REVIEW

Biochar as a potential soil remediation agent for heavy metals in agriculture

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Abstract: Biochar is one of the most concerned research hotspots at present, which is a stable and carbon-rich solid produced by pyrolysis of organic biomass under anoxic conditions. Biochar has abundant pore structure, functional groups, aromatic hydrocarbons and other characteristics, which enable it to improve soil physical and chemical properties, increase nutrient content, and regulate soil microbial community structure. In recent years, with the continuous research on biochar, the role of biochar in the remediation of heavy metal pollution has been further studied. The physical adsorption, ion exchange, electrostatic attraction, complexation reaction, mineral precipitation, redox and other functions of biochar are the main factors for repairing heavy metal ions. In addition, immobilization is the primary goal of biochar remediation of heavy metals in agricultural soils, because it can greatly reduce the risk of human health caused by heavy metals entering the food chain. This paper reviewed the current knowledge of biochar and its function in agricultural heavy metal soil. Based on the background of heavy metal pollution in agricultural soil in China, the possible remediation mechanism of biochar was discussed. It provides scientific basis for the development and application of biochar in the remediation of heavy metal pollution in agricultural soil in China.
Keywords: Repair agent, passivation fixation, carbon sequestration

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1 Introduction

1.1 Status of Heavy Metal Pollution in Agricultural Soil

With the rapid development of agriculture and rural economy in China, the agricultural ecological environment has been deteriorating, and soil pollution is the most profound problem. Soil pollution refers to any excessive element or compound that produces toxic reactions to biological communities or human beings through direct and indirect contact, resulting in unacceptable environmental risks (Abrahams, 2002; Vangronsveld et al., 2009). According to the latest survey report on soil pollution of agricultural cultivated land in China, the total exceeding rate of soil heavy metal sites in China is 16.1% (Warnock et al., 2007). Agricultural soil pollution in China is mainly manifested in the accumulation of fertilizer elements, a variety of heavy metal pollution, pesticide and organic pollutant residues and so on. Among them, heavy metal pollution is particularly serious, mainly including Cd, Hg, Cr, Pb, Cu, Zn and other heavy metals (Cheng et al., 2016).

1.2 Origin and Concept of Biochar

Biochar is now one of the most attention soil remediation and amendments, which is a carbon-rich solid produced by pyrolysis of organic biomass under anoxic conditions (Figure 1). Biochar originated in the Amazon Basin, once a soil called black soil (Terra preta) (Glaser et al., 2000), at that time, people created 'black soil' by burning wood, carbon residue of pottery making and animal bones. The black carbon in charcoal is an important component of black soil. These charcoals cause soil to be rich in nutrients such as potassium, phosphorus and nitrogen, especially organic matter, which can sustain plant growth for a long time. From 2006 to 2007, Lehmann, a famous scholar, published an article about black carbon in the journal Nature and proposed the concept of biochar (Lehmann, 2007), which he believed it was an effective carbon storage technology and was recognized by many scholars.

2 Characteristics and preparation of biochar

Biochar is a porous, fine particle, high carbon content and stable solid material produced by pyrolysis of various biomass materials at high temperature (Lehmann and Joseph, 2009). Biochar is mainly composed of C, H, O, N moreover its carbon content is very high (about 70%-80%). Its structure is mainly based on alkyl and aromatic structures, supplemented by many complex components. Meanwhile, biochar

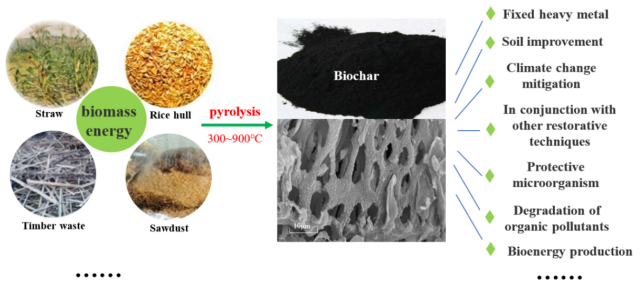

Figure 1. Raw materials and functions of biochar

has rich porosity structure, functional groups and aromatic hydrocarbons (Wu et al., 2017). The main raw materials of biochar are from a wide range of sources, mainly using solid wastes with high organic matter content, such as animal feces, agricultural and forestry wastes, industrial biological wastes, marine and aquatic organisms (Wang et al., 2021). The most common preparation method of biochar is pyrolysis at 300 - 900°C under anaerobic conditions. In the production process, the chemical properties (functional groups, cation exchange capacity and nutrient content), physical properties (pH value, surface area and pore size, etc.) and biological properties of biochar are affected by raw materials, preparation conditions and preparation process (Zhou et al., 2021).

3 Function and Applications of Biochar in Agricultural Soil

3.1 Function of Biochar in Agricultural Soil

Biochar can improve soil physical and chemical properties, increase nutrient contents, regulate the transformation of carbon and nitrogen, thereby reducing soil greenhouse gas emissions, carbon sequestration and emission reduction (Lehmann et al., 2006; Laird et al., 2010). In recent years, with the continuous research on biochar, its function is no longer limited to soil quality improvement. Biochar has also been proved to be able to inactivate inorganic pollutants, organic pollutants, heavy metal ions such as Pb^{2+}, Cu^{2+} and Hg^{2+} in soil to achieve the purpose of remediation of soil pollution (Lima et al., 2020; Chen et al., 2008).

The porous structure of biochar can provide living space and protection sites for soil microorganisms and improve their viability. The carbon source and phosphorus source of biochar are necessary elements for microbial growth and reproduction, which greatly promotes the activity and total amount of microorganisms (El-Bassi et al., 2021). At the same time, biochar can promote plant growth and yield by improving soil properties and nutrient fertility (Agegnehu et al., 2016). However, the characteristics of biochars prepared from different raw materials are quite different. For example, the pore structure of wood biochars (rice husk, straw, etc.) is better than that of organic biochars (sludge, pig manure, etc.). In addition, there are differences in microbial affinity of biochar. Previous studies have found that biochar application has a positive effect on common mycorrhizal fungi such as arbuscular and excisioncorrhizal (Wang and Wang, 2019). However, when the application amount of biochar is high, the abundance of microorganisms will be reduced due to the characteristics of biochar and soil environment. Excessive biochar (application rate $>$ 20% v/v, in green roof) will also make the soil temperature too high and increase the water loss (Chen et al., 2018). In addition, with the increase of time and the change of environment, biochar still has the possibility of decomposition, and its adsorption and soil nutrient regulation functions will also be reduced.

3.2 Application of Biochar in Agricultural Heavy Metal Contaminated Soil

When using biochar, the most direct way is to use biochar alone, using its own characteristics to repair. However, with the deepening of research, biochar has been found to have excellent affinity and plasticity (be improved), which can be combined with physical, chemical, biological and other technologies for targeted soil remediation and protection. For example, common physical modification methods include gas activation, ball milling, etc. (Sewu et al., 2019; Zhang et al., 2019). The intrinsic structure and physicochemical properties of biochar can also be improved by acid, alkali treatment and oxidation modification, so as to improve its adsorption capacity (Goswami et al., 2016; Jin et al., 2018). Biochar can also be combined with biotechnology to immobilize heavy metals by improving microbial functions related to heavy metals (Chen et al., 2019).

4 Mechanism of Biochar in Remediation of Heavy Metals

In recent years, biochar remediation of soil heavy metal pollution has been increasingly studied. Existing studies have confirmed that biochar can repair a variety of heavy metals common in agriculture (Table 1). Heavy metal ions are widespread and unstable in agricultural soil environment. They are easy to enter the human body through the accumulation of food chain, thus endangering human health. The essence of biochar remediation of soil heavy metal pollution is to adsorb it on biochar. However, there are many different adsorption mechanisms in the adsorption behavior. The adsorption stability of different adsorption mechanisms for heavy metals determines the safety of biochar after heavy metal remediation in agriculture. Therefore, it is particularly important to explore and enrich the adsorption mechanism of biochar for heavy metals (Figure 2). The mechanism of heavy metal remediation by biochar mainly includes the following aspects:

Table 1. The adsorption effects of various biochar on different heavy metals

Biochar raw materials	Pyrolysis temperature	Heavy metal species	Adsorption quantity/(mg • g^{-1})	Reference
spartina alterniflora	400°C	Cu(II)	48.49	Li et al., 2013
cattle manure	200°C	Pb(II)	132.8	Cao et al., 2009
pineapple peels	750°C	Cr(VI)	7.44	Wang et al., 2016
peanut vine	400°C	Cd(II)	89.6	Tong et al., 2011
flax shive	200°C	Zn(II)	32.5	El-Shafey et al., 2002
bagasse	400°C	Hg(II)	188.68	Krishnan and Anirudhan, 2002

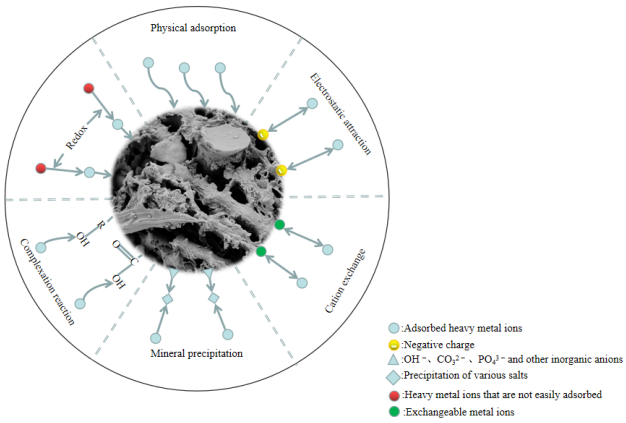

Figure 2. Schematic diagram of adsorption mechanism of biochar for heavy metals

4.1 Physical adsorption

Physical adsorption is mainly caused by van der Waals force between biochar surface and heavy metal ions. There are mainly two ways: one is adsorbed on the surface of biochar, and the other is diffused into the pores of biochar. The capacity of these two physical adsorption methods depends on the specific surface area of biochar and the number of aperture gap. Due to the weak strength of van der Waals force, the adsorption stability of physical adsorption is also poor, which is a reversible process (Qiu et al., 2021). Especially when the environment changes dramatically (such as, acid rain, alternation of dry and wet, surface aging of biochar, etc.), the heavy metals adsorbed by biochar are easy to decompose into the environment, resulting in secondary pollution (Shen et al., 2018).

4.2 Cation exchange

The adsorption mechanism of cation exchange is that some exchangeable metal elements are attached to the biochar matrix in the form of cations. When the initial concentration of contaminated heavy metal ions is high, they will exchange with metal cations. For example, sludge biochar has a good adsorption effect on Cr^{3+}, mainly because of the ion exchange between Cr^{3+} and Ca^{2+} and Mg^{2+} in biochar (Chen et al., 2015). The adsorption rate of this method is fast, and the maximum adsorption is obviously affected by pH (Zhou et al., 2017).

4.3 Electrostatic attraction

There are a lot of negative charges on the surface of biochar. When it adsorbs heavy metals, biochar will generate electrostatic attraction with positively charged heavy metal ions, so as to adsorb heavy metals (Uchimiya et al., 2012). The ability of electrostatic attraction is related to the pH value of the solution, the ionic strength and the number of charges carried (Dong et al., 2011; Wang et al., 2020).

4.4 Complexation reaction

Many oxygen-containing functional groups such as hydroxyl and carboxyl groups are produced on the surface of biochar during high temperature pyrolysis. These oxygen-containing functional groups can be used as an adsorption site of heavy metal ions in the process of biochar adsorption of heavy metals, form a polyatomic structure with specific metal ligand interaction, and form a more stable complex (Inyang et al., 2016).

4.5 Mineral precipitation

There are soluble salts such as $CaCO_3$ and $Ca_3(PO_4)_2$ in biochar, as well as OH^- , $CO_3{}^{2-}$ and $PO_4{}^{3-}$ and other inorganic anions. Some heavy metals will promote their release when they come into contact with biochar (Khan et al., 2021), under appropriate pH conditions, it will combine with heavy metal ions to form precipitation of various phosphates, carbonates and metal hydroxides (Qiu et al., 2021).

4.6 Redox

Biochar has the characteristics of oxidation or reduction, which can affect the adsorption mechanism and chemical behavior of variable valence heavy metals by changing the valence state of metal elements. For example, Cr^{6+} can be adsorbed to the surface of biochar by electrostatic interaction, but this adsorption is not stable. However, Cr^{6+} is reduced to Cr^{3+} by elemental carbon on the surface of biochar or H^+ in solution. The complex formed by Cr^{3+} and functional groups on the surface of biochar is obviously more stable than physical adsorption (Hsu et al., 2009).

5 Conclusion

As a new material, biochar has excellent plasticity and affinity, and has rich pore structure, functional groups, nutrients and mineral elements. Most of the raw materials of biochar come from agricultural solid waste, which not only greatly reduces the difficulty and cost of obtaining raw materials, but also provides a new way for the resource utilization of agricultural solid waste. The above characteristics of biochar determine that it has a very broad prospect and market in the remediation of soil heavy metal pollution. In the future, it may become a research hotspot to explore the joint heavy metals repair mechanism, improve the repair efficiency, and develop biochar with better performance. At the same time, exploring the application defects and limitations of biochar is also conducive to the practical application of biochar in agricultural restoration engineering.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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