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Current Research Status and Prospects of Biochar Materials for Remediation of Soil Heavy Metal Pollution

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Abstract. Soil heavy metal pollution is a serious environmental problem. Heavy metals such as cadmium and lead cause serious damage to soil ecosystems and affect human health. Therefore, the remediation of heavy metal pollution in soil is a hot topic in soil research. To ensure agricultural development and human health, various physical and chemical techniques are used for soil remediation. Traditional methods for heavy metal pollution control, such as bioremediation and adsorption, are often inefficient and cannot meet growing demands. With industrial development and population growth, effective methods for soil heavy metal remediation have become extremely important. People have explored this from various aspects and actively developed new materials and technologies. Biochar has gained popularity due to its high adsorption capacity and eco-friendly properties. Biochar materials and their derivatives have significant effects in treating soil heavy metal pollution. They have made a substantial contribution to soil restoration and environmental protection. In order to better control soil heavy metal pollution, the preparation, working principle, and various development directions of biochar have been extensively studied. In view of this, this article reviews the preparation methods of biochar materials, the mechanism of biochar adsorption of heavy metal pollutants, and the research progress of biochar application in soil heavy metal pollution control. The future development prospects of biochar are also discussed.

Keywords: Biochar materials, soil remediation, soil heavy metal pollution

1. Introduction

Heavy metal pollution is a widespread environmental issue in many countries, particularly severe in highly industrialized areas. Both water and soil are threatened by heavy metal pollution. The main causes include mineral extraction, industrial emissions, and the excessive use of fertilizers. They pose a serious threat to the ecosystem. Heavy metals are highly toxic and, unlike organic substances, they are non-degradable. They can only change their oxidation states and have a half-life exceeding 20 years. Some heavy metal elements can be absorbed by the human body, which are trace elements necessary for human growth and development, such as iron and zinc. However, excessive intake can also cause harm to the human body. Other heavy metal elements, such as lead, chromium, mercury, etc., are highly toxic to organisms and can harm their health when exposed or ingested [1].

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It can persist in the soil for extended periods, posing serious threats to ecosystems and human health. Pollution from heavy metals can severely affect the agricultural and ecological functions of soil. Accumulation of heavy metals can inhibit the reproduction and activity of soil microorganisms, which in turn impacts plant growth. The deposition of heavy metals in people's bodies can lead to various diseases, such as damage to the nervous system and cancer.

The traditional methods for remediating heavy metal pollution in soil primarily include bioremediation and adsorption techniques. Bioremediation utilizes plants or microorganisms to absorb, stabilize, or transform heavy metals. This encompasses various biological processes such as phytoremediation. Typically, heavy metals in the soil accumulate in the above-ground biomass of plants or become stabilized in the root zones. Although plants have significant potential for the absorption, stabilization, and degradation of heavy metals, their efficiency in absorbing these metals is often low. Furthermore, heavy metals pose a threat to plant growth and development.

Microorganisms can also be employed for heavy metal remediation. Yeast can adsorb heavy metal particles on its cell wall surface. It produces various enzymes to participate in this process. However, the vast diversity of microorganisms makes it challenging to select suitable strains, and most microorganisms exhibit low tolerance to heavy metals, which complicates their application.

The traditional adsorption method primarily uses clay minerals and lignin as adsorbent materials. Clay minerals are hydrous aluminum silicates with a layered structure and a particle size below two micrometers. They possess a high cation exchange capacity and surface charge, which allows for effective adsorption of metal cations. However, clay minerals show significant differences in the adsorption of various metal elements and are greatly affected by PH levels. Under extreme PH conditions, their adsorption capacity decreases, and recovery after adsorption involves complex processes [2]. On the other hand, Lignin has a molecular structure rich in hydroxyl and carboxyl functional groups. These functional groups can quickly bind with metal ions to form complexes. Nonetheless, lignin is also influenced by PH. Under acidic or alkaline conditions, it is prone to degradation, which affects its adsorption capability [3].

The efficient remediation of soil heavy metal pollution has become critically important. Biochar is a green and environmentally friendly functional material, which is the product of biomass pyrolysis under isolated air conditions. Due to its loose and porous structure and high surface area, biochar has strong adsorption properties and is used in various fields such as soil improvement and remediation. As an emerging soil remediation technology, it is highly valued in the field of soil heavy metal pollution control due to its wide sources, low cost, and green environmental characteristics. At present, research mainly focuses on expanding the scope of obtaining biochar raw materials, modifying biochar using physical or chemical methods, and combining it with other materials to form composite materials, such as nano biochar.

2. Biochar raw materials

Biochar material is a solid material produced by biomass pyrolysis under isolated air conditions. They have a high specific surface area and porous structure, and are increasingly being valued in the field of soil heavy metal pollution control. The raw materials of biochar are easy to obtain. It aligns with green and environmentally friendly concepts, using organic waste materials such as crop straw, livestock waste, wood chips, and sludge as raw materials. The thermal decomposition temperature and preparation process of the raw materials all influence their physical and chemical properties. With the deepening of current research, the scope of obtaining biochar raw materials should continue to expand.

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2.1. Crop straw

Straw is a commonly used raw material for preparing biochar. It is rich in organic components, including cellulose, hemicellulose, and lignin, which are high-quality raw materials for biochar. The yield of biochar prepared from straw is relatively high. Experiments have shown that biochar prepared from straw can effectively improve the white clay in Northeast China. The use of straw to produce biochar improves resource utilization and avoids environmental pollution caused by straw burning. In addition, straw is easy to obtain and inexpensive, further reducing the cost of straw biochar.

2.2. Animal feces

Animal manure can also be used to produce biochar. Compared to straw biochar, biochar produced from animal manure has a lower carbon content but is easier to produce and has a stronger ability to treat heavy metals. Biochar produced from different types of animal manure exhibits varying properties. Cow dung has a high fiber content and high moisture content. It is effective in remediating lead-contaminated soil. The lead concentration can be reduced by 70% to 89%. Chicken manure is an excellent organic fertilizer, and the biochar produced from it can increase the leaching rates of arsenic and cadmium in heavy metal-contaminated soils. Pig manure is rich in ash, aromatic groups, and polar groups. Biochar produced from composted pig manure can effectively remediate copper in soils [4]. Collecting animal feces and processing them for the preparation of biochar not only improves resource utilization but also avoids pollution of water sources by animal feces.

2.3. Sludge

The rich carbon content in sludge is a favorable condition for the preparation of biochar. Biochar made from sludge is mainly used for the adsorption of heavy metal ions in soil. Sludge biochar can increase soil PH, and the PH value rises with the amount of biochar used. The application of sludge biochar can increase the effective phosphorus content in soil. The increase is related to the preparation temperature.

2.4. Kitchen waste fermentation residue

Kitchen waste is usually collected and processed through centralized fermentation. This process produces kitchen waste fermentation residues, which are hard to degrade but rich in organic matter. Manually remove impurities like glass from the residues. Dry them and then process in a drying oven at 105°C for 4 to 5 hours. After that, treat the biochar with magnesium chloride, ferric chloride, or potassium hydroxide solutions to obtain modified biochar. Finally, combine it with other materials to create layered biochar composites [5].

3. Biochar production

Biochar is mainly prepared through methods such as thermal cracking, vaporization thermal cracking, and hydrothermal carbonization. In pyrolysis, there are two methods: fast pyrolysis and slow pyrolysis. Slow pyrolysis generates a greater yield of char and gas, while fast pyrolysis generates more bio-oil. Pyrolysis can be generally viewed as breaking down the biomass into smaller molecules through heating at high temperatures with low or limited oxygen. The process causes a change in the chemical composition of the biomass. After hydration or decomposition, the

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biomass develops a porous structure. Other products of pyrolysis are biofuels, coal tar, or other materials. Most processes control the pyrolysis temperature to below 600°C. Gasification pyrolysis breaks down biomass through reactions at temperatures greater than 750°C and occurs at limited oxygen levels, which produces lower yields of biochar. Hydrothermal carbonization also produces biochar and is done through mixing the treated biomass with water and putting it into a high-pressure reactor at closed conditions. Hydrothermal carbonization can occur at temperatures generally between 180°C and 230°C and reactions occur that can oxidize organic compounds, mainly those with carboxyl groups, and produce hydrocarbons, as smaller molecules condense together and polymerize to develop larger molecules. Aromatization reactions occur, which lead to a carbon rich solid material that is called biochar. Hydrothermal carbonization produces biochar, which is highly hydrophilic. After the reaction is completed, it is necessary to quickly cool the reactor to prevent the oxidation of biochar. Then, the biochar should be removed from the reactor, typically requiring filtration or centrifugation.

4. Absorption mechanism

The raw materials and preparation methods can affect the physicochemical properties of biochar. The adsorption of pollutants by biochar mainly takes two forms: physical adsorption and chemical adsorption. Physical adsorption mainly relies on van der Waals forces, while chemical adsorption is the interaction caused by chemical bonds during the adsorption process. The adsorption mechanism of biochar for heavy metals is related to the pore structure and abundant functional groups on the surface, which can be specifically divided into reaction mechanisms such as organic functional group complexation, co-precipitation, ion exchange, and electrostatic adsorption [6].

4.1. Surface complexation

The surface of biochar is rich in oxygen-containing functional groups such as hydroxyl and carboxyl groups, which can react with heavy metals to form a more stable state. The adsorbed heavy metals are not easily eluted. Research on the adsorption effect of heavy metals on biochar prepared from wetland plants revealed that heavy metals undergo complexation reactions with oxygen-containing functional groups.

4.2. Coprecipitation

The coprecipitation reaction usually occurs under alkaline conditions. When the pH is greater than 7, the concentration of hydroxide ions in the environment is high. During the adsorption of heavy metals by biochar, metal ions combine with hydroxide ions to form a large amount of hydroxide precipitate. This process converts metal ions into more stable forms. Therefore, it is believed that the mechanism of biochar adsorption of heavy metals is based on the precipitation reaction.

4.3. Ion exchange

Ion exchange technology utilizes the acidic oxygen-containing functional groups on the surface of biochar to remove heavy metal ions from soil. Heavy metal ions in soil will replace cations on the surface of biochar and bind with acidic functional groups. Research has shown that as the pyrolysis temperature increases, the adsorption capacity of magnetic biochar for heavy metal ions increases, thereby providing more ion exchange sites.

DOI: 10.54254/2755-2721/2026.KA27121

5. Material optimization

5.1. Biochar surface modification

Biochar has unique physicochemical properties, easy access to raw materials, and environmentally friendly characteristics, which have made it widely used in the field of soil heavy metal pollution. Current research on biochar mainly focuses on enhancing its adsorption capacity, improving preparation techniques, and combining it with other materials to produce biochar composites.

Biochar is used to treat heavy metal pollution in soil, mainly through its adsorption properties. In practical applications, biochar is often modified to improve its adsorption capacity and duration of action. One way is physical modification, which affects the surface properties of materials through ultraviolet irradiation, significantly increasing their specific surface area and surface functional groups. The removal ability of heavy metal ion Cr6+ by treated biochar has increased by 2-5 times compared to unmodified biochar [7]. The use of oxidants to modify biochar or doping P or N into biochar can effectively improve its adsorption capacity. Untreated biochar usually has poor surface structure and limited active sites. Optimizing the performance and structure of biochar can be achieved by doping nitrogen and phosphorus. This method promotes the electrostatic adsorption on the surface of biochar [8]. Modification with oxidants can increase the cation exchange capacity of biochar. Acid modification increases the specific surface area and number of surface functional groups of biochar, and also improves its stability. Modification of reed biochar with 1mol/L HCl solution, the specific surface area of the biochar increased from 58.75 m2/g to 88.35 m2/g [9]. The use of sulfuric acid and phosphoric acid to modify pig bone biochar can increase its microporosity by 263%. The principle of these improvements is that the carbon and oxygen content in biochar changes, and the acidic surface functional groups increase. This changes the hydrogen to carbon ratio and oxygen to carbon ratio of acidic biochar [10]. Modifying biochar with alkaline substances can increase its oxygen-containing functional groups, improve porosity. Experiments have shown that using sodium hydroxide to modify biochar is more effective compared to other alkalis. The adsorption capacity of walnut wood biochar modified with NaOH for heavy metals is increased by 2.6-5.8 times. Using potassium hydroxide to modify straw biochar, the specific surface area increased from 63.29 m2/g to 1358.37 m2/g [11]. The principle is that potassium hydroxide destroys the carbon layer structure of biochar, exposing more active sites and promoting the binding of biochar with heavy metals in the soil.

5.2. Nano biochar

Research on biochar at the nanoscale has made progress. There are differences between nano biochar and raw biochar in various aspects, and nano biochar can more efficiently adsorb heavy metals. Nano biochar is a type of carbon material prepared by ball milling, centrifugation, or ultrasonic degradation methods. Nano biochar can adsorb heavy metals on the surface and reduce the free metal ions in the soil [12].

Ball milling is a commonly used method for preparing nano biochar. Compared with other preparation methods, ball milling has lower equipment costs. By mechanically crushing biochar particles and reducing them to the nanoscale, biochar forms more microporous structures during this process.

The centrifugal method can also be used to prepare nano biochar. Centrifugal technology can quickly separate particles of different sizes, and centrifuge operation is relatively simple and suitable. Select biomass raw materials for pyrolysis under anaerobic conditions to generate bulk

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biochar, mix it with deionized water to form a suspension, and centrifuge at a specific temperature to separate nano biochar particles with a diameter less than 100 nanometers.

Ultrasonic degradation is another method for preparing nano biochar. During the ultrasonic treatment process, ultrasound can open blocked pores, thereby increasing the microporous structure. Long term ultrasonic treatment can separate small fragments adhered to the surface of biochar, thereby producing more nano biochar.

Experimental results show that nano-biochar can adsorb heavy metals like chromium in soil. Its fixation efficiency is higher than that of ordinary biochar. The primary fixation mechanisms are precipitation and ion exchange. Heavy metal ions in soil usually exist in cation form. The unique structure of biochar provides it with numerous active adsorption sites. Additionally, the presence of functional groups like carboxyl and hydroxyl enhances surface polarity and promotes ion exchange. After applying nano-biochar, the soil pH increased. This promotes the formation of insoluble hydroxides and reduces the mobility of heavy metal elements [13]. Experiments show that nano-biochar significantly improves soil moisture retention. It enhances microbial activity and organic carbon transformation. It also improves soil redox conditions. Additionally, it reduces carbon loss and salt accumulation. These effects support the growth of plant seedlings [14].

5.3. Biochar composite material

Biochar composites formed by combining biochar with other materials exhibit excellent adsorption capabilities for heavy metals such as cadmium. The composite material made from biochar and sepiolite (WBC + Sep) effectively adsorbs cadmium and transforms it into a more stable residual form. Compared to individual WBC and Sep, the composite WBC + Sep combines the properties of both materials [15]. It has more pores and functional groups. The method of fixing heavy metals in soil using this composite material mainly includes pore filling and complexation reactions. The composite material prepared by combining biochar with seaweed calcium silicate is highly effective in adsorbing Cd. The adsorption capacity of MB-CA is affected by pH, increasing with higher pH levels, peaking at pH 4. The reduction of Cd content in soil by MB-CA mainly occurs through the combination of anions such as CO2 and Cd to form precipitates, as well as coordination reactions between various functional groups in MB-CA and Cd. The above two composite materials fully demonstrate the excellent performance of composite materials formed by combining biochar with other materials. Biochar composite materials have bright prospects and great development potential.

6. Conclusion

Biochar is a material mainly prepared by the thermal cracking method, which is used for the treatment of heavy metal pollution due to its strong adsorption capacity. To address soil heavy metal pollution, various techniques have been applied. Compared to traditional methods for treating soil heavy metal contamination, biochar is more environmentally friendly and shows significant adsorption effects. The main mechanisms by which biochar adsorbs heavy metals in the soil include complexation, coprecipitation, and ion exchange. Current research focuses on expanding the range of raw materials, modifying biochar, synthesizing biochar composite materials, and reducing the scale of research. These studies aim to enhance biochar's adsorption of heavy metals in soil, prolong its effective time, and alleviate global soil heavy metal pollution issues.

Biochar is well-known for its excellent properties, but research on its negative impacts is relatively scarce. For instance, in high-carbon environments, biochar may be converted into carbon dioxide by soil microorganisms, potentially exacerbating the greenhouse effect. Moreover, most

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current studies focus on short-term laboratory experiments, lacking long-term research on biochar under natural conditions. Additionally, biochar material has some unresolved issues. For example, their effectiveness in soil tends to be short-lived. Once biochar has adsorbed soil heavy metals, it may become unstable. Furthermore, some biochar materials exhibit strong adsorption properties for only specific heavy metal elements, resulting in limited effectiveness. The integration of multifunctional biosensing research has become inevitable.

By addressing these shortcomings, biochar materials will have broader development prospects and better applications in the field of soil.

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