Preparation of biomass charcoal and its application in soil remediation

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Abstract. Biochar is a carbon-rich, highly stabilized substance has received widespread attention in the field of soil remediation. This paper discusses the preparation method of biochar and its application in soil remediation. The preparation process of biochar includes carbonization and activation, and its physicochemical properties mainly depend on the preparation conditions and the type of raw materials. Biochar can significantly improve the physical and chemical properties of soil, increase its water retention capacity and nutrient supply capacity, and reduce its bioeffectiveness by adsorbing organic pollutants and heavy metals. By applying biochar to the soil, the fertility of the soil can be effectively enhanced and crop growth can be promoted, thus realizing the sustainable development of agricultural production. It is hoped that this paper can provide a reference for the application of biomass charcoal in soil remediation.

Keywords: bio mass carbon, soil modification, soil remediation.

1. Introduction

Biomass charcoal is a carbon-rich, highly stable substance formed by high-temperature thermal cracking of biomass materials under anaerobic or partially anoxic conditions [1]. It has unique physical and chemical properties, such as high carbon content, large specific surface area, and cation exchange capacity, which have led to the widespread attention of biomass char in the field of soil remediation. With the continuous development of agricultural production, the problems of soil degradation and environmental pollution are becoming more and more serious, and the development of soil conditioners with multifunctionality has become the key to solve these problems. The preparation of biomass charcoal can not only effectively utilize agricultural waste and reduce environmental pollution, but also enhance soil quality and agricultural productivity, and realize the recycling of resources and sustainable development of the environment.

2. Preparation of biomass charcoal

The preparation of biomass carbon is mainly divided into two processes: carbonization and activation, which can be carried out step by step or simultaneously. Pretreatment of biomass can reduce the activation temperature, shorten the activation time or increase the yield of activated carbon. Pre-treatment methods mainly include de-ashing, pre-oxidation or soaking. Different fields have different performance requirements for activated carbon, so the preparation process needs to be adjusted and optimized according to the specific needs.

2.1. Preparation of raw materials

Biomass feedstocks for the preparation of biomass charcoal include a variety of natural substances and their derivatives, such as wood chips, organic wastes from agricultural and industrial activities, municipal solid wastes, animal and poultry manure, aquatic plants and algae, but most of the feedstocks come from agricultural wastes. The transformation of agricultural waste into biomass charcoal through pyrolysis can reduce the environmental pollution caused by agricultural waste and can be used as a renewable energy source to replace non-renewable energy sources.

2.2. Preparation methods

Biomass char is a black organic carbon-rich material with large specific surface area and high aromatization formed from biomass under high-temperature anoxic or oxygen-limited conditions through dehydration, decarboxylation, decomposition, reduction, etc. Through decomposition of macromolecules, polymerization of small molecules, and volatilization of gases, a stable carbon skeleton is finally formed. The main methods for the preparation of biomass char are pyrolysis, hydrothermal carbonization and microwave method [2].

2.2.1. Pyrolysis

Agricultural waste, such as straw, husk, corn cob, etc., mainly consists of lignin, cellulose, hemicellulose, lignocellulosic biomass is the main raw material for the preparation of biomass charcoal, and the characteristics of the biomass raw material is the primary factor affecting the nature of biomass charcoal. Biomass pyrolysis process is mainly the thermal decomposition of lignin, cellulose, hemicellulose three components, the decomposition temperature are: 315~400 ℃, 220~315 ℃, more than 400 ℃, cellulose and hemicellulose pyrolysis products are mainly some volatile substances, such as bio-oil and syngas, lignin pyrolysis products are mainly biomass char. Slow pyrolysis refers to the process of preparing biomass char by pyrolysis at a lower temperature (usually 400～600 ℃) with a heating rate of 0.1～1 ℃/s^{-1}, slow pyrolysis residence time is longer, and the mass fraction of its biomass char can be as high as 60% [3]. The slow pyrolysis process is influenced by two factors, namely the peak temperature and the carrier gas. A peak temperature of 600 ℃ helps to produce biomass char with high carbon sequestration potential and increase the total yield of biomass char. The carrier gas (nitrogen or carbon dioxide) required for this process must be of high purity, and a constant flow rate should be maintained during the preparation process. Slow pyrolysis is one of the most widely used techniques for the preparation of biomass char, with a lower pyrolysis temperature and a slower heating rate. During the slow pyrolysis process, the biomass undergoes thermal cracking, polymerization, and condensation, which can take place over a longer period of time, which is favorable for the generation of biomass char. Rapid pyrolysis method is to further increase the heating rate, shorter pyrolysis time, biomass from the low temperature oxygen deficiency state quickly warmed to a higher temperature to occur rapid decomposition, to ensure rapid and uniform heat transfer and rapid release of volatile products, to generate a large number of condensable volatile components, and a small amount of coke, the method of bio-oil yield is higher, the product of about 65% of bio-oil, about 20% of biomass char, biogas content The biogas content is only 15% [4]. Flash pyrolysis is a new pyrolysis technology proposed to further increase the yield of bio-oil, with an increased heating rate and a more significant reduction in pyrolysis time, which produces a large amount of volatile gases instantly at the beginning of pyrolysis, and requires a higher particle size of the biomass feedstock of <0.2 nm, with a yield of bio-oil of about 80%.

2.2.2. Carbonization

Hydrothermal carbonization is a reaction in which biomass is dissolved in water in a closed vessel and heated to 300 ℃ [5], the process is spontaneously exothermic and the carbon in the original biomass is transferred to the product. Different components undergo different conversion paths in the hydrothermal carbonization process. Cellulose and hemicellulose are sugars, and as the temperature increases, glycosidic bond hydrolysis, monosaccharide degradation, and the generation of intermediates such as 5-hydroxymethylfurfural are generated to further polymerize into spherical carbon materials. The structure of lignin is relatively stable, and demethylation, alkylation and condensation reactions occur during hydrothermal carbonization, accompanied by the breakage of carbon-carbon bonds and hydrolysis of carbonyl groups to form an amorphous hydrothermal carbon structure. In addition, parameters such as temperature, pressure, and residence time affect the properties of biomass char. This method does not require dehydration pretreatment of biomass feedstock, is simple and controllable, and is easier to achieve a homogeneous carbonization process, but it has a lower carbonization temperature, and the stability of the prepared biomass char is poor.

The biomass char prepared by the carbonization method usually contains a large number of oxygen-containing functional groups, which are widely used in environmental remediation, and the carbonization process reduces the oxygen content of the biomass.

2.2.3. Microwave

Taking biomass as raw material, under the premise of isolating oxygen, adding certain catalyst or microwave absorber to realize the rapid heating of biomass, using microwave heating to make biomass pyrolysis, it can realize more efficient pyrolysis, and the main products of this technology are pyrolysis oil, pyrolysis gas, and biomass charcoal. Compared with the traditional pyrolysis process, it has the advantages of low required temperature, fast heating speed and short processing time, and the prepared biomass char has a large specific surface area and rich functional groups.

2.3. Properties of biomass charcoal

Generally speaking, the physicochemical properties of the biomass char obtained will be different due to the different materials used to prepare biomass char and the preparation conditions such as temperature, oxygen content and time, and the environmental function of biomass char is mainly determined by its physicochemical properties. However, the constituent elements of biomass char are mainly carbon, hydrogen, oxygen and nitrogen, among which carbon has the highest mass fraction, and alkyl and aromatic structures are the most important components of biomass char, which give biomass char the potential to sequester carbon and be used as organic fertilizer.

2.3.1. Pore structure of biomass charcoal

The pore structure of biomass char is formed during pyrolysis or carbonization. Factors such as pyrolysis temperature, heating rate, raw material type and particle size all have an effect on the formation of pore structure. Biomass charcoal has a very complex pore structure with different pore sizes. The specific surface area of biomass char is usually determined by its porosity. Biomass charcoal pores can be categorized into small pores (<0.9 nm), micropores (<2 nm), and macropores (>50 nm) according to their pore size. Macroporosity can affect the aeration and water retention capacity of soil, as well as provide a place for microorganisms to survive and reproduce; small pores can affect the adsorption and transfer of molecules by biomass charcoal [6].

Biomass charcoal Biomass charcoal has an important role in its ability to hold nutrient ions, and this ability is achieved through the retention of water. It is because biomass charcoal has a rich pore structure and an abundance of surface functional groups that it has a certain degree of water holding capacity. The porosity of biomass char changes with the preparation temperature, such as biomass char prepared from dewatered sludge from a sewage treatment plant, the pore structure of biomass char in the temperature range of 300-900 ℃ enhances with the increase of preparation temperature. The porosity of biomass char prepared from corn stover also increased with the increase of preparation temperature, and the number of micropores and small pores of the char reached the maximum value at 900℃, and then decreased with the further increase of preparation temperature. This is due to the fact that the higher pyrolysis temperature leads to fewer polar functional groups on the surface of the biomass char, and the surface hydrophobicity is enhanced, and thus it is not easy to retain soil interstitial water. By optimizing the pyrolysis process parameters, the pore structure parameters (e.g., porosity, pore size distribution, etc.) of biomass char can be regulated to meet different application requirements.

2.3.2. Chemical properties of biomass charcoal

Biomass charcoal is a carbon-containing polymer, and infrared Fourier transform photoacoustic spectroscopy (FTIR-PAS) analysis has shown that the surface of biomass charcoal is rich in oxygen-containing functional groups such as -COOH, -COH and -OH. These functional groups give the biomass char good properties such as adsorption, hydrophilic or hydrophobicity, buffering of acids and bases, and ion exchange, and these properties give the biomass char the ability to be used in soil applications. The -COOH and -OH on the surface of biomass charcoal make its surface negatively charged, and the results of the potentiometric measurements on the colloidal sliding surface showed that the zeta potential values of biomass charcoal became more negative with increasing pH, indicating that the dissociation of -COOH and -OH increased the number of negative charges on the surface of biomass charcoal. Therefore, the abundant oxygen-containing functional groups on the surface of biomass charcoal can generate a large number of negative surface charges, and therefore the cation exchange capacity (CEC) of soil can be increased by applying biomass charcoal to the soil.

2.3.3. Stability of biomass charcoal

Biomass charcoal has a highly carboxylated, aromatic structure and high C content, with very low solubility and a very high melting and boiling point, and this structural feature determines that it is more chemically and biologically stable than the parent carbon from which it originates, more resistant to microbial decomposition, and more stable than other organic matter in the soil, and the carbon in biomass charcoal is estimated to remain in the environment for up to 1,000 years. The stability of biomass charcoal as a stable carbon pool in the global carbon cycle is an important property that affects its use as a soil carbon sink, and this stability is also affected by the surrounding environment.

The main processes affecting the stability of biomass charcoal in the environment include physical decomposition, chemical decomposition and biological decomposition. The physical decomposition process is mainly the process of biomass char crushing and decomposition caused by physical erosion and the physical migration process under the action of rainfall and runoff, such as the crushing and decomposition caused by dry-wet cycle, freezing-thawing cycle, and root penetration, and the scouring and migration of surface runoff, etc. The chemical decomposition process mainly includes the dissolution process of biomass char under the action of water solution, as well as the oxidizing action. The chemical decomposition process mainly includes the dissolution process of biomass char under the action of aqueous solution, and the chemical oxidation process mainly caused by oxidation, such as the release of soluble biomass char, the increase of oxygen-containing functional groups on the surface of biomass char, and the enhancement of hydrophilicity, etc. The biological decomposition process is the process of biomass char due to the action of dry-wet cycle, freeze-thaw cycle and root penetration. Biodegradation processes are processes in which biomass char is utilized due to metabolism of soil organisms and catalytic degradation by enzymes, such as microbial mineralization [7].

3. Soil modification by biomass charcoal

3.1. Changes to soil physical properties

Global research on biomass-based charcoal originated with the recognition of black soils (Terra Preta) in the central Amazon Basin. In these black soils, the upper soil layers have a lower bulk density than the lower soils, which is where biomass charcoal comes in. Biomass charcoal has a porous structure, which effectively increases the void content of the top soil layer and reduces the bulk density, thus improving the permeability of the soil. This structure facilitates water and air circulation in the soil, providing a better growing environment for plant roots.

In addition, the porous nature of biomass charcoal absorbs and retains water, reduces evaporation of soil moisture, lowers the tensile strength of the soil and increases the water-holding capacity of the soil, which helps to keep the soil moist under drought conditions.

3.2. Adjustment of soil ph

Due to the nutrient uptake in the plant growth process makes the plant body contain a certain amount of Ca^{2+}, Mg^{2+} and other metal cations, in order to maintain the charge balance in the body, the plant will accumulate a certain amount of alkali (organic anions) in the body during the growth process, some studies have shown that the application of biomass charcoal in the acid and sandy soils can greatly increase the soil's ability to absorb and retain K^+, Na^+, Ca^{2+}, Mg^{2+} and NH_4^+ absorption and holding capacity of soil [8]. Rice husk charcoal can significantly reduce soil acidity, increase the number of soil exchangeable salts and soil salts saturation (BSP), which can lead to a decrease in soil exchangeable and soluble aluminum content [9]. During pyrolysis, these bases are concentrated, making biomass char alkaline. Therefore, biomass charcoal can be used as an amendment for acidic soils to neutralize soil acidity and increase soil pH. Novak et al. showed that when walnut shell biomass charcoal (pH 7.3) was added to acidic soil, the pH of the soil increased from 4.8 to 6.3 [10].

Different soils require different degrees of conditioning. Analysis of biomass char made from different crop residues at more than ten kinds of 400°C conditions revealed that the alkali content of biomass char prepared from leguminous materials is higher than that of biomass char prepared from non-leguminous materials, which indicates that the type of material also has an effect on the alkali content of biomass char. Therefore, it is possible to change the raw materials used to prepare biomass charcoal to obtain biomass charcoal materials that are suitable for the soil.

3.3. Carbon sequestration in soil

Biomass charcoal, as a highly stable carbon-rich material, can play a role in locking the carbon in biomass in the process of production and storage to avoid entering the atmosphere through microbial decomposition, etc. At the same time, it can convert the organic carbon fixed by plant photosynthesis into inert carbon, so that it will not be rapidly mineralized by microorganisms, which can play a positive role in increasing sinks and reducing emissions, reducing greenhouse gas emissions and influencing climate change. The effect of the plant is to increase sinks, reduce greenhouse gas emissions, and influence climate change.

Biomass char is produced by charring organic waste at high temperatures in an anoxic or low oxygen environment. This process converts the carbon in the organic material into a stabilized carbon-based solid substance known as biomass char. The carbon in biomass char comes from carbon dioxide absorbed by plants through photosynthesis. When this organic material is converted into biomass charcoal, the carbon is stabilized in the structure of the biomass charcoal and is not easily decomposed by microorganisms or released back into the atmosphere: this is the "carbon negative effect" of biomass charcoal. Therefore, the application of biomass charcoal in soil can realize the transformation of unstable organic carbon in biomass to stable biomass charcoal, and achieve the effect of long-term carbon sequestration.

At the same time, biomass charcoal has a large specific surface area and porosity, which can improve the structure and water retention capacity of the soil. These properties make the carbon sequestration of biomass char in soil more significant, because the stabilized soil structure and good water retention capacity help to reduce carbon loss and release. Therefore, applying biomass charcoal to soil can realize the conversion of unstable organic carbon from biomass to stable biomass charcoal and achieve long-term carbon sequestration.

Biomass charcoal is a win-win strategy for mitigating global warming and addressing global food security. Biomass charcoal is expected to be a long-lasting carbon sink due to its high chemical stability, high carbon content and ability to be stabilized in the soil over a long period of time.

3.4. Increase microbial activity in the soil

Biomass charcoal can enhance biostability through interactions with environmental components, and it is able to form stable organic matter-biomass charcoal agglomerates by adsorption of organic matter on the surface and by interaction with soil particles or by solidification of mycorrhizal secretions, mycelium, and polysaccharides. After the addition of biomass char, the available components of biomass char trigger the activity of soil microorganisms, and it has been found that the addition of biomass char prepared from 2.5% rice straw (500 ℃) to the cultivated layer of paddy soil, and the high content of total organic carbon in the soil after one year's incubation experiments indicate that it can promote the co-metabolism of microorganisms and enhance the mineralization of C in biomass char. However, the mechanism of the effect of material charcoal on the environmental functions of soil and agroecosystems is not yet fully understood. Biomass charcoal showed the functions of promoting crop growth, improving soil nutrients and microbial activity during the short-term experiments, but the mechanism of these beneficial effects of biomass charcoal remains to be explored, and the long-term effects of biomass charcoal application need to be further investigated.

4. Remediation of soil by biomass charcoal

Biomass charcoal can improve the physicochemical properties of soil, improve the microbiological environment of soil, adsorb soil organic matter and reduce the bioeffectiveness of toxic elements. The porous structure and rich oxygen-containing functional groups on the surface of biomass charcoal make biomass charcoal have a strong ability to adsorb toxic substances, which can not only improve soil properties and increase soil fertility by changing the physicochemical properties and microbiological properties of the soil [11], but also increase the content of soil organic matter (SOM), improve the content of effective soil nutrients, change the soil microbiological environment and promote plant growth [12]. environment and promote plant growth [12]. By applying biomass charcoal, the concentration and toxicity of organic pollutants in the soil can be effectively reduced, improving soil quality and promoting crop growth. In addition, biomass charcoal can be used as a green and sustainable soil amendment for improving the water and fertilizer retention capacity and microbial activity of the soil to promote the sustainable development of agricultural production.

4.1. Adsorption of pesticide organic residues

Biomass char from high temperature pyrolysis mainly immobilizes organic pollutants through surface adsorption. The biomass carbon prepared under such conditions is less rich in pore structure and huge specific surface area, and its own polarity will be stronger, so that the biomass carbon can be very good affinity to organic substances, so as to remove organic pollutants such as pesticides, petroleum hydrocarbons and so on more effectively.

Biomass charcoal can adsorb organic pollutants such as pesticides, reducing their chemical activity and toxicity in the soil. These organic pollutants are usually adsorbed on the porous structure and surface functional groups of biomass charcoal, thus reducing their concentration and toxicity in the soil. The adsorption capacity of biomass charcoal for pesticides is 2000 times higher than that of soil, and even a small amount of biomass charcoal (0.05%) applied to soil can effectively reduce the toxic effects of organic pollutants on plants, and reduce the accumulation of pesticides and other organic pollutants in plants [13].

4.2. Adsorption of heavy metal pollution

Biomass charcoal has a strong adsorption capacity, which can adsorb heavy metal ions in the soil and immobilize heavy metals on the surface or inside the pores of biomass charcoal through mechanisms such as electrostatic attraction, ion exchange, complexation reaction and precipitation, thus reducing the mobility and bioeffectiveness of heavy metals in the soil. , Adding biomass charcoal to the soil can increase the adsorption capacity of the soil for heavy metals. Biomass charcoal can decrease the mobility of heavy metals in the soil by increasing soil pH, thus providing immobilization of heavy metals. Beesley and Marmiroli found that the concentration of Cd and Zn in the soil leachate decreased by 300-fold and 45-fold, respectively, after biomass charcoal produced at 400 ℃ was applied to the soil. The results showed that the addition of biomass charcoal had the effect of passivating soil heavy metals and reducing their bioavailability and transport [14].

Meanwhile, different kinds of heavy metals have different chemical properties and toxicity, so the adsorption capacity of biomass charcoal on them will be different. At the same time, the concentration of heavy metals will also affect the removal effect of biomass charcoal, generally speaking, the removal effect of biomass charcoal is more significant in the case of low concentration of heavy metals. For soils contaminated with high concentrations of heavy metals, the single use of biomass charcoal may be difficult to achieve the desired removal effect. Zhu Yuanfang et al. [15] measured the effect of two kinds of biomass charcoal on heavy metal forms in composite polluted soil, and the experimental results showed that cow dung biomass charcoal was more effective than rice husk charcoal in removing the heavy metals Cu, Pb, Zn, and that corn stover charcoal could adsorb Cd^{2+} and Pb^{2+} in aqueous solution more effectively. Therefore, for different composite polluted soils, different biomass charcoals should be selected for their remediation according to local conditions.

5. Conclusion

This paper reveals the remarkable effects of biomass charcoal in improving soil physical structure, regulating soil pH, sequestering carbon and enhancing soil microbial activity through a detailed study of biomass charcoal preparation and its role in soil remediation. The porous structure and rich surface functional groups of biomass charcoal provide it with excellent adsorption capacity, which can effectively adsorb organic pollutants and heavy metals in soil and reduce their bioefficacy, thus improving the soil environment and promoting the healthy growth of plants. At the same time, biomass charcoal is also highly stable and can exist in the soil for a long time to play a lasting role in remediation. In the future, with the in-depth research on biomass charcoal, its application prospects in agriculture, environmental protection and other fields will be broader, and it is expected to become an important tool to promote ecological sustainable development.

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