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Research progress in preparation and application of biological carbon

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Abstract: *Biochar is a carbonaceous material generated by pyrolysis of biomass under the condition of low oxygen content. Because of its large specific surface area, developed pore structure and rich oxygen-containing functional groups on the surface, it has a good adsorption and fixation effect on organic pollutants in soil, water and sediments. It is considered as an ideal and universal adsorption material and is widely used in the field of environmental pollution control. This paper reviews the preparation, application and defects of biochar. In order to provide reference value for the improvement of potential value and utilization rate of biochar.*

Keywords: *biochar, adsorbent, application*

1. Preparation of biochar

1.1. Preparation of raw materials and processes

The raw material for preparing biochar is usually biomass materials with wide sources and low cost, such as agricultural waste, forestry waste, animal manure, etc. These wastes are rich in nutrients such as carbon, nitrogen, phosphorus, lignin and cellulose, so they are very suitable for preparing biochar. Up to now, the preparation methods of biochar can be divided into carbonization technology, liquefaction technology, gasification technology and microwave pyrolysis technology[1].

The main purpose of carbonization is to produce carbon, and the long-term cracking at a low heating rate of about 500℃ is called the process of biomass carbonization. According to the difference of heating temperature, heating rate and reaction residence time, carbonization technology can be divided into four types: slow pyrolysis, medium pyrolysis, fast pyrolysis and flash pyrolysis.

The slow pyrolysis reaction is carried out at a low heating rate at 400℃-650℃ for 1-2 days, and the average yield of biochar is about 35%. Some scholars have found that biochar was made from corn residue, cow dung and corn straw by anoxic carbonization at 300℃ for 2 h, and analyzed by FTIR. The results show that the functional groups of biochar from different materials are similar to those of activated carbon straw, and they all contain absorption peaks[2]of hydroxyl groups, aromatic groups and oxygen-containing groups. In this paper, three kinds of biomass, namely poplar branches, water hyacinth and corn stalks, were used as raw materials to make biochar. The prepared biochar was analyzed and characterized, and the influence of pyrolysis temperature on the physical and chemical structure of biomass char was explored[3]. Liang and Hou Jingwen found that the yield of biochar prepared from reed decreased by 9.79% from 350℃ to 700℃. Wang Dou, et al. studied the adsorption of methyl orange by biochar prepared from earthworm dung, and got the conclusion that increasing the pyrolysis temperature, the carbon yield and C,H,O,N content decreased, but the ash content and specific surface area increased[4]. The rapid pyrolysis method is to react at 400℃~550℃ for 1~2s at a rate of 1000℃/s, and the final char formation rate is 12%, which is usually called flash pyrolysis. Rapid pyrolysis has high heating rate and high bio-oil yield. Some quick cracking technologies include: vortex reactor cracking process, ablation cracking process, rotating cone reaction process, boiling fluidized bed cracking process, circulating fluidized bed cracking process, thermal cycle vacuum cracking process, entrained bed reactor process, Auger kiln cracking process and cyclone cracking process[5].

Liu Ronghou et al.[6]studied the effect of biomass rapid pyrolysis reaction temperature on the yield, water content, density, viscosity and composition of bio-oil. The change of heating temperature and rate will cause the change of material ratio in the product. In order to obtain high-yield biochar, the reaction conditions should be controlled at a lower temperature and a slower heating rate, but too low a temperature will lead to incomplete carbonization, and the extension of carbonization time will reduce the carbonization rate[7]. By comparison, the output value of biochar using slow pyrolysis process is the best, and the requirements for raw materials are not high.

Biomass gasification is a process of converting biomass raw materials into gas at high temperature by using oxygen or oxygenates in the air as gasification agent. The by-products contain biochar and biomass extract[8]. Zhao Hongtao et al.[9]found that pine sawdust was used as raw material, and the effects of gasification temperature and gasification equivalent ratio on gasification process were analyzed. The components of gasification gas, tar and biochar were further analyzed, and the optimal gasification intensity of pine sawdust in fluidized bed gasifier was determined. At the same time, the feasibility of mixed gasification of poplar sawdust and pig manure was also studied. Some scholars have found that gasification converts the internal energy of carbon in biomass into combustible gas through two continuous reaction processes, and the generated high-grade fuel gas can be directly used for production and life, or can be generated by internal combustion engines or gas turbines for cogeneration, so as to realize efficient and clean utilization of biomass[10]. Ying Hao, Tu Junling and others found that the reaction temperature in gasification is an important factor[11,12]that affects the steam gasification characteristics of sawdust.

Microwave pyrolysis reaction is to heat biomass to 400-500℃ in the absence of oxygen, and crack it into low molecular organic vapor in a short time, and then quickly cool it to obtain the liquid fuel with the maximum liquid yield[13]. Ravikumar C et al.[14]studied the microwave-assisted pyrolysis of corn cob, corn stalk, sawdust and rice straw under constant conditions. Some scholars have also studied the potential application of microwave pyrolysis of Carya cathayensis shell to produce carbon-based solid products[15]for the treatment of polluted water. Many scholars have studied using iron (Fe) and cobalt (Co) particles as susceptor by microwave pyrolysis, and using bagasse to produce nano-material biochar. By analyzing the physicochemical properties of biochar by Raman spectroscopy, X-ray diffraction and other characterization techniques, the influence of susceptor composition on the quality of biochar[16]has been studied. Tharaneedhar V studied the adsorbent used to remove methylene blue from water from corncob microwave pyrolysis waste. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were used to analyze the surface characteristics[17]of corncob after microwave pyrolysis. Microwave pyrolysis of biomass to produce biochar or nanomaterials can improve the utilization value of pyrolysis solid products, and the prepared biochar is an economical, environmentally friendly and effective biological adsorbent[18]for wastewater treatment.

1.2. Physical and chemical properties of biochar

The physical properties of biochar include specific surface area, pore structure, bulk density, etc. The chemical properties include pH, carbon content, hydrogen-carbon ratio, oxygen-carbon ratio, ash content, volatile matter, functional groups and cation exchange capacity, etc. The physical and chemical properties of biochar directly affect its adsorption performance.

In terms of physical properties, biochar has good air permeability and water absorption. Adding biochar into soil can improve the properties of sandy soil to a certain extent, and it is also conducive to the growth of soil microorganisms, and can promote the absorption of nutrients by plants to a certain extent. In terms of chemical properties, biochar is mainly composed of C, H, O, N and P, of which carbon accounts for the highest proportion, reaching more than 60%. Biochar has large specific surface area, porosity and high aromatization. Generally, the pH value of biochar is alkaline. Thanks to the above characteristics, biochar has good adsorption performance. With the increase of pyrolysis temperature, biochar prepared at different temperatures is rich in mineral elements. Different biomass and different pyrolysis methods have great influence on the specific surface area of prepared carbon. Due to the decrease of polar functional groups on the surface, the specific surface area of biochar increases, while the water-holding capacity of biochar decreases. With the increase of pyrolysis temperature, the basic groups in biochar increase and the acidic groups decrease, so the total functional groups decrease and the density of functional groups decreases. The differences and diversity of biochar prepared from different pyrolysis temperatures and biomass make it show different environmental effects. In recent years, it is considered by scholars as a new type of green adsorption material, and it is also widely used in environmental problems such as greenhouse gas emission reduction and soil moisture.

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2. Application of biochar

2.1. Soil modification

In agricultural production, a large number of waste biomass such as straw are discarded or burned, while the technology of biomass carbonization returning to field solves the problem of waste biomass resource utilization, and at the same time overcomes the disadvantages caused by straw returning to field, which has obvious advantages. At the same time, biochar directly carbonized and returned to the field plays an important role in crop growth, soil water storage and fertilizer conservation, improving fertilizer utilization rate, increasing yield and improving quality. The technology of direct carbonization of biochar into fields, whether as an application form of biochar or a new potential form of fertility, is of great significance to the sustainable development of agriculture, the realization of a virtuous cycle of agricultural production and the increase of farmers' production and income[19].

Carbon has strong adsorption capacity for heavy metal ions in soil, which can obviously change the occurrence form of heavy metals in soil and reduce the content of exchangeable heavy metals, thus reducing the availability of plants. However, some studies also believe that exogenous carbon can effectively reduce the available content of soil polluted by sudden heavy metals, but for soil polluted by metals, the addition of exogenous carbon will increase the activity of heavy metals. Meng Lingyang et al. found that peat, activated carbon and weathered coal can effectively reduce the content of available cadmium in the soil polluted by sudden cadmium, but enhance the activity of cadmium in the contaminated soil[20].

On the one hand, the surface of biochar contains some easily-decomposed carbon sources and nitrogen sources (Gheorghe et al,2009), which is beneficial to microbial activities, which is the reason why biochar can increase the number and activity of soil microorganisms at the initial stage. On the other hand, the gap of biochar has great variability, ranging from one nanometer to tens of nanometers, even tens of microns. The porous structure and huge surface area of biochar can store water and nutrients, and become a micro-environment where microorganisms can live (Kolb et al ,2009), which provides a hotbed for the growth of special groups of microorganisms, thus promoting the circulation of soil nutrients. Of course, the effect of biochar on soil microorganisms may be mainly based on the change of soil environment, and its internal mechanism needs further discussion[21].

The current research shows that biochar application can promote soil enzyme activities related to the utilization of mineral elements such as N and P, but decrease the soil enzyme activities involved in ecological processes such as soil carbon mineralization (Lehmann et al. , 2011) Because of the adsorption of biochar, the action of biochar on soil enzymes is complicated. On the one hand, the adsorption of biochar on reaction substrate contributes to the progress of enzymatic reaction and improves the activity of soil enzymes; on the other hand, the adsorption of biochar on enzyme molecules protects the binding sites of enzymatic reaction and prevents the progress of enzymatic reaction (Czimczik and Masiello,2007; Derenne and Largeau,2001; Lehmann and Joseph,2009; Lehmann et al,2011)。 Jin(2010) thinks that the change of soil enzyme activity is closely related to the ecological function of biochar, and its changing trend contributes to the stable existence of biochar in the soil environment[22].

2.2. Environmental pollution control

The adsorption of heavy metals by biochar is related to its physical and chemical properties (oxygen-containing functional groups, mineral composition, aromatic structure, etc.), and the properties of biochar depend on the composition of biomass raw materials, pyrolysis temperature, pyrolysis technology and pyrolysis conditions. Therefore, the adsorption capacity and mechanism of different biochars to different heavy metals are different. The main mechanism can be divided into two major mechanisms: the "lime effect" of biochar and the adsorption of biochar. Therefore, before applying biochar to remediate contaminated soil, it is necessary to examine soil properties (especially soil fertility) and the types of pollutants[23]contained in the soil in detail.

Traditional oxidation technology still needs to invest oxidant reagent. With the aid of electrocatalysis, biochar can be used as cathode material to realize the production of active particles by reducing oxygen. The content and distribution of oxygen functional groups, pore structure and specific surface area, primary ash and secondary inorganic components play a key role in the adsorption of pollutants, activation and catalysis of oxygen in the process of biochar water treatment. How to obtain biochar with high specific surface area and multistage pore structure, how to adjust the content and

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distribution of oxygen functional groups, and how to regulate the composition and content of inorganic components play a decisive role in the excellent performance of biochar in adsorption, catalysis and electrocatalysis[24].

Air pollution is an important environmental problem facing the world at present. A large number of studies show that carbonaceous materials have been widely used in the prevention and control of sulfur-containing gases, especially activated carbon. Activated carbon is a common desulfurizer, which can effectively convert H_2S into elemental sulfur[25-28]by catalytic oxidation. Biochar has adsorption properties similar to activated carbon, and most biochars are alkaline[29, 30]. Therefore, biochar may replace alkali-modified activated carbon for the removal of H_2S. In a word, the adsorption of pollutants by biochar is related to its specific surface area, pore size distribution and ion exchange capacity. Carbon is more suitable for removing inorganic pollutants, and the removal mechanism includes complexation with oxygen-containing functional groups, ion exchange and precipitation[31].

2.3. Mineralization potential

Although biochar is considered to be a relatively stable additive, fresh biochar may release a certain amount of organic carbon and N and P nutrients, promote soil microbial activities and enhance soil respiration (Kolb et al., 2009). Deenik et al. (2010) and Zimmerman(2010) found that the amount of volatile and unstable organic carbon in biochar was positively correlated with the amount of carbon dioxide released. Mumme et al. (2014) found that adding hydrothermal carbon can promote the growth of methanogens and increase methane production. The main reason is that hydrothermal carbon itself has a certain amount of highly available organic carbon, whereas pyrolysis carbon with low organic carbon content has no such effect. Hamer et al. (2004) also proposed that biochar entering the soil can provide a certain amount of carbon source[32]for the growth of some microorganisms.

3. Outlook

A large number of studies show that the yield of biochar can't reach a satisfactory value under the current process and production technology. In the process of pyrolysis of biochar, a large number of by-products, such as wood vinegar, pyrolysis gas and tar, will be produced. While using the waste heat of straw burning in farmland to prepare biochar, it may produce harmful substances and greenhouse gases higher than that of straw returning. Peng Changsheng and others found things we mentioned before. Pyrolysis of biomass by solar energy to prepare biochar, which combines biomass energy with solar energy, is a new technology with economical cost and energy saving.

At present, the raw materials for biochar preparation in most research institutes are generally qualitative, which will lead to the reduction of energy utilization and waste of resources. In the future research, we should give priority to the combination of different loads, and find the most suitable element ratio, which is conducive to improving the utilization rate and comprehensive performance of materials.

Because biochar is produced by cracking organic biomass, it has caused the loss of organic matter. However, these organic matters are essential parts for the production of humus soil, and the organic matters that produce biochar can be directly returned to the field and placed in the soil, which can also achieve the effect of improving the soil. Some scholars have shown that biochar does not necessarily make the soil more fertile, and the porous structure of biomass will lead to the propagation of strains. Studies have shown that in many cases, the addition of biochar will accelerate the decomposition of non-biochar organic substances by microorganisms, which will inevitably lead to the loss of biochar in the soil. Long-term burial of carbon in soil may change the soil structure, resulting in the release of CO_2 into the atmosphere. The argument that carbon is permanently preserved in soil needs further study. Some scholars have found that the soil with biochar can't reduce CO_2 emission after four years of application.

However, the adsorption capacity of biochar prepared by different biomass materials and methods is uneven. Because the physical and chemical properties of biochar are easily disturbed by external conditions, the surface charge conduction and adsorption of biochar is unstable, and the polluted ions are easily decomposed and released, which leads to secondary pollution. In addition, the complexity of the natural environment should be taken into account, and these factors will limit the application of biochar in environmental pollution control to a certain extent. Therefore, how to keep the excellent adsorption performance of biochar composites is a hot spot of biochar application research.

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