Characteristics of biochar and its role in the remediation of heavy metals in soil

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Abstract. With the increasing threat of soil heavy metal pollution to the quality of agricultural products and human health, biochar has been widely studied as a substance that can effectively adsorb heavy metals. This study reviewed the preparation of biochar as well as its types and properties and discussed the role and potential risks of biochar in the remediation of heavy metals in soil. Heavy metal pollution in the soil mainly comes from industrial pollution discharge, good drainage, the usage of chemical fertilizers, pesticides and other illegal applications, and it has great influence on plants, human health and soil environment. Biochar can not only adsorb heavy metals in the soil effectively, but also keep the soil fertile and improve crop yields. In addition, different properties of biochar are controlled by different raw materials and production conditions, such as pH, specific surface area and cation exchange capacity. These properties also determine their different interaction mechanisms. The direct effects mainly include complexation, reduction, ion exchange, electrostatic attraction and precipitation, while the brief effects affect the mobility and bioavailability of heavy metals in soil. The risk of biochar application that provides the basis for the production and utilization of biochar in the future was also discussed in the end.

1. Introduction

According to the data from the 2014 China Soil Pollution Survey, 16.1\% of soil contaminated sites exceeded the permitted limits of the second-level soil environmental quality standard, 82.8\% of which were polluted by heavy metals [1]. Soil heavy metal pollution and its management is a challenging problem facing the whole world. This is due in part to volcanic activity or weathering of the parent material, which may lead to high levels of heavy metals in some soils themselves [2]. Furthermore, large amounts of heavy metals (HMs) have been released into the environment due to human activities, such as mining, grinding, smelting, wastewater irrigation and sludge application [3-6].

Heavy metals in soil are non-biodegradable and are remnant in the environment. A large number of heavy metals will not only affect soil fertility and crop yield, but also affect human health [6-7]. In order to reduce soil contamination, people have adopted a series of physical remediation (e.g., guest land methods, thermal desorption technology, vitrification technology), chemical remediation (e.g., elution methods, immobilization and electrokinetic methods) and methods of bioremediation (e.g., microorganisms and plants to fix the soil) [8-9]. However, these traditional repair technologies are limited by poor feasibility, high cost, low efficiency and high secondary risk. One of the most effective remediation methods is in situ remediation of soil contaminated by heavy metals [10]. The commonly used soil additives are lime, \cite{11}, phosphate materials \cite{8}, red mud \cite{12-13}, bentonite \cite{13}, zeolite \cite{14} and biochar \cite{15}, among which biochar is a new soil modifier that has attracted extensive attention of researchers in recent years \cite{16-17}.
Biochar is a porous and carbon-rich material with abundant functional groups and large specific surface area. Many researchers have reported significant reductions in heavy metals in soils treated with biochar [17]. In addition, the researchers found that the biochar also promoted seed germination and plant growth in the contaminated soil [18-19]. Moreover, the production and preparation of biochar is considered as a management method for the disposal of large amounts of organic waste [20-22]. However, biochar applications do not always yield encouraging results [23]. It also has some potential risks to soil to a greater or lesser extent [24-25]. To provide a thorough analysis of biochar, this study reviewed and discussed 1) types of biochar; 2) properties of biochar; 3) preparation of biochar; and 4) the role and potential risks of biochar in the remediation of heavy metals.

2. Heavy Metals in Soil

2.1. Main types and sources

Heavy metals refer to about 60 elements with a density of 4.0 or 45 elements with a density of 5.0. The heavy metals that have serious effects on soil mainly include Hg, Pb, Cd, Cr, As, Zn, Cu, Ni and other elements, among which Hg, Cd, Pb, Cr, As and other elements have significant biotoxicity [26]. There are two main sources of heavy metal pollution in cultivated land: natural factors (soil parent material), and human industrial and agricultural activities [27-29]. Heavy metal elements in the parent material are relatively stable and not easy to be absorbed by plants, while heavy metal elements caused by human activities generally have high level of activity and are easy to be absorbed and accumulated by plants. With the development of economy and society, the contribution of human activities has exceeded that of natural sources.

2.1.1. Atmospheric deposition

Heavy metals discharged from industrial production could enter farmland through waste water, rainwater and atmospheric sedimentation, which are the main sources of heavy metals in the soil of agricultural products. With the process of urbanization, a large number of factories and township enterprises are gradually moving to the suburbs and rural areas. Due to the ignorance of environmental protection, excessive heavy metals are discharged in the soil of agricultural production areas and leads to pollution. For example, the input amount of cadmium, arsenic, mercury and other elements in farmland soil of Beijing accounts for more than 50% of the total [30-34]. Approximately, 86% of cadmium pollution in the farmland soil of Chengdu Economic zone in China, is affected by dry and wet atmospheric deposition [33].

2.1.2. Sewage irrigation

Sewage irrigation generally refers to the use of certain treatment of urban sewage to irrigation fields, forests and grasslands. Although the use of sewage to irrigate farmland effectively alleviates the problem of water shortage in China, urban sewage containing industrial wastewater leads to serious excessive levels of cadmium, mercury, copper and other heavy metals in the soil of irrigated farmland [35]. Such pollution irrigated areas are most common in arid areas in the west and north of China. For instance, the content of heavy metals Pb, Cd and Cr in Taiyuan sewage irrigated areas far exceeds their local background values, and the accumulation amount increases year by year [36].

2.1.3. Pesticide and chemical fertilizer large-scale application

Pesticides, fertilizers, plastic films and other agricultural supplies have a great promotion effect on the development of agriculture. However, some pesticides contain heavy metals such as mercury, arsenic, cadmium and lead, long-term abuse and unreasonable application of pesticides will aggravate the content of heavy metals in the soil. In addition, the application of phosphate fertilizer is the second largest source of high levels of heavy metals in the soil. Due to the natural cadmium associated with the production of raw phosphate ores, less than 20% of the cadmium can be absorbed by plants, and the rest would accumulate in the soil [32]. The stabilizers used in the production of agricultural plastic film are
rich in lead and cadmium, and their large-scale use is also a major source of soil heavy metal pollution [39].

2.1.4. Waste piling and dumping
Heavy metals in solid wastes are easy to migrate to the surrounding soil and water bodies, and the scope of pollution is generally centered on waste dumps. In Zhejiang, Guangdong and other major e-waste disposal areas, farmland, in general, is seriously polluted, and the main pollutants include Cd, Cr, Cu, Ni, Pb, Zn [37]. A study of the soil near the waste dump in Wuhan and the chromium residue dump area in Hangzhou found that Cd, Hg, Cr in the soil in these areas were all higher than the local soil background values, and their contents decreased with the increase of distance [38].

2.2. Effects of heavy metals on soil
Table 1 shows the effects of common heavy metal pollutants on plants, human health and soil environment. Although moderate amounts of heavy metals can effectively promote plant growth, excessive amounts of heavy metals cause serious harm to plants, humans and soil environment.

2.2.1. Effect on crop growth
When crops are poisoned by heavy metals, plant height, leaf length, tiller number and other internal factors such as photosynthetic rate all have a certain influence, leading to the growth and development of crops and yield decrease. When the metal chromium content is high, the germination and early growth of maize seeds are significantly inhibited, and high copper content will cause the tillering of rice decreases, and the yield also decreases significantly [33].

2.2.2. Effect on human body
Compared with crops, soil contaminated by heavy metals has indirect toxicity to human body. Heavy metals pass through the food chain and accumulate in large quantities in the body. Due to the similar physiological properties of cadmium and calcium, cadmium will affect the human skeletal system after entering the human body, which is known as "Itai-Itai disease" [40]. In addition, the world - shocked Minamata disease in Japan is also caused by a large number of mercury poisoning.

2.2.3. Effect on the soil environment
Heavy metal pollution in farmland has strong invisibility. Heavy metals stay in soil for a long time, and their toxicity is also accumulating, forming complex chemical effects. In addition, the increase of heavy metal content will also have an impact on the types of microorganisms, resulting in a decrease in the number of microorganisms and a decrease in the enzyme availability of microorganisms. This further reduces soil fertility and poses a serious threat to the sustainable development of ecological environment.

| Heavy metal | Plants | Human body | Soil environment |
|-------------|--------|------------|-----------------|
| Pb          | Pb affects the quality and yield of crops. High concentration of Pb will lead to the shrinkage, slow growth and decline in yield. | Highly toxic, affects the urinary system, and can lead to death in severe cases | The biomass and enzyme activity of soil microorganisms were reduced |
| Cd          | Cd will remain in the plant, causing the leaves to turn yellow and the plant tissue to die and wilt | Extremely toxic, 20 minutes after poisoning can cause nausea, vomiting, diarrhea and other symptoms. | Inhibit the metabolic function of soil microorganisms and reduce microbial activity |
Cr  Excessive chromium can cause the root system to become shorter, leading to stunting.

Hg  Mercury can reduce chlorophyll content and cause leaves and stems to turn brown or black.

As  A small amount of As can boost crop production, but too much of it stunts plant growth, causing leaves to curl up or wither and hindering root growth.

Cu  Excess copper inhibits crop growth by inhibiting the absorption of nutrients.

Zn  Too much Zn will damage the root system of the plant, inhibiting root growth and causing plant dwarfism.

3. Biochar

3.1. Characteristics of biochar
Biochar has the characteristics of large surface area and porous porosity. Different pore sizes can not only promote the growth of soil microorganisms but also absorb soil pollutants. The larger specific surface area also enables the biochar to have abundant functional groups on its surface, in which the oxygen-containing functional groups make the biochar surface negatively charged, thus having strong electronegativity and strong ability to exchange metal cation and electrostatic adsorption [41-44]. Biochar has a pH of 6.0 to 12.0 and can be used as a modifier for acidic soils. The functional groups and ash composition on the biochar surface are the key reason for its alkaline nature [45].

3.2. Controlling factors of biochar characteristics
Biochar is a carbonized product of organic matter. Previous studies (as illustrated in Table 2) show that biochar can be simply divided into plant-derived biochar (e.g., Wheat straw), animal-derived biochar (e.g., cow manure, chicken manure) and sludgy-derived biochar (e.g., municipal sludge) according to the sources of organic matter [46]. The different feedstocks of biochar lead to various characteristics such as surface area, pH value, ash content, cation exchange capacity, which affects the ability of biochar to adsorb heavy metals. Plant-derived biochar generally has a high carbon content and a developed pore structure with a large specific surface area. Meanwhile, animal biochar and sludge biochar have a higher proportion of ash content, which leads to higher cation exchange capacity (CEC) [47]. In addition to the feedstocks, the pyrolysis temperature is another major factor affecting the properties of biochar [48-51].

Table 2. Characteristics of common biochar

| Biochar feedstock | Pyrolysis Temperature(°C) | Biochar PH | Absorbed Heavy metals |
|-------------------|---------------------------|------------|-----------------------|
| Wheat straw       | 350-500                   | 10.4       | Cd, Pb                |
4. Application of biochar in soil remediation

Different production raw materials and different pyrolysis conditions in the production process can cause different characteristics of biochar (such as cationic exchange capacity (CEC), active functional group). These characteristics can influence the mobility and bioavailability of heavy metals in soil through direct and indirect effects [52].

4.1. The direct effect of biochar on soil fixation of heavy metals

Biochar can fix heavy metal substances in soil through physical adsorption, electrostatic adsorption, ion exchange, complexation, precipitation and redox (Figure 1, Table 3). The physical adsorption is affected by specific surface area and porosity, and the larger specific surface area and porosity are conducive to the physical adsorption of heavy metals by biochar. The electrostatic adsorption of biochar to heavy metals depends on the pH of the environment and the zero-charge point (pHPZC) of biochar. The increase of pH value can increase the adsorption of heavy metals by biochar, and the electrostatic adsorption will also be enhanced with the increase of initial concentration of heavy metals [53-54]. Ion exchange depends on the electronegativity of the biochar surface. Strong electronegativity can lead to a high CEC and release cations such as Ca$^{2+}$ and Mg$^{2+}$, so that it can exchange with heavy metal ions on the biochar surface [55]. Complexation depends on the types of functional groups in biochar, such as $\text{--OH}$ and $\text{--CO}$, which provide binding sites for HMs to form the binding compound, thereby increasing the specific adsorption of the metal. Precipitation depends on the specific minerals contained in different biochar, which may form metal oxides such as Pb, Cd, Cu, and chloride and sulfate deposits. The redox reaction also depends on the types of functional groups in biochar. Biochar contains a variety of functional groups such as quinones and phenolic hydroxyl groups, which enable it to store and transfer electrons. It can oxidize As (III) or reduce Cr (VI), thus effectively fixing heavy metals [56].

| Material                | Original Concentration (mg/kg) | Metal(s)       |
|-------------------------|-------------------------------|----------------|
| Soybean stover          | 700                           | Pb             |
| Cassava stem            | 350                           | Cd, Zn         |
| Peanut, rice, canola    | 400                           | Pb             |
| Rice hull               | 500                           | Cd, Cu, Pb, Zn |
| Sludge                  | 400                           | Cd, Zn         |
| Woody biomass           | 900                           | Ni, Cr, Mn     |
| Chicken manure          | 500                           | Cu             |

Figure 1. The direct effect of biochar on soil fixation of heavy metals
Table 3. Reaction type, mechanism and application of direct interaction between biochar and heavy metals

| Reaction type       | Mechanism                                                                 | Application                                                                 | References |
|---------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------|------------|
| Physical adsorption | The heavy metals are adsorbed on the surface or diffused into the pores  | Rice straw biochar has better adsorption capacity for Cd and Ni at 700 °C. | [57]       |
| Electrostatic adsorption | The biochar surface charge adsorbs and immobilizes heavy metals by electrostatic interaction. | The removal rate of Cr (IV) was higher for HCL-BC with larger surface area and lower surface negative charge | [58]       |
| Ion exchange        | The surface salt ions of biochar can be replaced with heavy metal ions to fix heavy metals. | Ion exchange is dominant in animal-derived biochar fixation Cd and Cu.       | [59]       |
| Complexation        | Biochar surface functional groups provide heavy metal binding sites to form complexes that immobilize heavy metals. | The sulfhydryl modified rice straw biochar can be prepared by using sulfhydryl ethanol through catalytic esterification, and its adsorption capacity to Cd is increased by 3 times (45.13 mg/g). | [60-61]    |
| Precipitation       | The mineral components in biochar ash can precipitate with heavy metals to fix heavy metals. | C2O42- and CO32- in rice straw biochar can form PbC2O4 and Pb3(CO3)2(OH)2 precipitation with Pb, which is the main mechanism of fixing Pb. | [62-63]    |
| Redox               | The gain and loss of electrons between biochar and heavy metals changes the valence of heavy metals and reduces the toxicity and mobility of heavy metals | The phenolic hydroxyl of biochar can act as electron donor for Cr (VI), which will be oxidized to quinone group and complexed with adsorbed Cr (VI) | [64]       |

4.2. The indirect effect of biochar on fixation of heavy metals in soil

4.2.1. Effects of biochar on soil pH
Since most biochar is alkaline, the soil pH increases with the application of biochar. This enhances the hydrolysis of heavy metals in the soil, and then improves the adsorption of heavy metals and accelerates the transformation of heavy metals to oxidizable and residual states [65]. In addition, the increase of pH also enhances the complexation of heavy metals, and then reduces the desorption of heavy metals in the soil.

4.2.2. Effects of biochar on soil cationic exchange capacity
Abundant cation exchange sites on the surface of biochar also increase the soil cationic exchange capacity (CEC) with the massive application of biochar, thus significantly reducing the concentration of soluble and transportable heavy metals in the soil [66]. Ma showed that the CEC of the soil was effectively increased after biochar was applied, thus increasing the adsorption amount of Cu and Pb in the soil.
4.2.3. Effects of biochar on soil mineral composition
Biochar also has a large number of minerals on its surface, which are released into the soil as biochar is applied. These released minerals may form mineral facies on the surface of biochar and adsorb heavy metals from the soil [67]. Bian used laser etching technology to analyze the restored biochar and found that Cu and Pb in the biochar increased significantly while K, Mg and P decreased significantly; this indicates that biochar may enhance its fixation of heavy metals by releasing minerals into the soil.

4.2.4. Effects of biochar on soil organic carbon content
Biochar can release dissolved organic matter in the soil, thus increasing organic matter amount and reducing the mobility and bioavailability of heavy metals [68]. For example, with the increase of soil organic matter, Pb in the soil would change from an unstable state to a relatively stable organic binding state, which reduces the uptake of Pb by plants.

5. Conclusion
Undeniably, Biochar plays an essential role in remediation of heavy metal pollution in soil. This study aimed to create a comprehensive picture of biochar by providing analysis of types and properties of biochar and its preparation and illustrating the role and potential risks of biochar in the remediation of heavy metals in soil. Overall, summary of findings are as follows.

First, we observe that soil heavy metal pollution and its treatment is a challenging problem facing the world today. Moreover, most of the rest of the mainly from the pollution discharge, sewage irrigation, atmospheric sedimentation, as well as the application of sludge, pesticides, fertilizers, agricultural film, and other farmland applications.

Also, according to previous study findings, heavy metals in the soil also have a certain impact on plants, human health and the soil environment. Different degrees and types of heavy metals can lead to vegetation growth inhibition and even death. For human health, the mild may cause poisoning, diarrhea and other symptoms, and in severe cases may endanger human life. In addition, heavy metals inhibit the activity of microorganisms in the soil.

Furthermore, we explore biochar, a porous carbon-rich material with rich functional groups and large specific surface area. Studies have shown that biochar can effectively adsorb heavy metals in soil. In addition, it can also effectively enhance soil fertility and promote the crops growth. According to different production materials, biochar can be divided into plant biochar, animal biochar and sludge biochar. Due to different raw materials and different pyrolysis conditions in the production process, the pH, specific surface area, CEC and active functional groups of biochar differ. These differences also determine the interaction mechanism between biochar and heavy metals. Their main interactions include physical adsorption, electrostatic adsorption, ion exchange, complexation, precipitation and redox. The larger the specific surface area leads to the stronger CEC, causing the stronger the adsorption of heavy metals. In addition, biochar also introduces soil remediation by influencing the mobility and bioavailability of heavy metals. Overall, although biochar plays an active role in remediation of soil heavy metal pollution, it can affect the ecological environment and human health in the production and application process.

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