

The Research Progress of Biochar for Heavy Metal Soil Remediation was Briefly Discussed

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Abstract

Due to its structural advantages, biochar has developed pore structure, large porosity, surface potential energy, and more oxygen and nitrogen functional groups on the surface, which can adsorb and solidified heavy metals and organic pollutants in contaminated soil to achieve the purpose of repairing contaminated soil. At the same time, adding an appropriate amount of biochar to the soil can also enhance soil nutrition and improve water retention performance, and promote the good development of microbial systems. At present, it has become a research hotspot of contaminated soil remediation. In this paper, the preparation technology of biochar, the remediation mechanism of biochar and heavy metal pollutants, as well as the development prospect and precautions are described, in order to provide theoretical reference for the study of biochar in soil remediation.

Keywords

Biochar Heavy; Metal; Soil Remediation.

1. Preface

China is a big country in industry, agriculture and manufacturing. With the development of modern industry and mineral resources, single or mixed pollution of heavy metals and organic matter in soil has become a major environmental problem. On April 17, 2014, the Ministry of Land and Resources (now the Ministry of Natural Resources) and the Ministry of Environmental Protection (now the Ministry of Ecological Environment) jointly issued the "National soil Pollution Survey Communiqué", which found that the quality of China's soil environment is worrying, including inorganic pollutants as the main type of soil pollution, accounting for about 82.8% of the soil pollution exceeded the standard area. Soil inorganic pollutants are not easy to detect, slow but harmful, and can continue to accumulate in the soil, through the direct or indirect contact of human activities to human life brings irreversible impact, and ultimately directly damage human health and human development.

Biochar material is a high carbon porous refractory aromatic material formed by pyrolysis and retorting of biological raw materials under certain controlled conditions. In recent years, biochar not only has stable chemical properties, but also has developed pore structure, large porosity, surface potential energy, and more oxygen and nitrogen functional groups on the surface, which can adsorb and solidified heavy metals and organic pollutants in contaminated soil to achieve the purpose of repairing contaminated soil. At the same time, adding an

appropriate amount of biochar to the soil can also enhance soil nutrition and improve water retention performance, promote the good development of microbial systems, thereby solidifying soil pollutants, reducing the absorption of heavy metals in crops, and increasing crop yield. Therefore, biochar has great development prospects in soil pollution remediation, water purification and air pollution. At the same time, with the rapid development of agriculture, forestry and animal husbandry in China, a large amount of crop straw, livestock manure and agricultural residue will be produced every year, which provides a steady stream of raw materials for the preparation of biochar.

2. Preparation of Biochar

2.1. Preparation Method

Biochar is a regenerative material made from porous carbon which is rich in oxygen and nitrogen functional groups by thermochemical treatment of biomass raw materials. According to different treatment methods, the preparation of biochar can be divided into thermal cracking method, hydrothermal carbonization method, chemical treatment method and gasification treatment method, among which thermal cracking method is the most commonly used preparation method for industrial production and laboratory preparation of biochar. Thermal cracking method is to dehydrate, decarboxylate, polymerize and isomerize carbon-containing raw materials to obtain highly aromatic stable porous carbonized materials by controlling certain conditions (temperature rise rate, holding time, oxygen content, temperature, etc.) from treated or untreated carbon-containing raw materials. In the process of pyrolysis, about 1/3 of the raw materials for the preparation of biochar are carbonized into carbon structural materials, 1/3 into crude oil products, and the remaining 1/3 into gaseous substances that can support combustion.

2.2. Preparation of Raw Materials

The raw materials for the preparation of biochar are simple and widely sourced. As long as the biomass contains high cellulose, it is the natural raw material for the preparation of biochar, such as all kinds of wood, crop straw, domestic waste, sludge and feces, etc., are the raw materials for the preparation of biochar. The physical and chemical properties of biochar are relatively stable, mainly manifested as good thermal stability, stable physical and chemical stability and biological inertness. This is mainly because biochar has highly aromatic carbon elements, and carbon atoms are closed to each other, and there is a stable carbon chain structure. In addition to a stable carbon structure, biochar also contains a variety of inorganic carbonates, minerals and ash, of which carbon accounts for more than 80% of the total content in biochar, and also includes inorganic elements such as oxygen, nitrogen, hydrogen, phosphorus and metal elements such as magnesium, potassium, calcium.

2.3. Pyrolysis Temperature

The yield of biochar is directly related to the product and pyrolysis temperature. All biochar are alkaline substances, and with the increasing pyrolysis temperature, the pH value of the prepared biochar also shows a rising trend, mainly because there is a large amount of carbonate in biochar, and the carbonate becomes alkaline after hydrolysis. With the increase of pyrolysis temperature, the organic acid in the raw material is gradually converted into ash, and the content of carbonate generated by the reaction gradually increases. As a result, the pH value of biochar increases with the pyrolysis temperature. With the increase of pyrolysis temperature, the pore number of biochar gradually increased, the pore structure of biochar gradually matured with the increase of temperature, and the internal micropores also developed more complete. Secondly, with the increase of cracking temperature, many elements such as oxygen, hydrogen and nitrogen in the raw material are consumed and volatilized, and the amount of

carbon gradually accumulates, resulting in the decrease of oxygen-carbon ratio, hydrogen-carbon ratio, oxygen-nitrogen and carbon ratio. With the increase of cracking temperature, organic matter such as alkane group, methyl group (-CH₃) and methylene group (-CH₂-) gradually disappear, and the increase of aromatic components leads to the decrease of hydrophilicity.

The ash content of pyrolysis products also increases with the increase of pyrolysis temperature, and the volatile components of raw materials gradually decrease during pyrolysis. Studies have shown that the pyrolysis reaction of biochar raw materials is mainly hemicellulose in the range of 200~260 °C, mainly cellulose in the range of 270~350 °C, and mainly lignin in the range of 280~500 K. With the increase of pyrolysis temperature, the yield of biochar decreased gradually, and when the pyrolysis temperature further increased, the carbon yield basically stabilized.

2.4. Heating Rate

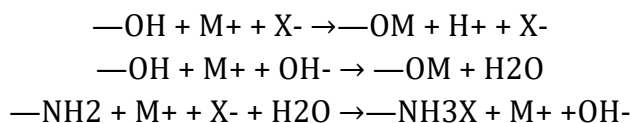
The preparation of biochar can be divided into slow pyrolysis and fast pyrolysis according to the heating rate of pyrolysis and the holding time. Studies have shown that low pyrolysis temperature (<400 °C), slow pyrolysis and prolonged holding time can promote the development of biomass particle size for preparing biochar. In contrast, slow pyrolysis is conducive to the retention of functional groups containing oxygen and nitrogen, which is conducive to the full development of biochar and increase the production of charcoal in biochar, and fast pyrolysis is conducive to the output of biochar oily substances.

3. Mechanism of Biochar Remediation of Heavy Metal Contaminated Soil

Biochar has been widely used in heavy metal pollution, organic pollution and water pollution in urban polluted soil, but the mechanism of biochar on soil remediation is complicated and not fully understood. At present, the known mechanism involves ion exchange, cationic π interaction, surface complexation precipitation, electrostatic interaction and so on.

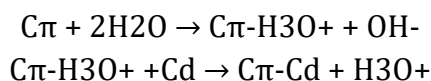
3.1. Ion Exchange

There Are A Large Number Of Oxygen-nitrogen-containing functional groups attached to the surface of biochar, such as carboxyl group (-COOH), amino group (-NH₂) and other basic groups can adsorb metal cations or anions through ion exchange, the specific reaction is as follows:



3.2. Cationic π Action

The complex electrostatic interaction between metal cations and aromatic substances in biochar leads to the mutual adsorption of heavy metal cations and biochar. The cationic π action of biochar in different systems is also different. Studies have shown that the higher the arylation degree of groups in biochar, the more frequent the conjugation of cationic π with aromatic structure, the more easily the negative charge functional group on the π orbital changes, the more easily the functional group loses electrons, and the stronger the electrostatic interaction with heavy metal cations. Specific reactions are as follows:



3.3. Complexation with Oxygen-containing Functional Groups

The surface of biochar is rich in carboxyl, hydroxyl, amino and other oxygen-containing functional groups, which can adsorb heavy metal cations by complexation. As the pyrolysis

temperature of biochar increased, the carbonization level of biochar increased, the ratio of oxygen-carbon, hydrogen-carbon and oxygen-nitrogen to carbon gradually decreased, and the hydroxyl, carboxyl and amino groups on the oxygen-containing functional groups underwent dehydrogenation and deoxygenation reactions, and the hydroxyl, carboxyl and amino groups gradually disappeared. The electrostatic reaction between heavy metal ions and biochar is also gradually reduced. Studies have shown that the adsorption rate of biochar and heavy metal cation decreases with the increase of pyrolysis temperature of biochar, and the biochar prepared by low temperature pyrolysis can effectively complex with heavy metal cation because the surface contains more oxygen functional groups.

3.4. Precipitation

Biochar can promote the hydrolysis of heavy metal cations to produce metal hydroxide, and biochar can further form carbonate or phosphate precipitation with metal cations, so as to achieve the purpose of solidifying heavy metal cations. Studies have shown that biochar can induce lead ions to produce lead phosphate or lead carbonate precipitation, and this precipitation reaction accounts for about 85% of the adsorption. The higher the phosphorus content in biochar, the more it can promote the production of phosphate mineral precipitation. Pb ion is mainly precipitated in the form of lead-chlorophosphate, and Cd ion precipitates with biochar biochar to produce carbonate precipitation and phosphate precipitation.

3.5. Electrostatic Action

There are a large number of negatively charged functional groups attached to the surface of biochar (with cation exchange capacity), which can promote the electrostatic interaction of heavy metal cations, and the adsorption strength of metal cations depends on the variable charge amount of surface functional groups. Some experts and scholars have shown that the higher the pH value of biochar, the more negative charge carried by the surface functional group, and the stronger the adsorption of heavy metal cations. The higher the cation exchange capacity (CEC) of biochar, the stronger the electrostatic interaction with metal cations.

4. Development Prospects and Precautions

Biochar can be widely used in heavy metal and organic pollution of soil and water, and is an effective green remediation material. However, the research on biochar remediation still has the following problems:

(1) The process of biochar remediation of soil heavy metal pollution is complicated, and different types and contents of biochar should be selected for remediation and treatment according to different heavy metal pollution. Secondly, biochar will migrate and transform after entering polluted soil, accompanied by rainwater loss. Therefore, the amount, frequency and influence of biochar addition on soil microbial population need further study.

(2) At present, studies on biochar remediation of heavy metals in soiled soil are limited to laboratory pot experiments or short-term field trials, and no long-term field observation and effect evaluation studies have been conducted;

(3) Biochar remediation of heavy metals in contaminated soil is restricted by many factors. According to the type and pollution degree of heavy metal pollutants, it is necessary to select different types of biochar and control the addition amount. Therefore, it is necessary to establish a set of remediation technology and treatment system for heavy metal pollution in contaminated soil.

(4) Biochar itself may carry some toxic and harmful substances, and when added to the soil, it will affect the local material structure, nutrient transmission system and microbial population distribution in the soil. At present, the state has not formed relevant standards for the remediation of soil heavy metal pollution by biochar, and there is no requirement on the

amount and type of biochar added. After that, it is necessary to establish a regulatory framework for biochar remediation of heavy metal pollution in soil, ensure the safety and standardization of the use of biochar, and ensure food health and human physical and mental health.

(5) The research on biochar modified materials is also the current research direction, such as improving the porosity of biochar, increasing the specific surface area, adding specific functional groups in biochar, and improving the utilization rate of biochar.

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