified biochar is limited by its low adsorption capacity. It is essential to have the pure biochar modified to obtain an improved adsorption capacity (Tan et al. 2022). There are many ways to chemically, physically, or biologically modify the properties of biochar (Rajapaksha et al. 2016). These methods include the treatment with steam, acids, alkali, metal oxides, carbonaceous materials, clay minerals, organic compounds, and biofilms (Sizmur et al. 2017). The objectives of these treatments are generally to (i) increase the surface area of the biochar, (ii) modify or enhance the surface properties of the biochar, or (iii) use the surface as a platform for embedding another material (or organism) with beneficial surface properties (Sizmur et al. 2017), thus achieving more efficient removal of contaminants. Physical activation of biochar using steam or chemical activation of biochar using acidic and alkaline solutions is usually carried out after pyrolysis. However, chemical activation before pyrolysis has been reported to give superior performance (Sizmur et al. 2017). Meanwhile, nowadays, more attention is being paid to sustainable development and circular economy. Circular economy approaches for converting raw low-value biomass into high-value adsorbent materials are now a hot research topic. Osman, for example, has synthesized value-added materials such as biochar using low-value waste cereal waste (Osman et al. 2020b) and giant manzanita (Osman et al. 2020a). This method is considered to be up-cycling and stabilizing and can support and promote the concept of a circular economy, as well as being considered as a pathway to cleaner production (Suárez-Eiroa et al. 2019).

In this paper, a comprehensive review of the synthesis and modification of biochar is presented. Meanwhile, the adsorption mechanism, adsorption kinetics, and isotherms of biochar are also discussed to further understand the relationship between biochar properties and its heavy metal adsorption capacity, and to provide new perspectives on the application of biochar in heavy metal remediation. Since the handling and disposal of saturated adsorbed biochar has not been fully resolved, the risks of biochar to the environment as well as its safe disposal and challenges to avoid secondary pollution of the environment are reviewed. At the same time, the economic viability of biochar in industry and its sustainability, and an assessment of the life cycle of biochar are also discussed with the aim of better understanding the significance of the application of engineered biochar in heavy metal remediation.

Factors Affecting Biochar Production

Biochar feedstock is an important factor affecting the preparation of biochar, and the type of feedstock will vary depending on the region. For example, in southern Thailand, the widespread availability of oil palm and rubber tree waste makes it more common to be used as biochar feedstock (Sutarut et al. 2023). Biochar can be prepared through pyrolysis (Huang et al. 2020), hydrothermal carbonization (HTC) (Zhang et al. 2018), gasification (Wang and Wang 2019), retort carbonization (Adeniyi et al. 2023a) and torrefaction (Chen et al. 2021b), among which pyrolysis is the most commonly used method and mainly discussed in this work, retort carbonization and torrefaction are relatively new processes for the production of biochar. The conversion process from biomass to biochar is shown in Fig. 1.

Temperature

The pyrolysis is carried out under oxygen-free conditions at 300–900 °C (Wang and Wang 2019). The temperature of pyrolysis is an important factor in determining the characteristics of biochar. Biomass consists of cellulose, hemicellulose, and lignin, the content of which varies with the type of feedstock (Wang and Wang 2019). Pyrolysis is the process of breaking the structure of the above three components and transforming them into biochar as well as bio-oil and syngas. The pyrolysis process involves the conversion of three main components, with hemicellulose being the most readily decomposed component, followed by cellulose, while lignin is the least efficiently decomposed and leaves the highest residue in the solid residue. Most of the gases released in the process were similar, including carbon dioxide, carbon

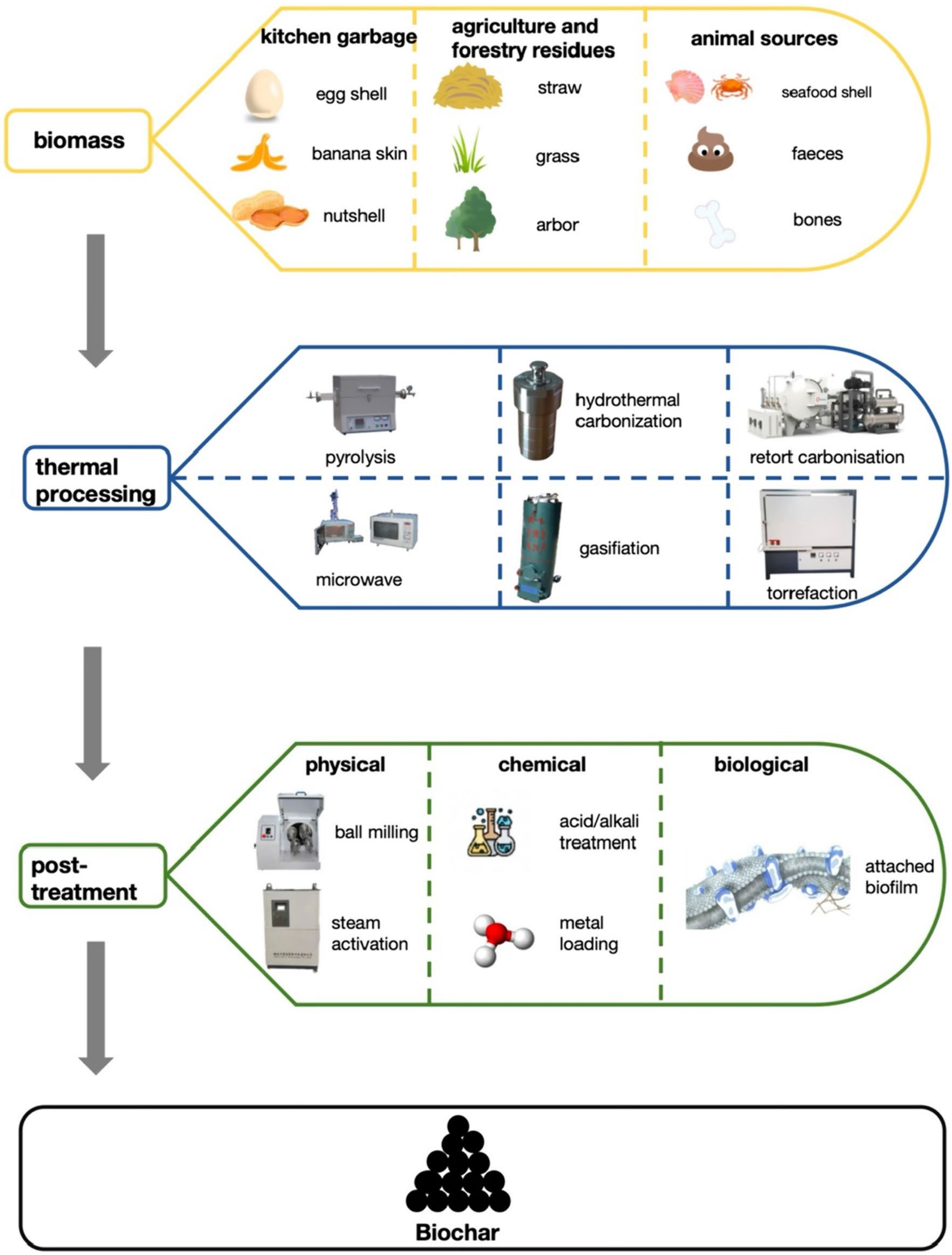


Fig. 1 Process and method to convert biomass to biochar

monoxide, methane, and some organic matter. Biochar is synthesized in horizontal tube furnaces at 700 °C and above, with low heating rates (10 °C/min), and also under three different atmospheres: N_2, CO_2 and H_2O. In addition, the temperature of pyrolysis also has an impact on the distribution of biochar, bio-oil, and syngas. Bruun et al. (2011) found that as the temperature increased, syngas production increased and biochar production decreased, the amount of bio-oil went up and then went down. The bio-oil was found to be the richest product at 525 °C, with the yield of syngas and biochar is approximately 10% and 25%, respectively. Das et al. (2021) selected maize stems, black crops, and pine needles as substrates. The biochar yield was found to be the highest at 400 °C followed by 500 °C and the lowest biochar yield was found at 600 °C.

The process of holding biomass under hydrothermal conditions for a period of time and converting the biomass into carbon material is known as hydrothermal carbonization (Alterkaoui et al. 2022). The temperature of hydrothermal carbonization was normally below 250 °C (Wang and Wang 2019). The temperature played an important role in the structure and properties of produced biochar. In general, with the increase in temperature, the yield of biochar and the number of acidic functional groups decreased, while the amount of basic functional groups, ash content, and pH increased (Yang et al. 2019b). Zhou et al. (2019b) investigated the effect of different hydrothermal carbonization temperatures (180, 210, 240 °C) of several poultry manures on the yield of manure biochar. They found that the yield of biochar gradually decreased with increasing temperature, with the highest yield of 66% being reached at 180 °C. Zhang et al. (2018) used eucalyptus sawdust to prepare KOH-modified biochar for Cr^{6+} adsorption at different hydrothermal carbonization temperatures. It was found that the modification carried out at a hydrothermal carbonization temperature of 220 °C and modified with 0.05 mol/L KOH was able to obtain a high biochar yield (47.61%) and the highest adsorption rate of Cr^{6+} reached 92.16%, with a maximum adsorption amount of 46.08 mg/g, which is an effective way to remove toxic Cr^{6+}. Ortiz et al. (2020) explored the effects of pyrolysis temperatures (673, 773, and 873 K) and feedstock (nuts and almond shells) composition on biochar yields and physical–chemical properties. They found that the yield of biochar depends strongly on the pyrolysis temperature. The authors found that the yield of both nut and almond shell biochar decreased with increasing pyrolysis temperature. Gasification requires higher temperatures of around 700–1000 °C. In the temperature range of 700–850 °C, primary vapors and liquids are converted to gaseous olefins, CO_2, H_2, CO, water, phenolic and aromatic hydrocarbons. A further increase in temperature from 850 to 1000 °C involves the conversion of secondary products to H_2, methane, CO, water, carbon dioxide, tar, and biochar (Patra et al. 2021). It takes place in the presence of a gasification medium, which can be air, oxygen (O_2), steam (water) or carbon dioxide (CO_2). Biomass gasification has a high potential for application in waste treatment compared to other existing technologies such as landfilling and incineration, as it can produce a wide range of products with utilization value. The high temperatures in the gasifier at the time of gasification may result in the loss of functional groups such as hydroxyl, carboxyl, and carbonyl groups (You et al. 2017). As a result, the functional groups of gasified biochar are generally less abundant than those produced by other thermochemical processes such as pyrolysis and hydrothermal charring (You et al. 2017). However, gasified biochar can also be used as a carrier for the adsorption of some pollutants due to its large porosity and specific surface area (Liu et al. 2020a).

Retort carbonization is a type of carbonization in which the flue gases from the distillation process are re-combusted in the heating zone, thus providing more heat for the distillation process (Ighalo et al. 2022a). Retort carbonization systems are characterized by controlled heating conditions, efficient energy use, and by-product recovery (Narmatha et al. 2020). These systems have attracted attention for their ability to produce biochar with desirable characteristics (Adeniyi et al. 2023b). However, it has been found that differences in temperature and feedstock affect the biochar yield from retort carbonization. Chandrasekaran et al. (2019) investigated the retort carbonization of julienne flowers and observed a biochar yield of 29.6% at 500 °C. Ighalo et al. (2021) observed a biochar yield of 28.57% from dried almond (Terminalia catalpa) leaves at 494 °C. Djousse Kanouo et al. (2018) prepared biochar using maize and eucalyptus bark by retort carbonization at 280 °C and found that the average yield of biochar varied with the feedstock from 33% for maize biochar to 68% for eucalyptus bark biochar. Chandrasekaran et al. (2021) investigated the carbonization of prosopis julius larwood and casuarina quisetifolia wood at different final carbonization temperatures varying from 400 to 700 °C. They found that charcoal yield at 400 °C and fixed carbon content at 700 °C obtained from casuarina wood were the highest at 41.15% and 87.78%, respectively.

Torrefaction is carried out in the absence of oxygen and is aimed at producing solid fuels such as coked charcoal or biochar. Torrefaction is classified as dry torrefaction and wet torrefaction (Chen et al. 2021b). In the dry firing process, biomass can be roasted in a dry, non-oxidizing (inert) or oxidizing environment, typically at temperatures between 200 and 300 °C. In the wet torrefaction process, the biomass is roasted at 180–260 °C and the biomass content is increased with a solution of water and dilute acid. The main objective of wet torrefaction roasting is to upgrade solid biomass as an alternative to coal (Chen et al. 2021b). Simonic et al. (2020) analyzed the effect of torrefaction temperature and time to determine the optimal operating parameters of the torrefaction process. They found that the optimal torrefaction time and temperature for oak and mixed wood was about 1.2 h at 260 °C.

Heating Rate

Pyrolysis is divided into slow pyrolysis, fast pyrolysis, and flash pyrolysis (Ighalo et al. 2022b) according to the difference in temperature-increasing rate. Faster heating rates favor the evolution of fuel (liquid and gaseous) products (Ighalo et al. 2022b).

Slow pyrolysis is a robust and energy-efficient process. During slow pyrolysis, the yield of biochar is the largest compared to gas and liquid products (Tan et al. 2021). At heating rates below 10 °C/min, the chemical bonds are broken down and the structure of the biomass is affected, rearranging the structure into a more stable matrix and thus inhibiting the formation of volatiles (Tan et al. 2021). Yu (Yu et al. 2019)'s team investigated slow pyrolysis in the temperature range of 350–600 °C using a fixed-bed reactor. They found that the biochar yield decreased from 32.7% at 350 °C to 20.7% at 600 °C, while the carbon content gradually increased up to a maximum of 91.6%. Moreover, the microporous structure developed rapidly at 500 °C. Wang et al. (2022) investigated the slow pyrolysis of corn cobs, corn stover and spruce wood at 600 °C and also characterized the yield and properties of the products, focusing on solid biochar. The results showed that the yields of biochar and condensate from corn cob, corn stover, and spruce wood were comparable. However, their gas releases and yields differed significantly, which was mainly related to the different chemical compositions (i.e., hemicellulose, cellulose, lignin, and inorganic species).

Fast pyrolysis can produce biochar with more advantages by applying heat in a short time at a higher temperature. In the fast pyrolysis process, the biomass is rapidly heated at 600–1000 °C under anaerobic conditions to produce pyrolysis vapors and biochar (Tan et al. 2021). Fast pyrolysis has a relatively fast heating rate (10–10,000 °C/min) and a short residence time (0.5–5 s) but maximizes bio-oil yield (Tan et al. 2021). The biomass is rapidly heated and the released pyrolysis vapors are rapidly transported from the pyrolysis reactor (Wang et al. 2020a). Incomplete pyrolysis of biomass occurs if the temperature is too low, or the particles of the feedstock are too large. This easily leads to rapid mineralization in soil when the biochar is applied to the soil. Thus, the particle size of feedstock has to be small enough and the heat is required to be high enough to ensure complete carbonization during pyrolysis. Fluidized bed and pyrolysis centrifuge reactor (PCR) are commonly used as the reactors in fast pyrolysis.

Flash pyrolysis, also known as ultra-fast pyrolysis, is characterized by high heating rates and high temperatures, with vapors residence times typically less than one second, allowing rapid cooling of the pyrolysis vapors and rapid removal of coke from the system (Ighalo et al. 2022b). Kristina Maliutina et al. (2017) investigated the flash pyrolysis reaction of chlorella vulgaris and palm kernel shell at 600–900 °C and found that the highest bio-oil yields of 60.22% and 73.74% were obtained during the pyrolysis of chlorella vulgaris and palm kernel shell at 800 °C and 600 °C, respectively. Gholizadeh et al. (2020) found experimentally that as the heating rate gradually increased, the amount of fuel product increased significantly and the residual charcoal yield decreased significantly. This is due to the flash pyrolysis of biomass, which produces more fuel products at higher heating rates (Varma and Mondal 2017) Exploring the effect of heating rate in flash pyrolysis is difficult to carry out because the pyrolysis process is conducted at very high temperatures in a very short period (less than 1 s) (Ighalo et al. 2022b).

Residence Time

The residence time is one of the important factors affecting the yield and properties of biochar, such as specific surface area and pore size, therefore, residence time is an important factor affecting the adsorption performance of biochar (Yuan et al. 2023). Zhao et al. (2018) investigated the effects of residence time on the yield of biochar produced from rapeseed. They found that the biochar yield decreased with the increase in residence time. The effect of production conditions (pyrolysis temperature and residence time) on the basic properties and nutritional traits of biochar from different feedstocks (maize stover, rapeseed straw, wheat straw, and peanut hulls) was investigated by Wang et al. (2020c). An increase in pyrolysis duration could improve biochar pH, electricity conductivity (EC), ash content, stability, and nutrient content, especially below 500 °C.

Catalyst

Catalytic processes play an important role in biochar production (Cheng and Li 2018). Common catalysts include metal salts, metal (alkaline earth and transition metal) oxides, and zeolites (Jiang et al. 2013; Sert et al. 2011; Shao et al. 2010). Reduced tar is important for the production of clean syngas from biomass and is also very dependent on the use of catalysts. When a reversible reaction occurs, catalysts can catalyst both forward and reverse reactions (Bohlouli and Mahdavian 2021). Different base, acid, and enzyme-based catalysts are being used to produce biochar (Chi et al. 2021). Qin et al. (2023b) produced renewable biochar and green chemicals by catalytic pyrolysis from poplar using iron nitrate and zinc chloride as additives. The additives contribute to the production of furfural in biochar, promote the production of H_2, and inhibit the production of CO.

Types of Biochar and Biochar-Supported Adsorbent

Pure Biochar

Biochar with No Modifications

Biochar can be obtained from diverse sources. The material riches in cellulose, hemicellulose, and lignin can be used as raw materials for biochar production, including agricultural and forestry waste, manure, sludge waste, and kitchen scraps. For example, corn stalk (Zhang et al. 2019b), corn cob (Wang and Wang 2019), bagasse (Neolaka et al. 2020), cow manure (Zhang et al. 2021a), pig manure (Lee et al. 2020), sewage sludge (Singh et al. 2020), wood chips (Mokrzycki et al. 2020), and coconut shell (Samsudin et al. 2019) was reported to be raw materials for biochar production. The biochar made from different feedstocks was found to exhibit various properties since the raw materials themselves were different owing to their diverse compositions and structures. Till now, a great number of studies have investigated the effectiveness of biochar produced from various raw materials. For example, Deng et al. (2020) prepared low-cost banana stem biochar using pyrolysis (used at 500 °C) for the removal of heavy metal ions (Zn(II), Mn(II) and Cu(II)) from aqueous solutions. The experimental results showed that the initial solution pH affects the ability of biochar to adsorb heavy metal ions in both mono and polymetallic systems. The adsorption of Cu(II) by biochar was highly selective compared to Mn(II) and Zn(II). Biochar produced by the microalga Spirulina was used to study the adsorption efficiency of heavy metals, i.e., Cd(II), Cu(II), and Pb(II) by Moon et al. (2023). It suggested that biochar at 200 °C showed a high removal rate of Cd(II), Cu(II), and Pb(II) by 95.21%, 96.02%, and 97.58%, respectively. Cao et al. (2019b) pyrolyzed pomegranate peel at 300 °C and 600 °C to produce biochar, and explored its adsorption capacity of Cu(II) in soil. It was found that the adsorption capacity of biochar produced by pyrolysis at 600 °C (51.92 mg/g) was stronger than that of biochar produced by pyrolysis at 300 °C (44.63 mg/g). Salem (2023) utilised bagasse biochar (SCBB) as a biosorbent material for Sr^{2+}. The removal rates of these solutions varied between low and high concentrations of Sr^{2+}, 29% and 73%, respectively. The removal of Pb^{2+} from wheat straw biochar at 600 °C was studied by Vaghela et al. (2022). A Box Behnken experimental design was used and the optimum value of Pb^{2+} (99%) was found at 2.90 (g/L) biochar dose, 0.022 (mg/g) heavy metal concentration and 309 (min) time.

Biochar with Alkaline Modifications

Although pure biochar has been widely used and proved to be an effective adsorbent for heavy metals, its adsorption performance may not always be satisfactory due to the trace amount of heavy metal and the complex environment where large quantities of interfering pollutants co-exist. Therefore, it is crucial to modify biochar appropriately to enhance its performance. In addition, it is found that various pretreatment of biochar before adsorption can not only increase the adsorption efficiency of pollutants but also eliminate or reduce the interference of byproducts in the adsorption process (Zhou et al. 2019a). Biochar modification methods include chemical modification, physical modification, mineral adsorbent impregnation, and magnetic modification (Rajapaksha et al. 2016), among which chemical modification is commonly used. It includes acid modification, alkali modification, oxidant modification, metal salt or oxidant modification, and carbonaceous material modification.

Alkali modification can improve the alkalinity of biochar, and optimize the pore characteristics of biochar (Li et al. 2020b), and some can also improve the content of oxygen elements (Li et al. 2016). At present, the commonly used types of alkali modification are using sodium hydroxide, potassium hydroxide, and potassium carbonate. Wang et al. (2023) and his team prepared biochar from cassava stems, rubber wood, and bagasse, and then further modified it with KOH to remove hexavalent chromium. The results showed that the pore characteristics and redox capacity of the modified biochar were improved, and the KOH-modified rubberwood biochar showed the highest removal rate of Cr(VI), which was 6 times higher than that of the unmodified biochar. Yang et al. (2022) found that the specific surface area and total pore volume of biochar changed significantly when the biochar was treated with NaOH at 300 °C and 400 °C, and the pollutants Cr^{3+} were effectively adsorbed by the alkali-treated biochar. Yuan et al. (2020) used rice straw as the raw material to produce biochar and modified it with Fe^{2+}/Fe^{3+} and NaOH, which greatly increased the adsorption capacity of Cd. They also found that Fe-modified biochar had a C-O-Fe structure formed on the surface of biochar, which was considered to contribute to a sharp increase in adsorption capacity.

Biochar with Acidic Modifications

Apart from alkaline modifications, using acid as a modification agent is gaining attention to enhance the adsorption capacity of biochar. The main purpose of the acid modification is to remove impurities such as metals and introduce acid functional groups on the surface of biochar (Liou and

Wu 2009; Wang and Wang 2019). Oxidation of biochar by oxidizing agents such as sulfuric (Xu et al. 2023) and oxalic acids (Xie et al. 2023) may have added oxygen-containing surface functional groups to its surface, which increases the active adsorption sites on the surface of the biochar and thus removes pollutants. In general, strong acid treatment can introduce acidic functional groups to carbon-based surfaces, thereby increasing adsorption capacity through ion exchange and complexation (Yu et al. 2023).

Commonly used acidic acidifying compounds include sulphury acid, hydrochloric acid, nitric acid, oxalic acid, phosphoric acid, and citric acid (Rajapaksha et al. 2016). The impregnation ratio, type of acid, and activation temperature affected the properties of the resulting biochar (Panwar and Pawar 2022). Zhou et al. (2019a) studied the effect of hydrochloric acid, sodium hydroxide, deionized water, and ethanol pretreatment on Cr^{6+} adsorption capacity of straw biochar. They found that the adsorption capacity of biochar modified by hydrochloric acid was higher than that modified by the other three methods at the same pyrolysis temperature. This could be attributed to the impact of hydrochloric acid on the spatial structure of biochar, which in turn increases the number of adsorption sites for Cr^{6+} in biochar. Yu et al. (2021) found that the dehydration process of sulfuric acid during carbonization promotes the formation of the carbon skeleton of biochar and the oxygen-containing functional groups on its surface, which can provide sufficient adsorption sites for heavy metals to enhance the adsorption of Pb^{2+} and Cd^{2+}. It has been found that when nitric acid and potassium permanganate were co-modified with biochar, the specific surface area of biochar increased significantly (Qin et al. 2023a). Qin et al. (2023a) found that the specific surface area of potassium permanganate and nitric acid-modified coconut shell carbon was 3.02 times higher than that of coconut shell carbon, and the adsorption kinetic data of MHBC for Pb^{2+} and Cd^{2+} were more in line with the proposed second-order kinetic model, which indicated that the adsorption process was dominated by chemisorption.

Min et al. (2022) and his team modified the biochar of sludge and rice husk with oxalic acid. They found that modified biochar was 10 times more effective in adsorption than the unmodified ones. Meanwhile, the modified rice husk biochar was more efficient in adsorption than the modified sludge biochar, which was due to the differences in elements and functional groups of the raw materials.

Biochar with Oxidation Modifications

There are many other chemical modification methods, such as oxidation modification, which can enhance the adsorption capacity of biochar for heavy metals and also improve carbon retention rate and carbon stability. Oxidative modification can increase oxygen-containing functional groups. Zhang et al. (2021c) and his colleagues modified hickory wood chips biochar produced at different pyrolysis temperatures with hydrogen peroxide and found that the adsorption efficiency of heavy metals was improved due to a significant increase in the hydroxyl and carboxyl content of the biochar surface. Most experiments have confirmed that modification can significantly improve the adsorption capacity of biochar, however, it was found that the adsorption capacity of high-temperature biochar decreased under the treatment of hydrogen peroxide (Nie et al. 2019; Wu et al. 2017). For example, Encinas-Vazquez et al. (2021) prepared biochar from almond hardwood and olive branches and modified it with H_2O_2. The results showed that the maximum adsorption capacity of both materials for Pb^{2+} was reduced. The adsorption capacities of unmodified and modified almond biochar for Pb^{2+} were 40.32 mg/g and 24.81 mg/g, respectively, but the adsorption capacity of olive branch biochar before and after modification was unchanged and was about 12.84 mg/g. The different preparations and modifications of biochar for heavy metal adsorption are summarized in Table 1.

Biochar Immobilized with Microbe

It is well known that microbes have a good capability of removing heavy metals in the environment. However, the application of microbes in heavy metals remediation is limited due to microbial loss and growth inhibition (Chen et al. 2021c). Microbial immobilization technology is an environmentally friendly technique that attaches the microorganisms on to an insoluble substrate surface, which could significantly reduce microbial loss and improve microbial degradation efficiency (Luo et al. 2015). It also allows for the recovery of the microbial biocatalysts after the reaction has taken place (Liu et al. 2020b). Extensive research has been conducted using microbes through immobilization technology to remove pollutants such as heavy metals. The selection of carrier material is an important factor in microbial fixation (Rikmann et al. 2016). It always requires that the carrier has good properties in terms of its inertia, physical strength, stability, renewability, and cost (Liu et al. 2020b). Biochar is reported to provide stable and suitable conditions for the survival and activity of microorganisms. It was found that microorganisms removed pollutants mainly resulted from the oxidation and decomposition of pollutants and the immobilized cell had a higher adsorption efficiency than free cells (Huang et al. 2020; Lou et al. 2019). In addition, the biochar itself is a good adsorbent for heavy metals removal. In this regard, the immobilization of microbes on biochar could be a promising technology to enhance the heavy metals removal efficiency (Lou et al. 2019).

The loading modes of biochar and microorganism are shown in Fig. 2. The loading of microorganisms on biochar has three modes: adsorption, trapping, and covalent. In

Table 1 Pure biochar as an adsorbent for heavy metals removal

Feedstock	Preparation temperature	Type of process	Target pollutants	References
Sewage sludge	300 °C, 400 °C, 500 °C	Slow and fast pyrolysis	As(V) and Cr(III)	Agrafioti et al. (2013)
Corn straw	350 °C, 500 °C, 700 °C	Slow and fast pyrolysis	Zn(II)	Song et al. (2020)
Wheatgrass and cow dung	450 °C	Fast pyrolysis	Cd(II) and Sb(III)	Jin et al. (2018)
Black fungus	400 °C	Slow pyrolysis	Cr(VI)	Jin et al. (2018)
Corn straw	500 °C	Fast pyrolysis	Hg(II) and Atrazine alone or a mixture of the two	Tan et al. (2016)
Almond hardwood	750 °C	Flash pyrolysis	Pb(II)	Encinas-Vázquez et al. (2021)
Sludge	900 °C	Flash pyrolysis	Cd(II)	Chen et al. (2015)
Beet Root Powder	300 °C	Slow pyrolysis	Cr(VI)	Dong et al. (2011)
Corn straw	400 °C, 600 °C, 800 °C	Slow and fast pyrolysis	As(V)	Wang et al. (2021c)
Cotton stalk	250 °C, 350 °C, 450 °C, 550 °C, 650 °C	Slow and fast pyrolysis	Pb(II)	Gao et al. (2021)
Pomegranate peel	300 °C and 600 °C	Slow and fast pyrolysis	Cu(II)	Cao et al. (2019b)

Modified Biochar as an adsorbent for heavy metals removal

Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Biochar with acidic modifications						
Straw	300 °C, 500 °C, 700 °C	Slow and fast pyrolysis	Cr(VI)	HCl	HCl treatment greatly reduced the ash content of biochar, reduced the zero charge, and protonated the functional group, the total Cr removal rate reached 90%	Zhou et al. (2019a)
Bamboo hardwoods	550 °C	Fast pyrolysis	Cd(II)	CS_2、$FeSO_4$	After modification, the surface of biochar is rougher, the granular structure was larger, and the sulfur group increases the viscosity between S and Fe particles, making them more stable and providing a basis for the adsorption of Cd	Wu et al. (2019)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Wheatgrass and cow dung	450 °C	Fast pyrolysis	U(VI)	HNO_3	The volume and surface oxygen content of the biochar treated with HNO_3 were higher than that of the original biochar, and the formation of oxygen-containing functional groups (C=O and COO) was the reason for increasing the removal rate of U	Jin et al. (2018)
Coconut shell	800 °C	Flash pyrolysis	Multi-metal (Cd, Ni and Zn)	HCl	After HCl modification, the impurities on the surface of biochar were removed, and its specific surface area and porous volume were significantly increased, which was conducive to the adsorption of heavy metals	Liu et al. (2018)
Biochar with alkaline modifications						
Corn straw	800 °C	Flash pyrolysis	Mercury(II) and atrazine exist alone or in combination	KOH	After KOH modification, the specific surface area of biochar was increased by 2 times, and the oxygen-containing groups of biochar also increased, providing conditions for the removal of Hg(II)	Tan et al. (2016)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Dairy manure	300 °C	Slow pyrolysis	Pb(II) and Cd(II)	NaOH	After the modification of NaOH, the contents of C, H, and O of biochar increased, and the specific surface area and porosity also increased, which improved the adsorption capacity of heavy metals	Chen et al. (2019)
Rape straw	600 °C	Fast pyrolysis	Cd(II)	NaOH	NaOH treatment increased the surface area of biochar threefold and the total pore volume also increased, and it was these factors that increased its ability to remove Cd(II)	Li et al. (2017)
Ipomoea	350 °C, 400 °C, 450 °C, 500 °C, 550 °C	Slow and fast pyrolysis	Cd(II)	KOH	After KOH treatment, the surface area of biochar increased by 23 times, the content of C increased by 5 times, and the content of oxygen increased by 7 times, all of which made the final adsorption capacity of Cd increase	Goswami et al. (2016)
Rice husk, wood chips and their mixture	300–400 °C	Slow pyrolysis	Cd(II), Pb(II), and Zn(II)	NaOH	After modification, wood chip biochar has the largest average pore diameter, and rice husk biochar has the largest specific surface area, reaching 89.08 m^2/g, which can provide conditions for more adsorption of heavy metals	Lee and Shin, (2021)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Straw	300 °C, 500 °C, 700 °C	Slow and fast pyrolysis	Cr(VI)	NaOH	NaOH treatment has the greatest effect on biochar generated at 300 °C, the highest zero point charge, and contains rich aromatic CO and phenolic OH groups, and the adsorption capacity of Cr(VI) was enhanced	Zhou et al. (2019a)
Biochar with other chemical modifications						
Natural almond and natural olive biochar	750 °C	Flash pyrolysis	Pb(II)	H_2O_2	After H_2O_2 modification, the specific surface area of almond hardwood biochar increased by 2 times and the pore volume increased by 3 times, but the aromaticness (H/C) of olive biochar was slightly higher than that of almond hardwood biochar, and it had higher antioxidant activity. They all lay the foundation for effective removal of Pb(II)	Encinas-Vázquez et al. (2021)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Corn straw	350 °C, 500 °C, 700 °C	Slow and fast pyrolysis	Zn(II)	Oxidation modification: montmorillonite (silicon, alumina and magnesium oxide)	Montmorillonite modified biochar had a large surface area at a high pyrolysis temperature, and a large amount of water vapor was generated in the hydrothermal process, which greatly promoted the formation of mesoporous materials. In addition, during the pyrolysis process, the dehydroxylation and volatility of organic compounds increased with the increase of temperature, which provided adsorption sites for the adsorption of Zn	Song et al. (2020)
Corn straw	800 °C	Flash pyrolysis	Hg(II) and atrazine exist alone or in combination	Na_2S	Under the modified condition of Na_2S, the sulfur content was significantly increased by 101.29%, while the specific surface area was also increased by 1.7 times	Tan et al. (2016)
Peanut Shell	250 °C	Slow pyrolysis	Cr(VI)	Clay	The use of Kaolin and Bentonite effectively increased the specific surface area and average pore diameter of biochar, and enriched the mineral content and species on the surface of biochar, which was conducive to the removal of Cr(VI)	Wang Hai, (2019)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Ficus microcarpa aerial root	600 °C	Fast pyrolysis	U(VI)	$KMnO_4$	After potassium permanganate modification, the pore size of biochar increased, and the contents of O and Mn increased significantly, and it was found that Mn could interact with U(VI) to achieve the purpose of removing U	Li et al. (2019b)
Rice husk	300 °C	Slow pyrolysis	As(V) and Cr(VI)	Ca and Fe	The addition of Ca and Fe facilitated metal precipitation and electrostatic interaction to remove heavy metals	Agrafioti et al. (2014)
Rice husk	350 °C	Slow pyrolysis	U(VI)	Natural siderite	Various characterization results showed that magnetic biochar had a porous structure with large specific surface area, which provided more adsorption sites for U(VI) adsorption	Li et al. (2019a)
Straw	300 °C, 500 °C, 700 °C	Slow and fast pyrolysis	Cr(VI)	Deionized water and ethanol	The improvement of Cr(VI) adsorption effect was not significant, but it provided a new modification idea	Zhou et al. (2019a)

Table 1 (continued)

Modified Biochar as an adsorbent for heavy metals removal						
Feedstock	Preparation temperature	Type of process	Target pollutants	Method of modification	Enhanced features	References
Rice straw	400 °C, 600 °C, 800 °C	Slow, fast and flash pyrolysis	Cd(II)	Fe^{2+}/Fe^{3+} and NaOH	The basic groups or organic groups on the surface of biochar can chelate heavy metals and be fixed by precipitation. After iron activation, there were more C=O groups and iron oxides on the surface of biochar, forming more cadmium chemisorption/oxidation active sites	Yuan et al. (2020)
Thalia dealbata	500 °C	Fast pyrolysis	Cd(II)	$MgCl_2$	The specific surface area of biochar modified by $MgCl_2$ was increased by 15 times, and the amount of aromatic structure substances and oxygen-containing functional groups was increased, which helped to improve the adsorption capacity of Cd	Tao et al. (2019)

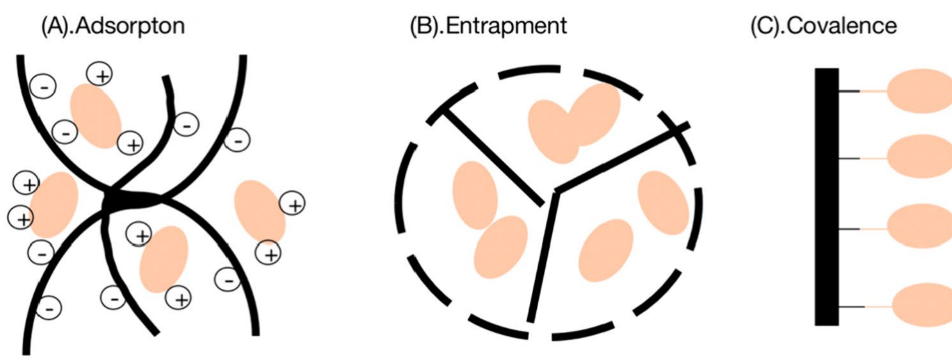


Fig. 2 Biochar and microorganism binding diagram

adsorption, microorganisms are immobilized on the support by physical absorption through π–π bonds (Mubarak et al. 2014). The captured grid structure can prevent the exudation of microorganisms to the carrier, and it has low toxicity to microorganisms. However, only small molecules from the external environment can freely enter and exit the carrier, so this method is not suitable for macromolecular pollutants (Wu et al. 2022). Trapping methods are further divided into different types: temperature-induced gelation, chemical/photochemical polymerization, etc. (Asgher et al. 2014). During cell entrapment, they are trapped in a supporting matrix, which helps to protect the cell from external invasion (Rodríguez-Restrepo and Orrego 2020). In the covalent bonding method of loading mode, the cells are fixed by chemical covalent bonding between microbial cells and biochar functional groups (Ha et al. 2022). This method improves the closeness of microorganisms and biochar, making the stability relatively high, and the microorganisms are not easy to fall off. Therefore, covalent fixation is preferred when there are unstable and variable factors in aqueous solution and medium.

Chen et al. (2021c) fixed Bacillus cereus WHX-1 on biochar by adsorption method, which improved the strain's reducing ability on Cr^{6+}. However, the microorganism was easily shed since the force between microorganisms and biochar was weak (Chen et al. 2016). The method is therefore suitable for the fixation of living cellular organisms (Wu et al. 2022). Chuaphasuk (Chuaphasuk and Prapagdee 2019) and his team proposed biochar immobilized with cadmium-resistant bacteria could improve the efficiency of cadmium extraction in suspension orchids and they found that the immobilized bacteria promoted the accumulation and transfer of cadmium. Huang et al. (2020) immobilized B. cereus RC-1 on the biochar made from rice straw, chicken manure, and sludge, respectively, to study their biosorption characteristics at different pH, reaction time, and initial Cd^{2+} concentration. When pH was 2–5, the total biosorption capacity of immobilized particles increased gradually. When pH is 6–7, the adsorption capacity tends to balance. The effect of reaction time on the adsorption capacity of Cd was controlled by the growth of cells. The Cd adsorption capacity of suspension cells increased as they were in the exponential period. At about 15–24 h, the number of cells reached a plateau and then declined, and the adsorption capacity of Cd decreased as a result. In addition, when the initial concentration of Cd^{2+} was less than 180 mg/L, its adsorption performance was greatly improved. Wang's team (Wang et al. 2021a) inoculated *Bacillus* K1 strain on rice straw biochar and magnetic rice straw biochar, respectively, to explore its ability to remediate cadmium-contaminated soil. They found that the bacteria-biochar composite had better Cd removal performance than the biochar alone and that the ferromagnetic modified biochar combined with bacteria was more effective in removing Cd than the unmodified one.

Biochar Modified with Metallic Materials

Metals are widely used as a modifier to enhance the adsorption properties of biochar for heavy metals removal. At present, the most commonly used metal modifiers are iron oxide (Samaraweera et al. 2023), zero-valent iron (Fe) (Wan et al. 2019), manganese oxide (Shaheen et al. 2022), metal sulfide (Khan et al. 2020), and zinc compounds (Yusuff et al. 2022). Also, several researchers have mixed biomass wastes with Fe_3O_4-rich plastic wastes to produce a ferromagnetic carbon composite through pyrolysis for water treatment applications (Osman et al. 2022a). Liu and his team (Liu et al. 2023) designed a composite material (M-BC) based on δ-MnO_2-modified biochar (BC) for the separation of U(VI) from synthetic wastewater. The results showed that the separation capacity of the modified biochar was 61.53 mg/g, which was significantly higher than that of the pure biochar (12.39 mg/g). It is noteworthy that the removal of U(VI) by MnO_2-modified biochar remained at 94.56% even after five times of recycling, indicating its good reusability and good potential for application. Khan et al. (2020) prepared MoS_2-modified magnetic biochar (MoS_2@MBC) for the adsorption of Cd(II) by hydrothermal method. After MoS_2 modification, the maximum adsorption capacity of biochar for Cd(II) is 7.81 times that of the original magnetic biochar, and the adsorption effect is very good. Among the metal-modified biochar, iron-modified biochar, with easy separation from aqueous solution as its main advantage, has drawn attractive attention (Wan et al. 2020). Moreover, the modification of biochar by iron has many other advantages such as stable adsorption properties, low cost, and easy regeneration (Abdel Maksoud et al. 2020; Tang et al. 2018). Researchers have made great efforts to prepare magnetic biochar. For example, optimization of conditions for the preparation of magnetically modified biochar using waste fir wood as raw material was carried out by Dong et al. (2022). They explored the effect of magnetic functionalization methods (impregnation and precipitation), iron solution concentration (0.01–1 M), and pyrolysis temperature (300–700 °C) on the characteristics of biochar and the adsorption capacity of Pb(II). They found that biomass prepared by precipitation with 1 M Fe(II)/Fe(III) precursor and pyrolyzed at 700 °C showed the highest adsorption capacity for Pb(II) (817.64 mg/g). The traditional processing of magnetic media is expensive (Zhang et al. 2009). However, microwave irradiation can facilitate uniform and rapid thermal reactions at a lower cost (Liu and Yu 2006; Zhang-Steenwinkel et al. 2005). Mubarak et al. (2014) synthesized new magnetic biochar using ferric chloride hexahydrate and single-stage microwave heating technology, which was called impregnated ferric chloride pyrolysis. Gao et al. (2018) synthesized nanoscale zero-valent iron-modified biochar and studied its removal ability of Cr^{6+} in solution. They found the removal efficiency of Cr^{6+} of this composite material was greatly improved under acidic conditions. Most of the iron modification process is completed by attaching iron oxide, which does not alter the original carbon skeleton structure of biochar (Yuan et al. 2020). In general, impregnating biochar with iron or iron compounds can improve its surface properties and has good potential in removing heavy metals (Zhang et al. 2020a). Wang et al. (2017a) found that the surface area of zinc-iron-modified biochar was increased to 518 m^2/g, which had a good effect on the adsorption process. Yap et al. (2017) successfully synthesized a new type of magnetic biochar (MB) from coconut shell (CS) for cadmium and lead removal. They found that the specific surface area of biochar after magnetic modification was improved, its porosity was well developed, and the surface porosity was widely distributed, and this is due to the fact that the impregnated ferric chloride evaporates from the cavities and pores, forming compounds which create new spaces. However, the magnetic modification of biochar for heavy metals removal does not always work well. In other words, the removal effects of different heavy metals by magnetic biochar are various. Trakal et al. (2016) found that the magnetization of wheat straw and grape biochar has no improvement on the adsorption of Pb^{2+}, but it showed good activity in Cd^{2+} removal even in the conditions with multiple metals existing (Michálková et al. 2014; Mohan et al. 2014). Although the exact mechanism resulting in the different performance towards the heavy metals adsorption is still unclear, the surface complexation of metal with hydroxyl and carboxyl groups played an important role in determining the heavy metals adsorption (Trakal et al. 2016). Meanwhile, the amount of iron ions addition is also a critical factor affecting the activity of derived biochar. Lyu et al. (2017) synthesized a novel nanoscale iron sulfide (ferrous sulfide) composite (CMC-FeS@biochar) for the adsorption of Cr^{6+}. In this process, FeS has successfully magnetized biochar by connecting with functional groups, and it was found that when the ratio of FeS: CMC: biochar was 3:3:1, the removal rate of Cr^{6+} reached the maximum.

Biochar Combined with Other Materials

Modification of biochar through various ways to improve its heavy metals removal has been extensively explored. Other than the traditional methods discussed above, some emerging approaches have also been investigated such as chitosan, metal–organic framework materials (MOF), and clay materials. These materials have been found to have a comparable effect to those traditionally used in the modification of biochar to improve heavy metal adsorption efficiency.

Chitosan has been studied extensively due to its renewable, biodegradable, abundant, and non-toxic properties. It can be used as an ideal material to combine with biochar for heavy metal removal research. Burk et al. (2020) used gasifier biochar (GBC) and chitosan-modified gasifier biochar (CGBC) made from pine wood to remove Cu^{2+} and Cd^{2+} from water. They found that the removal of Cu^{2+} and Cd^{2+} ions from water by pure gasified biochar was very high (86.2, 68.6 mg/g), and the adsorption capacity increased after chitosan-modified gasified biochar (112, 85.8 mg/g), which may be due to the amine groups in chitosan adsorbing Cu^{2+} and Cd^{2+}. Chen (Chen et al. 2021a) and others prepared a new type of biochar from ferrous sulfide nanoparticles and chitosan, and studied its U^{6+} ion removal performance in an aqueous solution. The results show that the composite has high stability and effective adsorption capacity for U^{6+}. Its high adsorption capacity is due to the large number of functional groups on the surface of the material, ferrous sulfide nanoparticles can react with hexavalent uranium. Ifthikar's team (Ifthikar et al. 2018) used activated sludge as raw material and added carboxymethyl chitosan to improve the stability of the biochar. When the ratio of chitosan to biochar in the composite was 2:1, the adsorption capacity of Hg^{2+} and Pb^{2+} was the strongest. Therefore, the adsorption capacity of pH for Pb^{2+} was explored under this ratio. They found that the adsorption capacity of Pb^{2+} increased as pH increased from 2 to 6, while the adsorption capacity of Hg^{2+} increased as pH increased from 2 to 3, and decreased as pH increased from 4 to 6. A multifunctional EDTA and chitosan biofunctionalized magnetic bamboo biochar adsorbent (ECMBB) was synthesized by Zhang et al. (2022a) for the co-adsorption of methyl orange (MO) and heavy metals (Cd(II) and Zn(II)). They found that the synthesized ECMBB composite enhanced the binding of cationic metals by introducing the amino group of chitosan and the carboxyl group of EDTA.

Metal–organic frameworks (MOF) are a material recognized to be able to effectively remove heavy metal ions from water (Zhu et al. 2021). It is porous, has an adjustable pore structure, contains rich functional groups (Chai et al. 2021; Fan et al. 2018; Mubashir et al. 2021; Seoane et al. 2016), and also can adsorb Cr, Cu, Pd, Sb, and other metal ions (Janiak and Vieth 2010). But because their powdery form is not suitable for practical applications, they need to be given a supporting material, and biochar is one such material. Zhu et al. (2021) and their team combined a recyclable magnetic metal–organic frame material with mushroom waste biochar to form a new material to treat metal element Sb^{3+} in water, and found the optimal conditions for high adsorption capacity materials.

Clay is widely used for the removal of heavy metals (Uddin 2017). The use of clay as an adsorbent has the following advantages: low cost, large supply, high specific surface area, excellent adsorption performance, non-toxicity, etc. There are many types of clays, of which montmorillonite and kaolinite are the most studied (Yao et al. 2014). Their negatively charged surfaces give them a high cation exchange capacity, and their high surface area and large porosity have prompted many researchers to use pure clays for the adsorption of heavy metal ions (Uddin 2017). Kakaei et al. (2020) found that bentonite and modified bentonite effectively adsorbed cobalt, copper, and lead from wastewater. Therefore, it is of great interest to investigate the adsorption capability of clays when used in combination with biochar. Hai et al. (2019) made a new material by mixing biochar prepared from peanut shells with kaolin and bentonite under magnetic agitation to adsorb Cr^{6+} from aqueous solutions. The results show that the adsorption of Cr^{6+} ions in wastewater to kaolin biochar is significantly higher than that of bentonite biochar. Es-sahbany et al. (2019) and Wang et al. (2020b) compared the Ni adsorption by using mixed layer clay and cow dung biochar, respectively, and found that mixed layer clay effectively removed up to 75% of nickel ions from wastewater, while cow dung biochar removed up to 96% of nickel ions. However, the biochar, in this case, resulted in more variations in the ion removal rate due to influencing factors such as pH.

Adsorption Kinetics

Studying the adsorption kinetics of heavy metals on biochar is an important step in exploring the adsorption process of biochar, which represents the adsorption abilities of different types of biochar in heavy metals remediation. It is widely adopted by most researchers while investigating the effect of biochar adsorption. Among the extensive studies, pseudo-first order, pseudo-second order, intraparticle diffusion equation, and Elovich equation have been predominantly estimated by fitting in the experimental data.

The assumptions of pseudo-first-order kinetic models are based on the control conditions of adsorption and diffusion. The original form and linearized form of this model are shown in Eqs. (1) and (2), respectively (Bogusz et al. 2015):

$$a_t = a_{\mathrm{eq}}\left[1 - \exp\left(-K_1 t\right)\right] \tag{1}$$

$$\ln\left(a_{\mathrm{eq}} - a_t\right) = \ln a_{\mathrm{eq}} - K_1 t \tag{2}$$

where a_{eq} is the adsorption capacity (mg/g) at the equilibrium time (mg/g), a_t is the adsorption capacity (mg/g) at any time, and t is the contact time (min), K_1 (L/min) is the rate constant of the pseudo-first-order equation.

The pseudo-second-order equation was developed on the assumption that the adsorption rate is controlled by the adsorption capacity and the concentration of the adsorbate (Dong et al. 2011). This model is applied when the process is dominated by the chemical forces of electron transfer between the pollutant and the adsorbent material (Song et al. 2020). The original form and linearized form of pseudo-second-order model are shown in Eqs. (3) and (4), respectively (Bogusz et al. 2015):

$$q_t = \frac{q_{\mathrm{e}}^2 K_2 t}{1 + q_{\mathrm{e}} K_2 t} \tag{3}$$

$$\frac{t}{a_t} = \frac{1}{K_2 a_{\mathrm{eq}}^2} + \frac{1}{a_{et}} t \tag{4}$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order equation.

The q_t and $t_{1/2}$ of the interparticle diffusion equation are linearly fitted. If a straight line passes through the origin, it indicates that the adsorption process is controlled by the internal diffusion of particles. If the line does not pass through the origin, then the adsorption process is also controlled by other adsorption processes, such as external diffusion steps (surface adsorption and liquid film diffusion) (Fan et al. 2016). The equation is as follows (Fan et al. 2016):

$$q_t = k_{\mathrm{d}} t^{0.5} + c \tag{5}$$

where q_t is the adsorption capacity at t time (mg g^{-1}), k_{d} is the intra-particle diffusion rate constant (g mg^{-1} min$^{-1/2}$), C is a constant (Fan et al. 2016).

The Elovich model is the adsorption occurred on the surface of a non-homogeneous object, which is controlled by multiple interaction mechanisms/processes (Wang et al. 2015a). This adsorption is regulated by a combination of reaction rates and diffusion factors (Fan et al. 2016). The original form and linearized form of the Elovich model are shown in Eqs. (5) and (6), respectively (Fan et al. 2016; Wang et al. 2015a):

$$a_t = \beta^{-1} \ln(\beta\alpha t + 1) \tag{5}$$

$$a_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

where α is the initial adsorption coefficient (mg g^{-1} min^{-1}), and β is the desorption coefficient (g mg^{-1}) (Fan et al. 2016).

The suitability of using any single model to describe certain adsorption processes varied case by case. It could be attributed to the diversity of adsorbent, namely the biochar and the various heavy metals involved in the process. Therefore, it is not reasonable to draw a solid conclusion on the fitness of these kinetic models to any individual adsorption process. This is the reason why researchers always evaluated the applicability of every common kinetic model in their studies and their findings were usually specific to the given process. For example, Zhang et al. (2019a) used sewage sludge as raw material to prepare biochar and modified this biochar with KOH, CH_3COOK, and CO_2 to study its adsorption performance on Pb^{2+}. They found that both the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation well described the adsorption behavior of sludge-based activated biochar. Agrafifioti et al. (2013) also used sewage sludge prepared as biochar to investigate its adsorption properties on As^{5+} and Cr^{3+}. But they observed the pseudo-second-order model as the best model in this process. Zhang et al. (2020d) used cow dung and earthworm composted materials to make biochar respectively, and then compared their adsorption capacity on Pb^{2+}, in which the adsorption process was explored by pseudo-first-order kinetic model, pseudo-second-order kinetic model, and Elovich kinetic model. As a result, the adsorption of raw biochar conforms to the Elovich kinetic model, while cow dung biochar and earthworm compost biochar conform to the pseudo-second-order kinetic model.

Adsorption Isotherm

In most research regarding the application of biochar in heavy metals removal, adsorption isotherm was frequently studied as a tool to disclose the adsorption mechanism and meanwhile evaluate the performance of biochar by delivering their maximum capacity of adsorption. A wide variety of adsorption models have been developed to study the surface adsorption phenomena.

The models most widely used in studying the adsorption isotherm of biochar on heavy metals are Langmuir and Freundlich models (Table 2). The Langmuir isotherm model, as one of the first proposed models, assumes that the adsorbent and the adsorbent are in an ideal state and is applied to the adsorption process of uniform adsorbent (Mozaffari Majd et al. 2022). The adsorption mechanism revealed by Langmuir's model is shown in Fig. 3 (Wang and Guo 2020). It illustrates the equilibrium of homogenous adsorption with monolayer. Alsuhybani et al. (2020) used modified magnetic nanoparticles to remove harmful lead ions from aqueous solution and found that the Langmuir adsorption isotherm model was able to describe the mechanism of this adsorption process. Different from the Langmuir isotherm model, a theoretical model with rigorous deduction and specific physical meaning, the Freundlich isotherm model is an empirical isotherm characterized by lacking physical meaning (Wang and Guo 2020). It is suitable for the adsorption study of rough surfaces and to represent the multi-layer adsorption on heterogamous surfaces (Mozaffari Majd et al. 2022; Zaheer et al. 2019). Goswami et al. (2016) utilized guava biochar to explore its ability to adsorb Cadmium (Cd) from water, and they found that the Freundlich mode was the best-fit model and consistent with that adsorption process. Temkin and Dubining–Radushkevich (D–R) models are also frequently applied in the field of biochar adsorption (Table 3). The Temkin model assumes that the adsorption process is a multilayer process, in which the interaction between adsorbent and adsorbent is considered (Temkin 1940). It has the disadvantage of ignoring concentration variations and assumes that the differential heat of adsorption across the molecular layer decreases with increasing coverage (Aharoni and Ungarish 1977; Kim et al. 2004). Encinas-Vázquez et al. (2021) and his team used natural almond biochar (NAB), natural olive biochar (NOB), modified almond biochar, and modified olive biochar (MAB and MOB) to remove pb^{2+}, and investigated their adsorption capacity. They found that the adsorption on modified olive biochar fit well with the Temkin model. The Dubinin–Radushkevich (D–R) isotherm model, developed from Polanyi's potential theory, is a semi-empirical model (Wang and Guo 2020). It assumes that adsorption is related to the volume of the adsorbent pores, it takes into account the pore structure of the adsorbent and it is applicable to adsorption on non-phase surfaces (Dubinin 1960; Hu and Zhang 2019). DR isotherm model is commonly used to describe physical or chemical adsorption processes (Alberti et al. 2012). Abdelnaeim et al. (2016) prepared biochar from a common reed (Australian reed) and explored its ability to remove Cu and Cd ions from an aqueous solution and found that the DR isotherm fitted the adsorption well. The equations for the above model are as follows (Fan et al. 2016):

Langmuir isotherm model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{8}$$

Freundlich isothermal equation:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{9}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{10}$$

Temkin isothermal equation:

$$e^{q_e} = \left(K_T \cdot C_e\right)^{\frac{RT}{b_T}} \tag{11}$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{12}$$

Dubinin–Radushkevich (D–R) isothermal equation:

$$\ln\left(q_e\right) = \ln\left(q_m\right) - \beta \varepsilon^2 \tag{13}$$

$$\beta = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{14}$$

$$E_a = \frac{1}{\sqrt{2\beta}} \tag{15}$$

where C_e is the equilibrium concentration, mg L^{-1}, q_e is the adsorption capacity at equilibrium time, mg g^{-1}, b is

Table 2 Langmuir and Freundlich models for adsorption isotherms

Raw material	Contaminants	Types of models						References
		Langmuir			Freundlich			
		q_{max}	b	R^2	k_f	$1/n$	R^2	
Rice straw	Cd(II)	8.40	NA	0.99	5.65	NA	0.94	Bashir et al. (2018)
KOH-modified rice straw	Cd(II)	15.50	NA	0.98	5.50	NA	0.95	Bashir et al. (2018)
Water hyacinth	Pb(II)	82.50	0.02	0.998	NA[a]	NA	NA	Zhang et al. (2020b)
Water hyacinth	Cd(II)	26.51	0.18	0.994	NA	NA	NA	Zhang et al. (2020b)
Water hyacinth	Cu(II)	19.14	0.02	0.985	NA	NA	NA	Zhang et al. (2020b)
Water hyacinth	Zn(II)	15.14	0.02	0.976	NA	NA	NA	Zhang et al. (2020b)
Wheat straw	Cd(II)	32.57	NA	0.99	2.08	1/0.84	0.84	Bogusz et al. (2015)
Wheat straw	Cu(II)	29.41	NA	0.96	1.09	1/1.37	0.75	Bogusz et al. (2015)
Wheat straw	Zn(II)	41.84	NA	0.99	5.02	1/2.102	0.94	Bogusz et al. (2015)
Enteromorpha	Cu(II)	254.00	0.6	0.99	143	1/0.5	0.93	Yang et al. (2019a)
Enteromorpha	Pb(II)	98.00	2.3	0.99	28	1/0.6	0.95	Yang et al. (2019a)
Eichhornia crassipes-20 °C	Cr(VI)	151.62	0.069	0.95	41.74	1/4.37	0.81	Zhang et al. (2015)
Eichhornia crassipes-30 °C	Cr(VI)	157.11	0.074	0.96	44.36	1/4.42	0.88	Zhang et al. (2015)
Eichhornia crassipes-40 °C	Cr(VI)	167.31	0.077	0.96	49.05	1/4.56	0.87	Zhang et al. (2015)
Wheat straw	U(VI)	8.70	0.17	0.98	2.50	1/0.31	0.89	Jin et al. (2018)
Cow manure	U(VI)	64.00	0.56	0.98	33.20	1/0.17	0.89	Jin et al. (2018)
Switchgrass-500 °C	Cu(II)	0.023	3.159	0.89	0.036	1/4.63	0.98	Han et al. (2013)
Switchgrass-700 °C	Zn(II)	0.087	0.37	0.98	0.018	1/3.71	0.84	Han et al. (2013)
Hardwood-500 °C	Cu(II)	0.072	1.106	0.88	0.046	1/2.49	0.99	Han et al. (2013)
Hardwood-700 °C	Zn(II)	0.082	0.366	0.98	0.021	1/1.94	0.99	Han et al. (2013)
Softwood-500 °C	Cu(II)	0.053	2.365	0.84	0.034	1/4.35	0.99	Han et al. (2013)
Softwood-700 °C	Zn(II)	0.027	1.97	0.99	0.014	1/3.329	0.93	Han et al. (2013)
Ca-impregnated rice husk biochar	As(V) and Cr(VI)	1000.00	0.003	0.88	5.14	0.81	0.98	Agrafioti et al. (2014)
Fe-impregnated municipal solid wastes biochar	As(V) and Cr(VI)	400.00	0.005	0.80	8.31	0.57	0.97	Agrafioti et al. (2014)
Fe^{3+}-impregnated municipal solid wastes biochar	Cr(VI)	454.55	0.005	0.83	8.67	0.59	0.99	Agrafioti et al. (2014)
Punica granatum peel biochar-300 °C	Cu(II)	51.02	0.03	0.98	0.80	0.79	0.92	Cao et al. (2019b)
Punica granatum peel biochar-600 °C	Cu(II)	53.19	0.18	1.00	0.79	0.79	0.92	Cao et al. (2019b)
Cotton stalk derived biochar-15 °C	Pb(II)	120.58	1.052	0.85	60.52	1/0.16	0.97	Gao et al. (2021)
Cotton stalk derived biochar-25 °C	Pb(II)	121.46	1.15	0.81	70.03	1/0.13	0.96	Gao et al. (2021)
Cotton stalk derived biochar-35 °C	Pb(II)	146.78	1.24	0.80	71.51	1/0.10	0.98	Gao et al. (2021)
Peanut shell with Kaolin-20 °C	Cr(VI)	15.58	0.0029	0.98	3.57	0.0064	0.995	Wang Hai, (2019)
Peanut shell with Kaolin-30 °C	Cr(VI)	68.98	0.0063	0.94	4.55	0.0083	0.992	Wang Hai, (2019)
Peanut shell with Kaolin-40 °C	Cr(VI)	76.62	0.13	0.80	9.61	0.0028	0.996	Wang Hai, (2019)

[a] *NA* not available

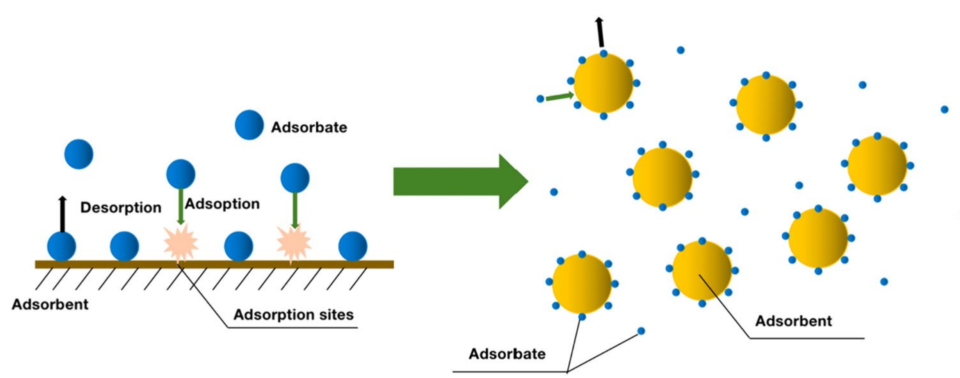


Fig. 3 The adsorption mechanisms revealed by the Langmuir isotherm model adopted from Wang and Guo (2020)

Table 3 Comparison of several models

Raw material	Contaminants	Types of models													References
		Langmuir			Freundlich			Temkin			Dubinin–Radushkevich				
		q_{max}	b	R^2	k_f	$1/n$	R^2	b_T	K_T	R^2	q_m	β	E	R^2	
Tea waste	Ni(II)	664.26	0.15	0.99	112.55	1/0.45	0.98	1.22	NA[a]	0.97	556.77	7.5	639.68	0.89	Shirvanimoghaddam et al. (2021)
Tea waste	Co(II)	373.53	0.417	0.87	112.79	1/0.33	0.98	2.17	NA	0.89	361.38	2.97	1016.66	0.66	Shirvanimoghaddam et al. (2021)
Natural almond biochar	Pb(II)	40.32	0.033	0.99	8.69	1/4.188	0.91	7.62	0.83	0.92	28.60	2.0×10^{-6}	NA	0.87	Encinas-Vázquez et al. (2021)
Modified almond biochar	Pb(II)	24.81	0.014	0.98	2.27	1/2.74	0.94	6.66	0.15	0.82	14.29	1.0×10^{-5}	NA	0.59	Encinas-Vázquez et al. (2021)
Natural olive biochar	Pb(II)	13.14	0.58	0.99	3.77	1/2.30	0.75	2.33	9.77	0.95	NA	NA	NA	NA	Encinas-Vázquez et al. (2021)
Modified olive biochar	Pb(II)	12.53	0.47	0.99	3.17	1/2.15	0.86	2.29	6.89	0.98	NA	NA	NA	NA	Encinas-Vázquez et al. (2021)

[a]*NA* not available

Langmuir's constant, L g^{-1}, q_{max} is the maximum adsorption capacity, mg g^{-1}, K_f is the Freundlich constant, L mg^{-1}, $1/n$ is the heterogeneity of adsorption sites, which is an indicator of isotherm nonlinearity, K_T is the equilibrium binding constant, L mg^{-1}; b_T is Temkin isotherm constant; R_T/b_T is related to the heat of adsorption, J mol^{-1}, q_m is the theoretical isotherm saturation capacity (mol g^{-1}), β is the Dubinin–Radushkevich isotherm constant (mol^2 kJ^{-2}) and ε is the Dubinin–Radushkevich isotherm constant. And "$1/n$" indicates the advantage of adsorption, when $1/n$ is less than 0.5, it indicates that the adsorbent is easy to be adsorbed on. When $1/n$ is greater than 2, it indicates that the adsorbent is difficult to be adsorbed on Shi et al. (2014).

Mechanism of Adsorption by Biochar

The mechanism of adsorption by biochar has been extensively studied. For inorganic pollutants such as heavy metals, the adsorption mechanism usually includes surface complexation, ion-exchange, metal ion complexation, electrostatic attraction, carboxylate complexation, π–π interaction, etc. In many cases, the adsorption process is a combination of various mechanisms (Abbas et al. 2018). Figure 4 lists some proposed mechanisms of biochar adsorption of heavy metals (Herath et al. 2021).

Surface adsorption is also called physical adsorption. This process does not form chemical bonds, and metal ions diffuse through the pores/cavities of the adsorbent (Shakoor et al. 2020). Among the numerous studies on biochar adsorption mechanisms, surface adsorption is one of the most popular proposed mechanisms. For example, the adsorption efficiency of Pb, Cd, Cr, Cu, and Zn on biochar made from sesame grass was in descending order and controlled by surface adsorption (Park et al. 2016). Liu et al. (2010) prepared pinewood biochar (P700) by pyrolysis and found that the mechanism of Cu^{2+} adsorption was mainly physical adsorption. The experiment showed that a thorough carbonization process occurred in P700, and almost all oxygen-containing groups were decomposed during the pyrolysis process, thus forming a rough surface and porous structure, which could be used as a good adsorbent for Cu^{2+}. In general, higher pyrolysis temperatures increase the adsorption capacity by increasing the surface area of biochar, as well as filling the voids (Abbas et al. 2018).

Ion exchange is the process of exchanging cations on biochar with heavy metal ions to achieve the purpose of removing heavy metal pollutants in contaminated sites. The team of Wu et al. (2021) used magnesium to modify coconut shell biochar to adsorb Cd and Pb by increasing its ion exchange capacity. They found that the ion exchange capacity of biochar was significantly increased after modification with Mg ions. The adsorption of Pb and Cd on

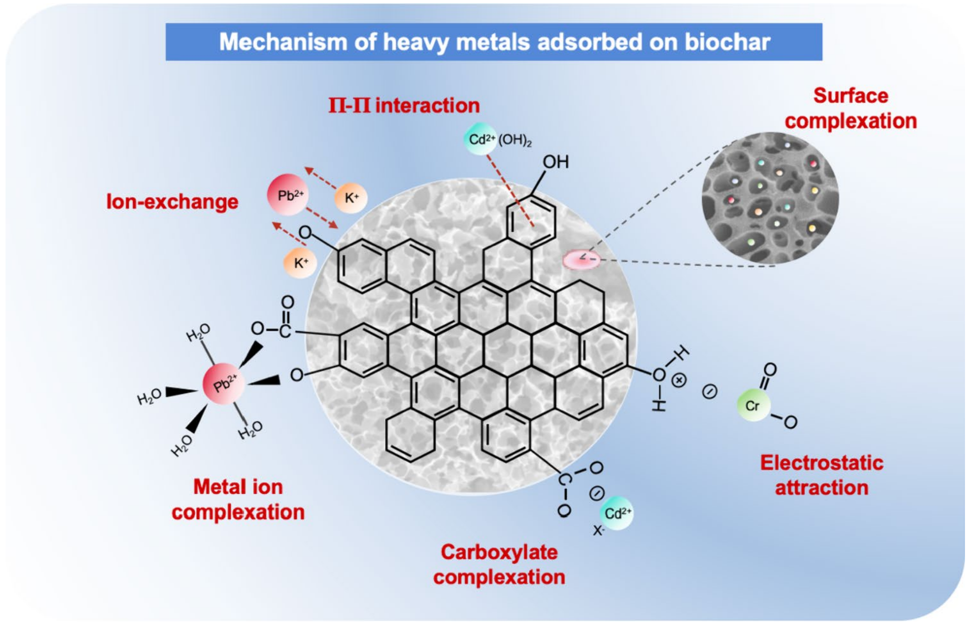


Fig. 4 Mechanism of heavy metals adsorbed on biochar (Herath et al. 2021)

Mg-modified biochar was found to be 49% and 59% higher, respectively, than those of unmodified biochar. Zhao et al. (2017) found that the size of heavy metals and the surface morphology of biochar were important factors affecting the heavy metals removal efficiency by ion exchange. Liu et al. (2010) also used pine biomass to prepare biochar (H300) by hydrothermal carbonization and found that it can adsorb a higher amount of Cu^{2+}, which is because the hydrothermal treatment produces more oxygen-containing groups on the surface of the carbon, resulting in a porous structure, which is conducive to the ion exchange process.

Complexation is the process of forming internal or external polyatomic complexes between metals and ligands on the surface of biochar (Shakoor et al. 2020). It has been found that plant carbon-based biochar could adsorb many heavy metals such as Pb, Ni, Cu, and Cd, by forming carboxyl and phenolic metal complexes on the surface of biochar. Xu et al. (2016) used hickory and bagasse biochar to remove Hg^{2+} in water and they found that the adsorption of Hg^{2+} on bagasse-derived biochar was attributed to the complexation reaction of Hg^{2+} with phenolic hydroxyl (CO) and carboxyl (COO) groups. Harvey et al. (2011) prepared biochar from Rockweed, honey mosquito, and loblolly pine, and the complexation of Cd with surface functional groups of biochar such as graphene structures was the primary mechanism for removing Cd. In addition, as mentioned above, some adsorption process is governed by multiple mechanisms. Wang et al. (2015b) investigated the Pb^{2+} adsorption process of peanut shell and Chinese-herb-residue-derived biochar and found that the adsorption mechanism involved functional group complexation, Pb^{2+}–π interaction as well as precipitation.

Electrostatic interactions are electrostatic reactions of heavy metals with charged surfaces of biochar, resulting in the fixation of heavy metals on biochar (Shakoor et al. 2020). It has been reported that heat helps to break up biochar's graphene-like structure in the process of biochar production, which benefits the adsorption of metal through electrostatic interactions (Keiluweit and Kleber 2009). Qiu et al. (2008) stated that rice and wheat straw biochar had a higher adsorption efficiency for lead due to the strong electrostatic interaction between the negatively charged biochar and positively charged lead ions. Moreover, Dong et al. (2011) found that at pH2, the electrostatic attraction between anion Cr^{6+} and cationic biochar surface contributed to chromium removal.

Application and Assessment Analysis of Biochar

Additional Applications of Biochar

In addition to being used as an adsorbent, biochar has many other applications. Many people prepare biochar from different raw materials, and then apply them as catalysts and support materials for photocatalysts (Chi et al. 2021), biodiesel production (Zhao et al. 2023a), preparation of biohydrogen, etc. Nanocomposites were successfully synthesized using biochar and photocatalysts such as TiO_2, ZnO, and Fe_3O_4 by Fito et al. (2022). The nanocomposites prepared by this method have high magnetic permeability, photocatalytic activity, electrical resistance, mechanical hardness, and thermochemical stability. Bhatia et al. (2020) prepared the catalyst by pyrolysis at 600 °C; optimized various reaction conditions to ensure maximum conversion of waste oil to biodiesel; and analyzed the fatty acid alkyl ester composition of biodiesel from waste cooking oil. The final conversion was 98.58% after 6 h of treatment under optimal conditions, and the catalyst could also be reused five times without deactivation. Taghavi et al. (2018) and his team used sargassum biochar as a catalyst for the thermal resolution of hydrogen from raw algal material, and the amount of hydrogen obtained was very low, only 3 mmol/g Sargassum. At the same time, biochar was found to have a significant effect on soil quality and fertility. It improved nutrient cycling in the soil and increased water and nutrient retention (Osman et al. 2022b). Biochar also can change the physics-chemical properties of the soil, such as increasing soil pH, cation exchange capacity, soil buffering capacity, retention capacity, and total porosity (Nath et al. 2022). It also increases the content of soil organic matter (Zygourakis 2017) and mineral elements (N, P, K, Ca, Mg, S) (Zhang et al. 2021b), after application, mineral nutrients can be returned to the soil, improving soil nutrients and productivity (Zhang et al. 2021b). Wang et al. (2021b) showed that the addition of biochar may increase crop yield, but was not related to application rate and crop productivity. When biochar was applied at rates of 10, 25, 50, and 100 $t·ha^{-1}$, crop yields were significantly higher compared to the control group without biochar, but at application rates of 40 and 65 $t·ha^{-1}$, the addition of biochar had no effect on crop yields. Theoretically, due to the abundance of carbon, oxygen, and other nutrients in biochar, its proper application helps to increase crop productivity, water, and nutrients, thus maintaining soil health (Osman et al. 2022b). Furthermore, biochar also helps to reduce greenhouse gas emissions such as carbon dioxide, methane, and nitrous oxide in the soil (Fawzy et al. 2020). These advantages are due to the effects of biochar on the physical, chemical, and biological properties of the soil, such as soil acidification, interaction with soil organic matter, stimulation of soil microbial activity and dynamics, etc. (Dai et al. 2020; Oni et al. 2019; Tenic et al. 2020). Cao et al. (2019a) prepared biochar from apple branches and forks. They explored the promotion of nitrate reduction by biochar in soil and plant roots and found that biochar reduced the nitrate (9.9–68.7%) and NO_x (6.3–19.2%) levels in the soils. Biochar is generally weak alkaline (Guo et al. 2020). The addition of weakly alkaline biochar to soil has also been found to improve crop nutrition by increasing alkaline cations in the soil. Therefore, higher pH biochar may be most suitable for application in acidic soil (Agegnehu et al. 2017), weakly alkaline biochar, on the other hand, is recommended for use in alkaline soils to maintain the balance of the soil environment by lowering the pH (Naeem et al. 2018).

It was found that biochar could also be used for animal husbandry. In recent years, some studies have been conducted on the effects of biochar on livestock when added to animal rations (Abakari et al. 2020; Al-Azzawi et al. 2021; Schubert et al. 2021). Co-feeding with biochar increased milk yield by 3.43%, increased protein-fat content by 2.63–6.32%, and reduced intestinal methanogens by 30% (Al-Azzawi et al. 2021). Goiri et al. (2021) found that a certain concentration of rations co-fed with biochar resulted in weight gain in chickens. The biochar may help maintain (Al-Azzawi et al. 2021; Eger et al. 2018; Mirheidari et al. 2020). This is a major source of greenhouse gas emissions from agriculture, and thus contributing positively to global climate change.

Fossil fuels, as a nonrenewable source, have brought a significant concern around the world. It is noteworthy that biochar can be used as energy storage. Recently, Zhao et al. (2023b) applied biochar to microbial fuel cells and evaluated the characteristic performance, electron transfer mechanism, as well as environmental and economic assessment. The biochar was used as an electrode material or catalyst in microbial fuel cells, which can effectively improve the efficiency of environmental remediation due to its properties of large surface area, conductivity, and porosity (Zhao et al. 2023b). Biochar, as part of the materials for energy production, should be evaluated and analyzed to the maximum extent possible in future research using more techno-economic analyses, material energy assessments, and life cycle assessments.

Economic Viability

When producing biochar in large quantities, the cost is a major component of marketing in practical applications. Economic feasibility depends to a large extent on the location of the project, the type of feedstock, the specific conditions, the associated costs, and the investment requirements of the technology to be used (Fawzy et al. 2022). However, the feasibility of the biochar production process depends mainly on the costs (Adamu et al. 2023).

The main cost of industrial biocarbon is operational costs such as the cost from production, maintenance, feedstock, transportation, labor, distribution, etc., which to some extent determine the long-term commercial viability of biocarbon (Ahmed et al. 2016). The cost of different raw materials contributes much to the overall cost and different types of feedstocks vary. For example, in Spain, the raw material cost of coconut husk fiber, which is used as a feedstock for biochar, is as high as US$775/tonne (Fornes et al. 2015), which is about twice the cost of feedstock for Greenwood biochar. The cost of production is also related to the cost of the equipment required in the plant, as the production cost for large-scale production of biochar varies because of the different treatment methods and equipment. Ahmed et al.

(2016) tabulated production costs for several countries and regions, with the UK having the highest production costs up to \$5668/tonne (Fornes et al. 2015). As a result, high production costs will affect the choice of biochar preparation method by the plant, which in turn will greatly affect the acceptance of biochar in the commercial sector.

Although the cost of biochar seems to be disappointing, it's worth noting that the economic studies focus on determining the cost of biochar production or assessing the economic feasibility of biochar production, while neglecting the carbon removal aspect. The carbon removal capability has become a new commercial venture in recent years (Haeldermans et al. 2020; Nematian et al. 2021; Zhang et al. 2017). Biochar can be featured as an agent for carbon removal purposes, so it is reasonable to include the carbon removal capacity while analyzing the economics of biochar. In the business model, the type of feedstock, choice of technology, pricing decisions, and the negotiation of favorable terms and prices are key to the success of carbon removal using biochar. The economic assessment showed that Fawzy's et al. (2022) project could be profitable with a selling price of €350 per tonne of this biochar (dry basis), the net present value amounts to €3,002,358, which makes the investment very favorable, with an internal rate of return of 22.35%, but they do not consider the sale of excess energy. The results of Fawzy's study demonstrated the feasibility of a biochar-based decarbonization system. Thus, the removal of large-scale biochar-based carbon by pyrolytic conversion has proven to be beneficial for the removal of elemental carbon from the air.

Life Cycle Assessment and Sustainability Analysis

Life Cycle Assessment (LCA) is a methodology for assessing the environmental impacts of all stages in the life cycle of a commercial product, process, or service (Mehta et al. 2022a). LCA evaluates every parameter that can affect environmental outcomes, such as greenhouse gas emissions and global warming potential (GWP) (James et al. 2022a). LCA includes the characterization and assessment of product life, which is often described as a "cradle-to-grave" system (Fawzy et al. 2022). LCAs have been conducted on biochar application and it suggested a great reduction in greenhouse gas emissions (James et al. 2022a). Figure 5 illustrates the life cycle analysis of biochar (Patel and Panwar 2023). Fawzy et al. (2022) and his team investigated the potential for carbon removal using biochar from a Spanish olive tree pruning residue. They calculated the carbon footprint of biochar in its entire life cycle and found that for every tonne of biochar produced (dry basis), approximately 268 million tonnes of carbon dioxide equivalent could be permanently removed from the atmosphere. Osman et al. assessed the impact of using carbon composite adsorbents prepared from pumice leaf by LCA. They found that for 1 functional unit (1 kg of residue leaves used as feedstock), the abiotic depletion of fossil fuels throughout the process and the GWP were quantified to be 7.17 megajoules (MJ) and 0.63 kg of carbon dioxide equivalent (CO_2 eq), respectively (Osman et al. 2022a). Rajabi Hamedani et al. (2019) and his team explored the environmental impact of biochar prepared from pig manure and willow, respectively. They found that willow biochar had a higher stable carbon content (80%) than pig manure biochar (33.7%) and had a lower environmental impact. Debela et al. (2019) suggested that the GWP of mangrove biochar is about 0.13 tonnes of CO_2/tonne of feedstock, depending on the quality of the feedstock and the yield of biochar in the pyrolysis process. The environmental effect (GWP) of biochar decreased with the increase in mangrove yield.

On the other hand, biochar has also been studied by many researchers for its circular economy which is known as recycling, reduction, reuse, and recovery of materials (Mehta et al. 2022b). This approach is now increasingly being adopted by many governments such as that of China, the European Union, and Japan (Mehta et al. 2022b). The EU's (European Union) circular economy strategy, which centers on wastewater by-products, generally assumes that by-products can be used directly in energy production and that substitutes can be converted into new products, but not just in agriculture (Bolognesi et al. 2021). Biochar is produced using local feedstocks under specially designed process conditions, avoiding the economic and environmental impacts of long-distance transport, promoting local business and employment, and increasing resource efficiency and local synergies, while the current recycling of biochar is in line with the requirements of the circular economy.

Industrial Scale Implementation

To meet the market demand for biochar, industrial-scale biochar production has to be achieved. However, currently, the production of biochar in industrial mode still faces some challenges. For example, it is not yet known whether biochar will maintain the same excellent properties when its production is increased to the industrial level (Crespo-Barreiro et al. 2023). Aiming to scale up the production of biochar from olive tree pruning, Crespo-Barreiro et al. (2023) studied the properties of biochar derived from three reactors (semi-pilot, pilot, and industrial scale) under specific production parameters. They found that 600 °C was the optimal production temperature since at this point the biochar had high stability and high carbon content. Meanwhile, it was found that the worst biochar properties were obtained in a semi-pilot reactor. The effect of scaling up from laboratory

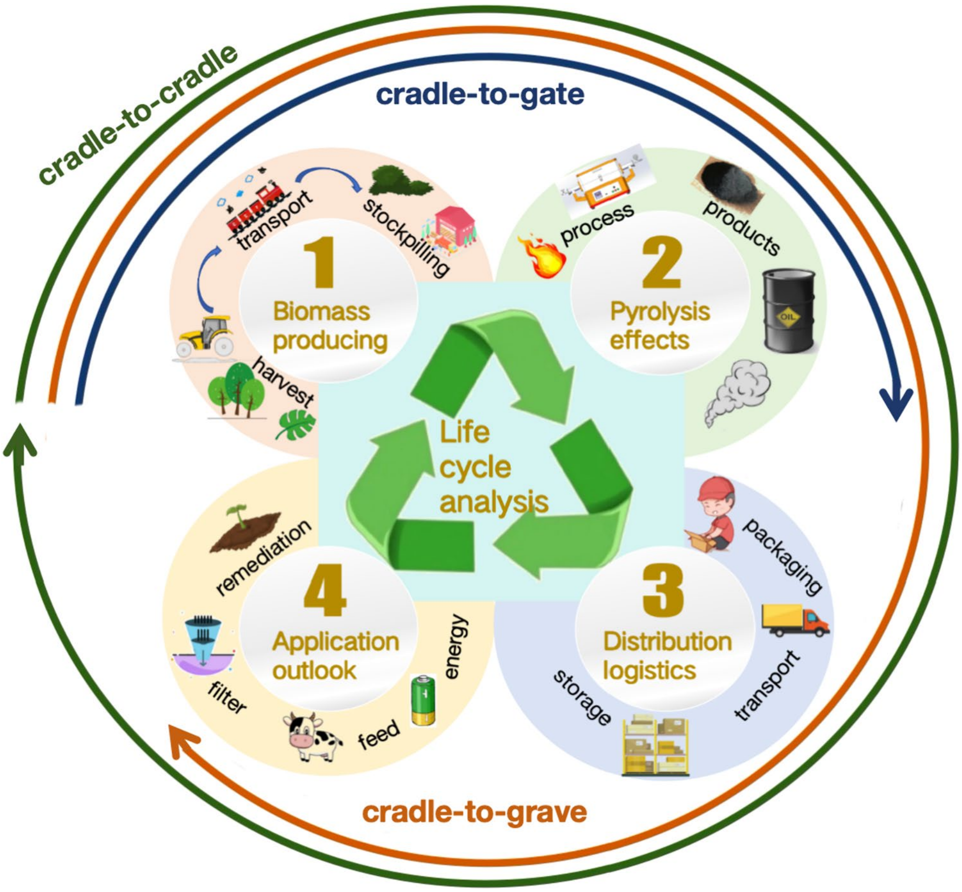


Fig. 5 The life cycle analysis of biochar (Patel and Panwar 2023)

scale to pilot scale production on the quality of biochar was also examined by James et al. (2022b). Under laboratory conditions, most of the biochar produced in the trial was highly efficient at removing zinc, however, the performance of the biochar declined when tested in the field.

Three different biomass slow pyrolysis systems are commonly used in rural and industrial use for heating technology routes and application models: rotary kiln (SCRK), vertical kiln (SCVK), and chain furnace (HCCF) (Cong et al. 2022). The common feature of these application models is the use of different types of equipment to convert agroforestry residues into char, syngas, and by-products such as bio-oil and vinegar fractions. The advantages of the rotary kiln (SCRK) and vertical kiln (SCVK) technologies are the higher quality and stability of the syngas (Cong et al. 2022).

Business analyses are essential to determine the feasibility of the selected process to be applied on an industrial scale. Zein et al. (2022) investigated the feasibility of a method for biochar production using pea waste (PW). Their research around the aspects of the location of the plant, biochar feedstock, cost analysis, total capital investment, operating expenditure summary, sensitivity analysis, and economics summary. They concluded that the production of biochar is feasible at present, but the selling price of bio-oil, a by-product of biochar preparation, would have to be increased significantly to generate a positive profit, which would also affect the sales volume of the bio-oil to a certain extent (Zein and Ansu 2022).

Environmental Risk Assessment and Safe Disposal

Environmental Risk Assessment

In addition to removing the heavy metals, biochar can also be applied to treat contaminants such as emerging pollutants and dyes (Chu et al. 2020, 2021; Eniola et al. 2023; Qiu et al. 2022; Sun et al. 2023). All of these applications could bring contaminations to the environment, where a critical environmental impact assessment should be conducted. One of the impacts is that the amount of carbon at the remediation site will be increased due to the release of carbon from the biochar, which may break the ecological balance (Wang and Wang 2019). Second, the most considered potential environmental risk of using biochar is its heavy metals leaching out into the surroundings. For example, Peng et al. (2021) conducted low-temperature magnetic pyrolysis (LMP) of municipal solid waste (MSW) in a pilot-scale continuous reactor to study the distribution and transformation of heavy metals

(HMs) in biochar, and to assess the environmental safety employing the risk assessment code (RAC) and the modified potential ecological risk index (MRI). They found that the total concentration of HMs in biochar was higher than the total concentration of HMs in municipal solid waste, and the exchangeable fraction of cadmium in biochar was at a high-risk level at 200 and 250 °C. At the same time, different heavy metals have different risks of impacting the environment. Wang et al. (2019b) and his team prepared sewage sludge (SS)-derived biochar using a combination of hydrothermal pre-treatment and pyrolysis (HTP) of SS at 300–700 °C. They conducted the environmental risk assessment of Cu, Zn, Cr, Ni, Pb, and Cd in biochar samples and found that Cr, Pb, and Cu had no or low-risk levels, indicating that they are less toxic to the environment. For Cd, it became a low risk in biochar obtained after hydrothermal treatment (220 °C) and high-temperature pyrolysis (500 °C). Zhang et al. (2020c) analyzed the chemical forms, leaching capacity, and environmental risks of cattle manure biochar (CMBC) derived at different temperatures. They found that in the risk assessment code values of cow dung, Cd and Zn are medium risk, Cu, Ni and Pb are low risk, and Cr is no risk, so the presence of Cd and Zn has a certain environmental risk, which is contradictory to Wang's et al. (2019b) conclusion that "Cd is a low-risk heavy metal when it is greater than 500 °C", which may be due to the difference in the referenced risk assessment codes and indices. Thirdly, it was noted the potential toxicity of biochar to microorganisms. Some studies have shown phytotoxic effects of copper and zinc levels in biochar on cucumber, bean sprouts and sorghum (Visioli et al. 2016). Similarly, high levels of VOCs were detected in biochar and observed to cause phytotoxicity in legumes (Buss and Mašek 2014). Dong et al. (2011) demonstrated that Fe_3O_4-modified biochar from bamboo had low potential cytotoxicity. Therefore, to promote the practical application of biochar, more toxicity studies regarding the bio-toxicity of biochar are needed in the future, and Wang and Wang (2019) suggests that toxicity tests could be carried out with fish, algae, daphnia, and luminescent bacteria.

Safe Disposal

It is critical to dispose of the biochar safely post application, especially the one with heavy metal contaminated, since improper disposal will cause secondary contamination (Gupta et al. 2020). The selection of the disposal method is determined by many factors, such as the cost of the technology, the development of the region, and the regulatory and political considerations (Gmar et al. 2022). In general, the most studied and applied methods include: incineration (Fernández-González et al. 2019), landfill (Dhillon et al. 2017), stable solidification (Chen et al. 2022), recycling and reuse (Bădescu et al. 2018), and some new disposal technologies are also investigated recently.

The use of incineration as a method of safe disposal not only reduces the volume and mass of biochar, but also helps to recover the heavy metals and energy in terms of heat. Incineration can significantly reduce the volume of metal-enriched biochar (up to 84–99%). The flue gas release process may contain volatile heavy metals (Ghosh and Maiti 2021). The landfill disposal method (Dhillon et al. 2017) is commonly used as a method of biochar disposal due to the advantages of simple operation and low cost, which is similar to the way we usually use landfills (Pandey and Shukla 2019). With this method, the biomass is dispersed on the land surface or can be buried in the ground, and the natural decomposition later completes the final disposal (Gupta et al. 2020). Biosorbents containing toxic metal ions should be desorbed before using this method to avoid secondary pollution (Gupta et al. 2020). Stable solidification is often used as a reliable and cost-effective technology and is always applied in conjunction with other disposal approaches. Chen et al. (2022) incorporated rice hull biochar (RBC) and yard waste biochar (YBC) as green additives to a standard binder for municipal solid waste incineration (MSWI) fly ash. The experimental results showed that the cured material with the addition of biochar obtained similar strength to cement-based cured material, providing a mechanically stable curing matrix for engineering applications.

As environmental issues have become a growing concern, new approaches using renewable energy sources or developing closed-loop systems for carbon recovery and reuse have been applied (Phule et al. 2023). Biochar is reported to have the ability to reabsorb heavy metals after regeneration, a property that can be used to increase the service life of the biochar and, to a certain extent, reduce the environmental impacts (Gupta et al. 2020). For this purpose, iron-modified biochar magnetic precipitation and centrifugal precipitation facilitated the regeneration process by easy recovering (Matsuda et al. 2016). Biochar regeneration and reuse methods can reabsorb heavy metals after regeneration. This property of biosorbents can be used to increase the lifetime of the biosorbent, which in turn reduces the need to generate new biosorbents, thus saving energy and protecting the environment (Gupta et al. 2020). Iron/iron oxide-modified biosorbents can also be recovered by magnetic and centrifugal precipitation (Matsuda et al. 2016). Waste biosorbents are mostly recycled for the production of bricks and cement for the construction industry, but their mechanical strength can be compromised by extensive use. In addition, heavy metals in biochar-based sorbents can be used to produce supercapacitors. For example, microwave oxidation with Ni^{2+} loaded biochar reduces the carbon content and increases the oxygen content, thereby increasing capacitance, charge/

discharge capacity, and power density (Wang et al. 2017b, 2019a).

Although the topic of safe disposal of used biochar has been considered, the attention paid to this aspect is still not adequate. The studies in literature mostly focus on the performance of the biochar but few studies carried enough insights into the final treatment of the used biochar, which may generate significant environmental problems. The discharge of pollutants from the disposal of contaminated waste biomaterials may pose both environmental and social issues, especially in developing countries (Gupta et al. 2020).

Status and Future Perspectives

To date, extensive studies on biochar have been conducted including the different properties of biochar that various raw materials introduced as well as different modification methods for their capacity improvement. Their mechanisms have also been investigated by looking through the adsorption performance. Thereby, great progress has been made toward the application of biochar in heavy metal remediation, which holds great potential to maximize the value of waste streams and avoid their environmental pollution. However, heavy metals, as hazardous materials, carry the risk of secondary pollution to the soil and water when the contaminated biochar is directly discharged into the environment. In this regard, the application of biochar as an absorbent for heavy mediation still faces great challenges. Safe and proper strategies have to be considered, e.g. the recycling and depositing of used biochar in a safe manner. Moreover, at present, biochar application as adsorbent, especially for heavy metal remediation, is mainly carried out in the laboratory. Industrial manufacturing is still on the way. Therefore, the large-scale production and application of biochar for heavy metal adsorption is yet to be investigated. Accordingly, its economic analysis will be necessary to understand its sustainability. Meanwhile, the potential environmental and ecological risks of engineering biochar must be carefully estimated. To anticipate and assess the environmental impacts arising from the application of biochar, complete environmental impact analysis is critical to commercialize the biochar and the countermeasures to prevent these impacts and damages have to be developed.

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Declarations

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