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Original Research

Research Progress on the Application of Biochar in the Remediation of Heavy Metals in Tailings Soil

Zeng-Rui Gu, Xin-Ying Hui, Hong-Jie Zeng, Qi-Chao Qu, Quzong Deji, Peng-Cheng Xie, Rui-Qing Huang, Wei Li, Jian Xiong*

Key Laboratory of Environmental Engineering and Pollution Control on the Plateau of Tibet Autonomous Region, School of Ecology and Environment, Tibet University, Lhasa 850000, China

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Abstract

The aim of this paper is to summarize the research progress on the application of biochar in the remediation of heavy metals in tailings soil. Through combing and analyzing the related literature, this paper summarizes the preparation and influencing factors of biochar, its main properties, the effect of remediation of soil heavy metal pollution and the remediation mechanism, as well as the application of biochar in the remediation of heavy metals in tailings soil. The study shows that biochar has good adsorption and passivation of heavy metals, which can significantly reduce the content of heavy metals in the soil and thus improve the soil environment. However, there are certain shortcomings in the study, such as the aging, regeneration and economy of biochar need to be further investigated. Therefore, future studies should deeply investigate the optimal conditions, economic feasibility and technical application of biochar in soil heavy metal remediation, with a view to providing new ideas and methods for the remediation of heavy metal pollution in tailings soil.

Key words: biochar, tailings soil, heavy metals, remediation

Introduction

The development and utilization of mineral resources is a double-edged sword. On the one hand, the development and utilization of mineral resources can promote global economic development; on the other hand, with the development of industry, the increase in the development of mineral resources has led to a larger number of abandoned mining areas, resulting in the accumulation of tailings [1-2]. Tailings stockpiles caused by mining activities are prone to degradation of soil physicochemical properties and structure, as well as heavy metal contamination and flotation drug residues [3], which have certain environmental hazards and are prone to pollute the environment such as soil, groundwater and atmosphere [4-5]. Heavy metals in soil are characterized by high toxicity, long action cycles, easy migration and transformation, and biological non-degradability. Heavy metals in soil can be absorbed by plants, go through the food chain enrichment, and ultimately directly affect human health [6]. In 2019, the total amount of tailings in China accumulated more than 17 billion tons, which is dominated by metal tailings [7], and the accumulation of tailings poses a greater threat to

*e-mail: jianxiong@utibet.edu.cn

the surrounding ecological environment as well as human health. Therefore, it is of great importance to improve the soil quality around the mining area and to reduce and control the content of heavy metals in the tailings.

At present, the remediation technologies for heavy metal contamination of tailings soil mainly include chemical remediation, bioremediation, nanomaterials remediation and joint remediation, etc. [7-9]. However, there are limitations in the restoration efficiency and practical application of these technologies under different environmental conditions. Chemical passivation technology is considered to be an efficient and low-cost method to amend the soil by adding exogenous organic or inorganic amendments to effectively immobilize heavy metals through surface adsorption, functional group complexation, or chemical precipitation, thereby reducing the activity of heavy metals [8]. The selection of passivation materials is the key to chemical passivation, and at the present stage, the passivation materials mainly include various types of phosphorus-containing substances, clay minerals, and biochar [10]. In recent years, biochar has been widely researched as a low-cost, ecologically safe, mass-marketable and excellent material for soil improvement and remediation. Numerous scholars have applied prepared biochar as well as modified biochar to the remediation of soil pollution. Li et al. [11] prepared biochar from tobacco straw and applied it for soil Cd remediation by loading polyethyleneimine to prepare modified biochar; Zhang et al. [12] investigated the passivation of Cd and Pb in soil by pine wood chips biochar and phosphate functionalized biochar. It has been found that biochar has good application prospects in metal mine contaminated soil and site remediation, etc. [13-15].

In recent years, scholars at home and abroad have increased their attention to and research on biochar, systematically exploring its performance and application in soil pollution remediation and improvement, environmental protection, and crop yield increase [16]. This paper summarizes and analyzes the preparation and influencing factors of biochar, the main physical and chemical properties, the effect in soil improvement, the mechanism of remediation of soil heavy metal pollution, and the application in heavy metal remediation of tailings soil, with a view to providing certain reference for future research on the remediation of heavy metal polluted soil by biochar, its application in heavy metal remediation of tailings soil, and the construction of green mines.

Biochar Remediation of Soil Heavy Metal Pollution

Introduction to Biochar

Biochar, also known as biomass charcoal, is a class of stable, highly aromatic, porous solid material with high organic carbon content produced by thermal cracking of biomass feedstock at high temperatures under anoxic or anaerobic conditions [17-19]. Biochar can be prepared from a wide range of raw materials, and currently the common raw materials for its preparation are agricultural wastes such as straw and husk, organic wastes such as municipal sludge and garbage, animal bones and feces, etc. [20-23]. As a suitable soil amendment material, biochar exhibits many advantages. Biochar has been proved by a number of studies to be characterized by high specific surface area, porosity, high pH, and strong solidification of heavy metals in soil [24]. It has been found that biochar has a stable carbon structure, which can exist in the soil for hundreds or even thousands of years without being degraded, and has a strong carbon sequestration effect [25], thus contributing to the mitigation of the greenhouse effect, and playing a role in increasing the soil carbon pool storage. Structure determines nature, as biochar has a relatively large specific surface area, rich porous structure, and a large number of functional groups on its surface, such as carboxylic acid, carbonyl, and hydroxyl, etc., which creates a strong adsorption capacity for heavy metals and other organic pollutants, and thus reduces the environmental risk of some of the pollutants. Biochar applied to the soil can provide a rich source of carbon to the soil [26], which in turn increases the soil organic matter content. Biochar application can improve the microstructure of the soil, as well as increase the abundance of soil microorganisms and significantly increase the activity of soil enzymes [27-28], which can help to enhance the yield of crops.

The physicochemical properties of biochar determine its application potential, and the selection of biomass feedstock, preparation method, pyrolysis temperature and time are the key to determine its physicochemical properties [29]. Therefore, the differences in biomass feedstock and preparation conditions have certain effects on the structure and performance of biochar. Meanwhile, the research in recent years mainly focuses on the adsorption effect of single biomass raw material biochar on single heavy metal solution under different preparation conditions, while there are fewer researches on the remediation of tailings with composite heavy metal contamination by different raw material biochar.

Preparation of Biochar and Influencing Factors

Biochar preparation methods mainly include pyrolysis, hydrothermal carbonization and microwave carbonization [30]. The physical and chemical properties of biochar, such as specific surface area, pore structure, type and number of functional groups, are closely related to its preparation method. Compared with pyrolysis, hydrothermal carbonization does not require drying and has a higher biochar yield [31]. Biochar prepared by hydrothermal and microwave carbonization methods contains high concentrations of organic matter and is not actually considered as a soil remediation material [32], thus pyrolysis is the most commonly used method for biochar preparation. Pyrolysis is the heating of biomass feedstock at high temperatures (300-1000ºC) under anaerobic or low-oxygen conditions, which causes chemical changes in the feedstock due to the increase in temperature and the cleavage of macromolecules into small molecules, resulting in the production of biomass oils, biochar, and combustible gases [33]. The physicochemical properties of biochar determine its potential for application as an amendment to improve the quality of soil environment. Although there are many factors affecting the physicochemical properties of biochar, biochar is produced by pyrolysis of biomass feedstocks, so biomass feedstocks and pyrolysis temperature are important factors affecting the physical and chemical properties of biochar [34-35].

Various kinds of solid waste biomass are commonly used as raw materials for the preparation of biochar, mainly including straw, animal manure, food waste, fruit peels and sludge. Biochar prepared by pyrolysis can be divided into fast pyrolysis process and slow pyrolysis process according to the different heating rates [36], and the biochar prepared by the two pyrolysis processes has different physicochemical properties [32]. Some researchers believe that the pyrolysis temperature can affect the specific surface area of biochar, thus affecting its adsorption capacity for heavy metal Cd [37]. And this difference in pyrolysis temperature leads to different specific surface area, pore structure, EC value, pH value, ash content and N and P content of biochar [38-40], which further affects the remediation effect of biochar on soil environment as a soil amendment. Numerous studies have shown that different pyrolysis temperatures and feedstocks affect the ash content, carbon content, aromaticity and pH of biochar, which in turn affects the remediation of heavy metal pollutants by biochar [41]. The composition, structure, and physicochemical properties of biochar are mainly influenced by the biomass feedstock and pyrolysis conditions. In addition, factors such as pyrolysis time, atmosphere conditions, and rate of temperature increase also directly affect the basic physicochemical properties of biochar [42]. Table 1 compares the differences in physicochemical properties of biochar prepared from different biomass feedstocks and different pyrolysis conditions.

Main Physical and Chemical Properties of Biochar

Biochar is a carbon-rich organic material obtained by pyrolyzing biomass under low or no oxygen conditions. The physicochemical properties of biochar mainly include pore structure, specific surface area, ash content, pH value, and the type and number of surface functional groups. A large number of studies in recent years have confirmed that biochar usually has a large specific surface area, high porosity, high pH, and a large amount of nitrogen, phosphorus, potassium and other elements. Studies have shown that biochar has a better sustained carbon sequestration capacity, and the carbon it contains can be sequestered for a long period of time, which can reduce the emission of greenhouse gases [50]. The unique pore structure of biochar can be effectively returned to the field to reclaim the soil, and the nutrients it contains can improve the soil nutrient status [51]. In the process of biochar pyrolysis preparation, the pore structure of the raw material is mostly preserved intact, and thus the prepared biochar generally has a larger specific surface area and a greater number of surface functional groups [52]. Biochar has a relatively stable porous aromatic carbon skeleton and rich functional groups within it, which to a certain extent determines its strong adsorption capacity and stabilizes heavy metals and other pollutants in the soil [53]. In addition, biochar has high carbon content and strong stability, and can exist in the soil for hundreds of years.

Different biomass feedstocks as well as different preparation processes can lead to differences in the physicochemical properties of the produced biochar. Biochar is usually alkaline due to the reduction of acidic functional groups during pyrolysis at high temperatures [54]. Vaughn et al. [55] found that the pH and K content of rice straw biochar were higher than that of wood biochar; another study [56] found that legume straw charcoal was better than non-legume straw charcoal

Table 1. Physicochemical properties of biochar with different feedstocks and pyrolysis conditions.

Preparation of raw materials	Pyrolysis temperature and retention time	Physical and chemical properties	References
Rice straw	700ºC, 2h	pH 9.98, specific surface area 288.3 m^2/g	[43]
Pig manure	600ºC, 1h	pH 8.70	[44]
Corn stalks	700ºC, 2h	specific surface area 285.317 m^2/g, average pore size 2.074 nm	[45]
Cattle manure	600ºC, 2h	pH 10.34, specific surface area 40.386 m^2/g	[46]
Rice husk	600ºC, 2h	specific surface area 297.36 m^2/g, average pore size 8.96 nm	[47]
Sludge	800ºC, 2h	specific surface area 137.86 m^2/g, Pores are dominated by 4.4 nm	[48]
Peanut shell	700ºC, 2h	ash content 2.43%, specific surface area 166.83 m^2/g, average pore size 3.01 nm	[49]

in terms of the improvement effect of acidic red soils, which may be related to the fact that legume straw biochar has a higher pH than that of non-legume straw biochar. This may be related to the higher pH value of legume straw biochar than non-legume straw biochar. In addition, pyrolysis temperature also affects the pore volume and specific surface area of biochar, etc. Park et al. [57] found that the specific surface area of sesame straw biochar increased from 46.9 to 289.2 m^2/g, and the total pore volume increased from 0.0716 to 0.1433 cm^3/g as the pyrolysis temperature was increased from 500 to 600ºC. The porous nature of the biochar, its large specific surface area, and the abundance of functional groups on the surface (-OH) were also found to be a significant factor. functional groups (-OH, -COOH,-C=O, etc.) on the surface of biochar make it have strong adsorption capacity for heavy metals [58].Deng et al.. [59] found that the surface functional group of biochar, -C=C-, plays an important role in the adsorption of Cd, whereas -C=O plays a major role in the adsorption of Cu. Therefore, the physicochemical properties of biochar determine its potential for remediation of soil heavy metal pollution, and it is a low economic cost, ecologically safe, wide source of raw materials, and renewable material for remediation of soil pollution; and at the same time, it can be applied to the removal of heavy metals and organic pollutants from water bodies by preparing biochar adsorbents [60].

Soil Amendment by Biochar

The ash in biochar contains mineral elements Ca, Mg, etc. and their oxides or carbonates, etc., thus biochar is generally alkaline and can be used for acidic soil improvement. The main reason why biochar can be used for soil amelioration is that biochar can increase the pH, soil ion exchange capacity and microbial activity of acidic soils [50]. Nitrogen, phosphorus, potassium and other elements contained in biochar can provide nutrients directly to the soil, which in turn improves the quality of the soil environment. Guo Xiongfei et al. [61] investigated the effect of applying biochar on soil nutrients through potting experiments, and the results showed a significant increase in soil total nitrogen and phosphorus content. Wang Guijun et al. [62] added biochar to different degrees of saline soils and found that the quick-acting nitrogen content of the soil decreased, and quick-acting phosphorus and effective potassium content increased. And some studies also found that the effect of biochar on soil nitrogen levels before and after its application did not change significantly [63]. Soil nutrient cycling and fertility improvement cannot be separated from the role of microbial communities, and Warnock et al. [64] suggested that biochar can indirectly affect plant-mycorrhizal interactions by changing the physicochemical properties of soil. It has been found [65, 66] that biochar affects the microbial-driven cycling and morphological transformation of mineral elements such as C, N, and P in the soil, which in turn improves soil fertility. The porous structure and surface properties of biochar can provide attachment sites and living space for microorganisms, which in turn can promote microbial communities to improve soil fertility.

Currently, biochar is mainly applied to improve acidic soils, improve fertility-poor soils and remediate heavy metal polluted soils [51]. Biochar surface is rich in oxygen-containing functional groups, which can provide more exchange sites and contribute to the increase of soil cation exchange, thus promoting the sequestration of nutrients in the soil [67]. Zhang Wen et al. [68] applied 20 t/hm^2 of charcoal biochar to the soil and found that the soil cation exchange value increased from 5.7 cmol/kg to 5.9 cmol/kg. Biochar application can reduce the accumulation of soil heavy metals in plant tissues. Khan et al. [69] demonstrated that application of biochar extracted from manzanita significantly increased spinach biomass and reduced Ni accumulation in spinach tissues. In addition, the soil improvement by biochar and the remediation of soil heavy metal pollution need to consider the amount of biochar applied, and the addition of the appropriate amount of biochar can often achieve a better soil improvement effect. At the same time, the porous structure of biochar can provide a certain habitat for soil microorganisms to help their populations to reproduce, and at the same time, it can also provide a place for enzymatic reactions, and achieve the effect of promoting and slowing down the enzymatic reactions [70], which to a certain extent can affect the activity of soil enzymes.

The main properties of biochar determine its potential for soil improvement. The main properties of biochar for soil improvement are summarized in Fig. 1.

Adsorption Mechanism of Soil Heavy Metals by Biochar

Heavy metals exist in soil in the form of exchangeable heavy metals, carbonate-bound heavy metals, iron and manganese oxide-bound heavy metals, organic matter-bound heavy metals, and residual heavy metals [71]. Biochar can effectively adsorb and passivate heavy metals in soil, and its passivation effect is closely related to the unique physicochemical properties of biochar itself, and the mechanism of passivation of soil heavy metals by biochar made from pyrolysis of different biomass raw materials is also different [48]. The mechanism of biochar on soil heavy metals mainly includes the following aspects: electrostatic effect, ion exchange, complexation effect, precipitation and physical adsorption, etc., and its interaction mechanism is shown in Fig. 2 [50].

Electrostatic Effects

The surface of biochar is rich in oxygen-containing functional groups, which can generate a certain amount of negative charges. These negative charges attach to the surface of biochar and attract positively charged metal

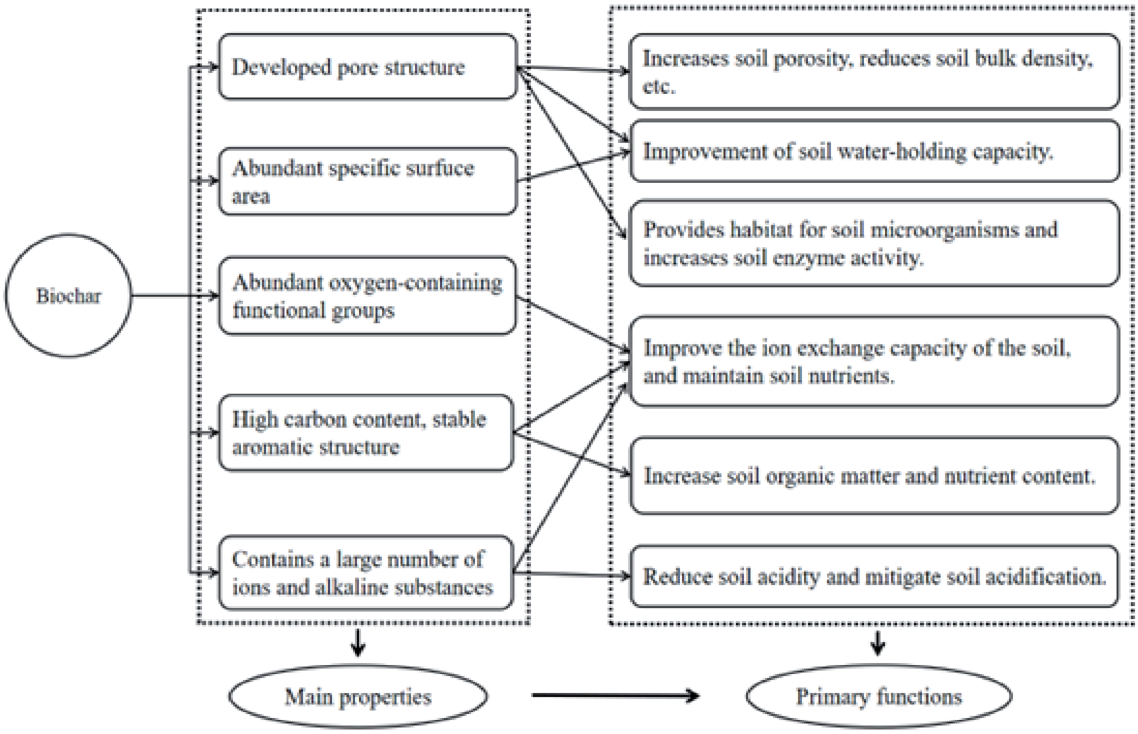

Fig. 1. Main properties and role of biochar.

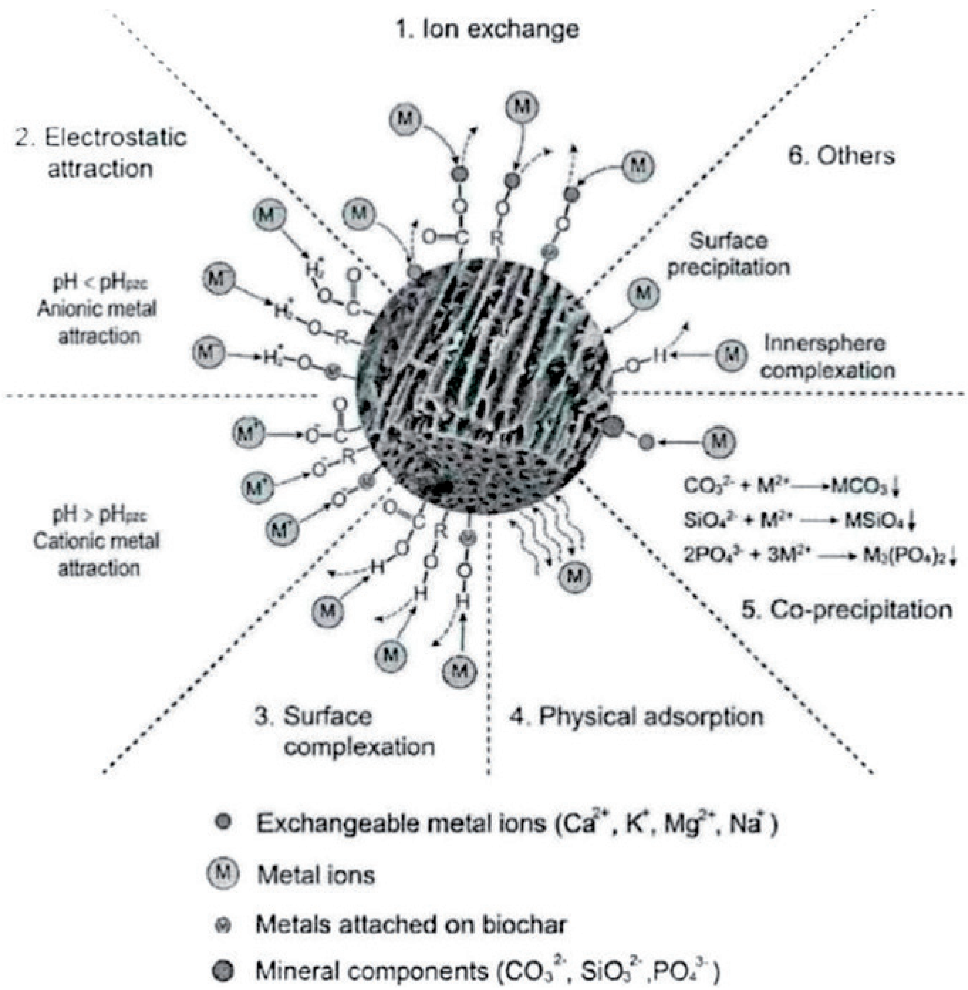

Fig. 2. Mechanisms of action of biochar on soil heavy metals.

ions through electrostatic action, thus realizing the adsorption of heavy metal cations in the soil [67], thus achieving the purpose of remediation of soil heavy metal pollution. The electrostatic interaction between biochar and heavy metal ions is closely related to the pH of the soil environment and the zero-charge point of biochar [72-73]. When the pH of the soil environment increases, the negative charge carried by the soil colloid increases to a certain extent, and more heavy metal cations are adsorbed through electrostatic action [74-75]. When the soil pH is greater than the zero-charge point of biochar, the surface of biochar is negatively charged and can be electrostatically adsorbed with heavy metal cations; conversely, biochar is electrostatically adsorbed with heavy metal anions [76]. In addition, the biochar formed from the pyrolysis of biomass has a large specific surface area and a developed pore structure, which increases its contact area with heavy metal ions and thus improves the electrostatic adsorption of heavy metal ions by biochar. The electrostatic adsorption of biochar with heavy metal ions was enhanced with the increase of the initial concentration of heavy metals [77].

Ion Exchange

Ion exchange usually occurs between H+ in oxygen-containing functional groups and metal ions. Under suitable environmental conditions, the oxygen-containing functional groups on the surface of biochar will shed H+ and provide sites for the attachment and binding of heavy metal ions, thus realizing the exchange of heavy metal ions and H+ . The ion exchange efficiency mainly depends on the size of heavy metal ions and the functional groups on the adsorbent surface [58]. High CEC of biochar can improve ion exchange effect between biochar particles and metal cations [78]. In addition, the application of biochar can increase the cation exchange in soil. Laird et al. [79] found that soil CEC increased by 20% after biochar application to soil and increased with the amount of biochar applied, thus contributing to soil fertility. However, at the same time, application of biochar to soils with high organic matter content may not increase soil CEC. Schulz et al. [80] found that application of biochar did not realize an increase in soil CEC.

Complexation Reaction

The surface of biochar possesses a large number of oxygen-containing functional groups, which can form stable complexes with heavy metal ions through surface complexation, thus reducing the effectiveness of heavy metals in soil. Some studies [81-82] found that Cu, Pb, Ag, and Al can be immobilized by complexation on the surface of biochar. The acidity and alkalinity of biochar is an important factor affecting the adsorption of heavy metals, and the increase in pH makes the negatively charged adsorption sites on the surface of the charcoal increase [83], and the electrostatic attraction and the dissociation of the organic functional groups are enhanced, thus improving the complexation of heavy metals.

Precipitating Effect

Precipitation is one of the important mechanisms for biochar to immobilize heavy metals in soil. The surface of biochar contains a variety of mineral components, and the anions dissolved by these mineral components, such as CO_3^{2-}, PO_4^{3-}, SiO_3^{4-} and Cl^- etc., can be combined with the heavy metal ions to form precipitation. It has been found that for cattle manure biochar with high phosphate and carbonate content, the formation of Pb phosphate and precipitation of Pb carbonate minerals is the main mechanism for adsorption and immobilization of Pb [84]. Biochar can affect the morphology of heavy metals in soil, mainly transforming them from the effective state to the residual state, thus immobilizing heavy metals and reducing their mobility in soil [85]. With the increase of soil pH, heavy metals in the soil will generate precipitates such as metal hydroxides. Jiang et al. [86] found that with the increase of soil pH, hydroxide precipitates of Cu^{2+}, Pb^{2+} and Cd^{2+} appeared in the soil, and biochar can be bound to the precipitates, which can reduce the mobility of heavy metals in the soil.

Physical Adsorption

The porous structure and large specific surface area of biochar can enable heavy metal ions to be adsorbed on its surface or diffuse into the micropores, thus realizing the physical adsorption of heavy metal ions by biochar. It was found that silica fertilizer ($Na_2SiO_3 \cdot 9H_2O$) was able to reduce the content of exchangeable Pb in soil through physical adsorption [87], and rice straw biochar containing Si was more significant in reducing the Pb content in soil [88]. Porosity and specific surface area are important factors affecting the physical adsorption of biochar. Generally, biochar prepared under high temperature conditions has larger porosity and specific surface area, and its ability to adsorb heavy metals is also larger [89]. Ji Haiyang et al. [90] used silk quilt waste as raw material to prepare biochar by pyrolysis at 300, 500, and 700ºC, respectively, and investigated its adsorption of Cd^{2+}, and the results showed that the specific surface area of the biochar prepared at 700ºC as well as the amount of adsorbed Cd^{2+} were the largest, which were 37.8 m^2/g and 91.07 m^2/g, respectively.

In addition, the mechanism of action of biochar on soil heavy metals is often not a single action, but a combination of multiple actions. Jiang et al. [91] conducted soil cultivation experiments using rice straw biochar, and the results showed that the adsorption of soil Pb(II) by rice straw biochar gradually increased with the increase of the addition amount, and it was concluded that Pb(II) was adsorbed and immobilized on the surface of biochar mainly through ion exchange and complexation with oxygen-containing functional groups on the surface of biochar. Ding et al. [92] investigated the effect of adsorption effect and mechanism of sugarcane bagasse biochar made at different pyrolysis temperatures on Pb. The experimental results showed that the adsorption mechanism of Pb by biochar made at low pyrolysis temperatures included complexation with functional groups, cation exchange and precipitation, whereas the biochar made at high pyrolysis temperatures mainly involved precipitation and intra-granular diffusion. Wang Hong et al. [93] found that the adsorption rate of water hyacinth charcoal on Zn and Pb in soil gradually increased with the increase of pyrolysis temperature and biochar addition, and that ion exchange and complexation were the main mechanisms of biochar remediation of soil heavy metal pollution. Table 2 summarizes the effect and mechanism of adsorption of soil heavy metals by biochar from different raw materials.

In summary, the solidification and stabilization mechanisms of biochar for different heavy metals are somewhat different; the passivation mechanisms of biochar produced under different biomass sources or pyrolysis conditions are also different due to the differences in their physicochemical properties. At the same time, the remediation of heavy metals in soil by biochar is often characterized by the co-existence of multiple mechanisms of action.

Hazards of Soil Heavy Metal Pollution

Due to natural or man-made reasons, heavy metal ions enter the soil environment and accumulate to a certain extent, exceeding the self-purification capacity

Table 2. Effectiveness of different biochar in adsorption of soil heavy metals.

Raw materials	Methods of preparation	Pollutants removed	Effects	Main mechanisms of action	References
Rice husk	600ºC High temperature cracking	Cu, Cd	$KMnO_4$ and NaOH were utilized to modify the biochar treatment, respectively. Soil cultivation experiments showed that the addition of biochar significantly increased the soil pH, and the effective state content of both Cu and Cd in the composite polluted soil was significantly reduced.	Cooperative interaction	[94]
Bark of poplar tree	600ºC High temperature cracking 2h	Cd	Potting experiments using poplar bark biochar (PBC600) and thiourea-modified poplar bark biochar (TPBC600) showed that the addition of biochar significantly affected the physicochemical properties of the soil. In the presence of TPBC600, acid-soluble and reducible Cd fractions were converted to oxidizable and residual state Cd fractions, effectively reducing the bioavailability of Cd in the soil.	-	[95]
Dregs of a decoction	Pyrolysis at 500°C for 2h	Cd, Cu	Using an indoor soil cultivation experiment, biochar reduced the soil content of Cu and Cd in the weakly acid extractable state by 9.00% and 6.82%, respectively, and increased the content of Cu and Cd in the residual state by 16.08% and 16.67%, respectively, as compared to the control.	Adsorption and immobilization, precipitation	[96]
Cow dung, rice straw	Pyrolysis at 350°C for 4h	Pb	Cow dung biochar treatment reduced soil TCLP extractive state Pb by 56.0% and rice straw biochar treatment reduced TCLP extractive state Pb by 35.8%.	Adsorption, ion exchange	[97]
Rice straw, wood chips	Pyrolysis at 500°C for 1h	Pb, Cd	Using HNO_3-$KMnO_4$ combined modified biochar, soil cultivation experiments showed that modified biochar could improve the soil structure, significantly increase the soil CEC and OM content, and enhance the soil's own immobilization of nutrients and heavy metals; meanwhile, the modified biochar-soil system mainly immobilized soil Pb and Cd through the pathways of ion-exchange, complexation reaction and precipitation.	Ion exchange, complexation, co-precipitation	[98]
Rice straw	Pyrolysis at 300ºC, 500ºC, 700ºC for 1h	Pb	Among the three different temperature rice straw biochar prepared (RSB300, RSB500, and RSB700) RSB500 and RSB700 had higher pH and surface area with higher metal removal capacity; RSB500 and RSB700 were more suitable for soil Pb remediation compared to RSB300.	Precipitation	[99]

of the soil, making the quality of the soil environment deteriorate, that is, causing soil pollution. Heavy metal elements that pollute the soil environment mainly include mercury, cadmium, lead and copper and other biotoxic elements. Heavy metals in soil are difficult to degrade, hidden, long-term accumulation, irreversible and highly toxic [100]. One of the major characteristics of soil heavy metal pollution is that it is difficult to degrade and more difficult to remove, and the vast majority of heavy metal substances can be decomposed by microorganisms such as bacteria and fungi in the soil by utilizing them, unlike ordinary organic matter. In addition, heavy metals in soil can be absorbed by crops and plants, and enter the animal body or human body through the food chain enrichment pathway, thus directly or indirectly causing harm to animal and human health; at the same time, heavy metals in soil can also be toxic to plants, and their accumulation in plants will cause changes in metabolic pathways, growth retardation, and yield reduction [101]. Heavy metals will continue to accumulate in the soil after entering the soil, changing the physicochemical properties of the soil and affecting the structure, abundance and diversity of the soil microbial community, thus affecting the stability of the whole soil ecology [102-103]. Some heavy metal elements (e.g., Zn, Cu, Mn, etc.) are necessary for plants and animals to carry out their life activities, but they can be harmful in excess of appropriate amounts [104]. Different heavy metal elements cause different hazards, such as Cd reduces the photosynthetic efficiency of green plants and inhibits further plant growth [104]; Pb has an obvious toxic effect on the root system of plants, resulting in thinning of roots, black color, and rotting of the root crown [105]. Soil heavy metal pollution can also seriously affect human health. Chronic Cu poisoning will cause vomiting, memory loss, etc. [105]; Pb will have more obvious damage to the nervous system of the brain as well as cardiovascular and cerebral vessels, etc. [106]. Fig. 3 represents the main impacts caused by heavy metal contamination of soil.

Therefore, the harm of soil heavy metal pollution should not be underestimated. The prevention and remediation of soil heavy metal pollution is of great significance for ecological environmental protection, human health protection and sustainable social development.

Application of Biochar in the Remediation of Heavy Metal Pollution in Tailings Soil

Potential of Biochar for Remediation of Heavy Metals in Tailings Soils

While mining and utilization of mines bring social and economic benefits, they also produce certain environmental pollution problems. As the tailings produced by mining contain heavy metals such as copper, lead, cadmium, etc., the disposal of tailings in stockpiles adversely affects the soil ecosystem [107]. For the soil around the mining area, the random accumulation and discharge of large quantities of waste rock, waste water, and sludge generated by industrial activities without effective treatment can lead to the migration of large quantities of heavy metals to the surrounding areas of the mining area [108]. At the same time, due to the specificity of mining activities and the complexity of the composition of the associated mineral metal elements [8], the heavy metal pollution of the tailings waste area and the surrounding soils is often accompanied by a variety of heavy metal composite pollution. In recent years, soil heavy metal pollution remediation technology is constantly developing, forming physical remediation, chemical remediation, biological remediation and joint remediation methods. The management measures

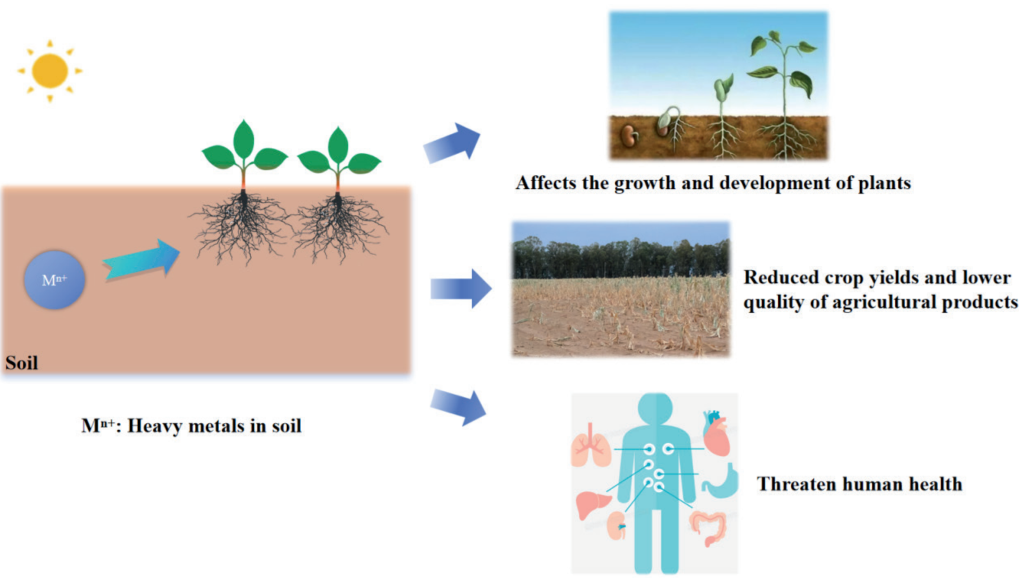

Fig. 3. Main hazards of heavy metal pollution of soil.

of tailings mainly include engineering remediation, chemical remediation and bioremediation [109], of which chemical remediation mainly includes techniques such as drenching, solidification and stabilization. Stabilization is a technology that stabilizes the tailings by adding organic or inorganic amendments such as biochar and lime to the tailings soil in order to reduce the concentration of heavy metals in the tailings through surface complexation, precipitation, ion exchange, and adsorption, thus reducing the mobility of heavy metals in the tailings [110]. Due to the special characteristics of the soil environment around the mining area, the use of in situ passivation technology to manage soil heavy metal pollution is simple, fast, and low-cost, which is suitable for the large-scale remediation of tailings soil. And the raw material of biochar has a wide source, which can be applied to the in situ passivation remediation of heavy metals in tailings soil.

Biochar is a promising material for remediation of soil heavy metal pollution due to its developed pore structure, large specific surface area and abundant oxygen-containing functional groups, which makes it a good application prospect in the in situ remediation of heavy metals in soil and the development of highly efficient heavy metal adsorbent materials. Biochar can effectively reduce the biological activity and toxicity of heavy metals in contaminated soil [111, 112], and has the role of remediation of heavy metal contaminated soil, thus reducing the environmental risk of soil heavy metals. The potential application of biochar in tailings heavy metal contaminated soils is enumerated in Fig. 4. Currently, studies [13-15] have shown that biochar has a better application prospect in metal mine contaminated soil and site remediation, etc.

Remediation of Heavy Metals in Tailings Soil by Biochar

In recent years, some researchers have explored the use of biochar for the remediation of heavy metals in tailings soil, and found that biochar has good remediation effect on soil heavy metal pollution. Fig. 5 represents the process of adsorption and removal of heavy metals from tailings soil by biochar. Table 3 compares the remediation effect of different biochar on heavy metals in mine soil. The study showed that surface modification treatment of biochar can realize the improvement and enhancement of biochar performance, which can help to improve the effect of biochar on the remediation of soil heavy metal pollution. Zhang Zezhan et al. [113] investigated the immobilization of Pb and Zn in tailings contaminated soil by preparing phosphate-modified biochar, and the results showed that the adsorption of heavy metals Pb and Zn by KH_2PO_4 modified biochar increased significantly. It was also found by [114] that the application of Hibiscus sabdariffa core biochar, sludge biochar and chicken manure biochar could directly immobilize heavy metal contamination in tailings and help to improve the stability of the tailings microbial community.

In addition, the use of biochar combined with phytoremediation and other methods to repair the tailings soil, to a certain extent, can reduce the effectiveness of heavy metals in the mining area and other soils, so as to achieve the enhancement of the effect of soil heavy metal management.Jun et al. [122] applied different amounts of lychee twig biochar to heavy metal contaminated soils in the mining area and promoted the growth of sunflower plants, of which the 5% biochar addition was

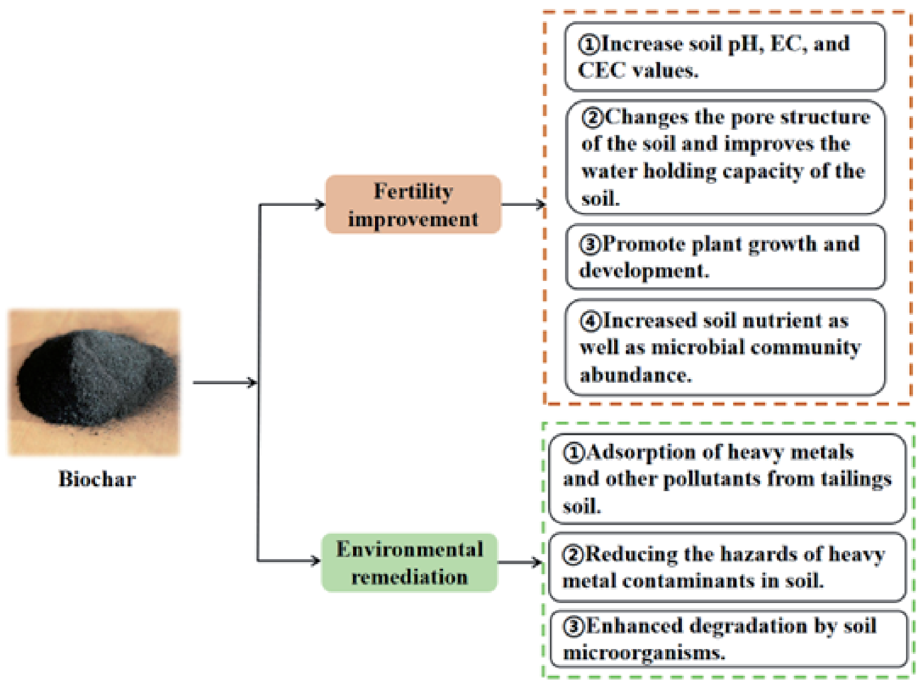

Fig. 4. Potential of biochar for heavy metal remediation of tailings soils.

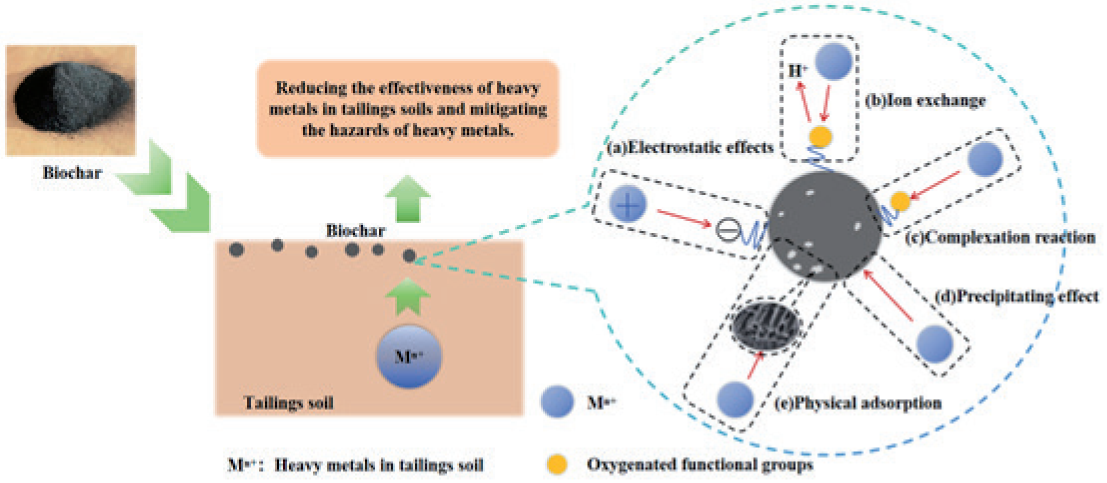

Fig. 5. Adsorption of heavy metals from tailings soil by biochar.

Table 3. Remediation effect of different biochar on heavy metals in tailings soil.

Raw material for biochar	Objects of restoration	Effects of the restoration	Mechanisms of action of biochar on soil heavy metals	References
Pig manure, fruit	Heavy metals in contaminated soil from agricultural land in mining areas	Pig manure biochar was better than fruit biochar in terms of remediation, and the remediation was better as the amount of both types of biochar added increased.	Adsorption	[115]
Soybean straw	Cu, Zn, Pb and Cd in soil contaminated by lead and zinc tailings	3% biochar can inhibit the decrease of soil pH caused by the pollution of lead and zinc tailings; biochar can significantly reduce the content of heavy metals in the roots of polluted soil cabbages, and 3% biochar can prevent the migration and enrichment of Cu, Zn, Pb, and Cd from the polluted soil of lead and zinc tailings to the aboveground part of cabbages.	Passivation	[116]
Rabbit excrement	Soil from a mining site in Spain	It was shown that biochar prepared at 450°C and 600°C applied with oilseed rape was able to reduce the content of As, Cu, Co, Cr, Se and Pb in the soil; the addition of biochar resulted in a decrease in the transfer factor of Co, Cr, Cd, Cu, Ni, Zn, Pb, and As in the soil, and the accumulation of these metals within the roots of the plants. In all cases, the addition of biochar increased biomass production.	Adsorption	[117]
Ginkgo biloba	Contaminated soil from a lead-zinc mine in Panzhihua, Sichuan Province	NaOH and nitrogen-doped modified treatment of Ginkgo biloba biochar were used for soil cultivation experiments, and the results showed that both modified biochars could achieve the stabilization of the active state Pb, Cd, and Cu in the soil, and at the same time, they could increase the pH and nutrient element content of the soil, in which nitrogen-doped modified biochars had a better effect of enhancing the nitrogen in the soil, and the NaOH-modified biochars had a greater increase of the phosphorus and potassium content in the soil.	Ion exchange, precipitation, complexation, adsorption	[118]
Rice straw, corn stalks	Soil of a lead-zinc mining area in Kaili, Guizhou	The addition of rice straw biochar and corn stover biochar for the release of heavy metals from the soil of lead and zinc mining area under acid rain leaching conditions showed that different biochar had different effects on the leaching of Pb, Zn, Cd and As. The addition of corn stover biochar significantly reduced the leaching of heavy metals Pb from the soil of the mining area, and its cumulative effluent was reduced by 49.11%, but it had a significant The rice straw biochar accelerated the release of Pb from the soil, and had no obvious effect on Zn and Cd, and both biochars had an activating effect on soil As.	Functional group complexation, ion exchange, precipitation	[119]

Table 3. Continued.

Corn stalks	Soil of the main mining area of Baiyun'ebo	The addition of biochar for indoor mining soil leaching experiments showed that biochar could alleviate the acidity of the soil to a certain extent and reduce the risk of heavy metal migration to the lower soil, and that biochar had the best passivation effect on Pb.	Ion exchange, complexation, adsorption, precipitation	[120]
Black pine, red willow	Soil from a mine in Idaho, USA (contaminated with Cd, Cu, Pb and Zn)	The application of both types of biochar significantly increased soil pH, while being able to reduce the bioavailability of Cd, Cu, Pb and Zn in mining soils.	Precipitating effect	[121]

the best, and the heavy metal concentration in the soil decreased significantly. Pandey et al. [123] applied 3% biochar to heavy metal contaminated soil and planted wheat at the same time, which showed that compared with the control group without biochar, the toxicity of heavy metals in soil and the toxicity of heavy metal enrichment in plants were reduced by biochar treatment, and it could promote the growth of wheat. Meanwhile, some researchers have used various raw materials to prepare biochar and explored its remediation effect on soil heavy metals in mining areas. Tao Ling et al. [124] investigated the control effect of prepared sludge-biotite co-pyrolysis biochar on heavy metals in contaminated soils in mining areas, and the results showed that after the addition of this biochar for the passivation of heavy metals in contaminated soils in mining areas, the content of Cu, Cd, Ni, Zn, and Cr in the soil was kept at a low risk level. In recent years, as a very potential, environmentally friendly, carbon sequestration function, and a wide source of raw materials for the remediation of soil heavy metal pollution, biochar has received more attention and research, and its application to the remediation of heavy metal pollution in tailings soil has a broader prospect.

Amelioration of Tailings Soils by Biochar

Biochar can increase the pH, conductivity, cation exchange and other factors of the soil to stabilize the heavy metals in the soil of the mining area [125], and at the same time, it is conducive to the improvement of the soil environment. It has been shown [126] that biochar can substantially increase the pH value of acidic mining soils contaminated by heavy metals, so that the quality of the soil can be effectively improved and the mobility of heavy metals in the soil can be reduced. The well-developed pore structure and rich specific surface area possessed by biochar can provide a good environment for soil microorganisms to survive and reproduce [127], and can also adsorb and desorb readily decomposable organic compounds [126], thus providing a nutrient source for microorganisms, which can help to increase the diversity of microbial communities. The structure and properties of biochar such as porousness, large specific surface area and large pH can have a certain effect on the structure and physicochemical properties of tailings soils and can serve to improve tailings soils to a certain extent.

Conclusion

Biochar, as a new type of soil environmental remediation material, can repair and manage the heavy metal pollution problems existing in tailings soil, and at the same time can realize soil improvement, which has good application prospects. Biochar can be prepared from solid waste biomass raw materials through high temperature thermal cracking. The preparation of biochar can realize the resource utilization of solid waste and the repair of soil and water environment, and achieve the goal of "waste for waste". However, most of the studies on the application of biochar in the remediation of heavy metal contamination in tailings soil are concentrated in the experimental stage, and there are few cases of practical application.

(1) When biochar is applied to soil, the improvement and restoration of soil environment is a long-term process, and it is also necessary to consider the effects of changes in the stability of biochar and its own structure on the soil and the restoration effect. In addition, the aging phenomenon of biochar also deserves attention and in-depth study, in which the impact and potential risk of biochar aging on the ecological environment such as tailing soil and atmosphere are not clear.

(2) Heavy metals in tailings soil are characterized by a long period of action and great harm. Biochar as an in situ chemical remediation material for heavy metal contamination of tailings soil has a single situation of remediation, while its long-term effect of remediation needs to be further explored. Thus, it can be combined with physical remediation, phytoremediation and other technologies to carry out joint remediation, with a view to realizing the enhancement of the remediation effect of heavy metals in contaminated soil, so as to achieve higher environmental and economic benefits. In addition, the feasibility of large-scale production, preparation and application of biochar needs to be further explored.

(3) The environmental problems caused by the stockpiling of tailings are relatively complex, and how to select the appropriate remediation technology

for heavy metal contamination of tailings soil according to local conditions needs to be further researched. In recent years, research on biochar in soil heavy metal pollution remediation and soil improvement has made some progress. As a potential, low-cost, and widely available raw material for in-situ remediation of soil environment, the optimal preparation conditions for large-scale application of biochar need to be explored in order to achieve the best remediation effect. Meanwhile, in order to improve the remediation effect of heavy metal pollution in tailings soil, the combination of biochar and different soil conditioners can be selected to optimize the remediation of heavy metal pollution in tailings soil.

Author Contributions

Z-R.G. wrote the paper as well as planned and supervised the project. X-Y.H. and H-J.Z. carried out the literature search and organization. Q-C.Q., Q-Z.D-J, P-C.X., R-Q.H. and W.L. were involved in summarizing the relevant content. J.X. revised the original manuscript.

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Competing Interests

The authors declare no competing interests.

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