

Preparation and Application of Modified Biochar for Arsenic Pollution Remediation

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Abstract

Aiming at the arsenic pollution problem that exists in the world and is difficult to completely repair, this article describes the causes and severe situation of soil arsenic pollution from the aspects of arsenic source and pollution status, summarizes the preparation methods, structural characteristics, functional group types and influencing factors of biochar, and expounds the specific methods of biochar modification. The application of modified biochar in arsenic contaminated soil and water remediation is introduced in detail, and the future research and application are prospected.

Keywords

Arsenic; Modified Biochar; Preparation Method; Remediation.

1. Introduction

Metalloid arsenic is an element that is ubiquitous in nature (atmosphere, soil, rock, water and other environmental media), has a certain toxic effect on the human body, and is easily carcinogenic. Arsenic in nature is mainly found in rock minerals. Common arsenic-containing minerals include sulfide minerals (such as pyrite, pyrrhotite, Maxi ore, galena, sphalerite, chalcopyrite, etc.), oxides Minerals (such as hematite, magnetite, ilmenite, etc.), silicate minerals (such as quartz, feldspar, mica, amphibole, pyroxene, etc.), carbonate minerals (such as calcite, dolomite, meteorite Iron, etc.), sulfate minerals (such as gypsum, barite, etc.) and other minerals (apatite, fluorite, etc.). Through the gradual disintegration of rocks and minerals through weathering or erosion, strong geological movement (such as volcanic eruption) or microbial activities, arsenic is released into the surrounding soil, and then gradually diffused through the transportation of wind or water. The release of arsenic under natural conditions rarely reaches the level of harmfulness to the human body. Most of the release, migration and pollution of arsenic are caused by human activities, including the mining, smelting and transportation of arsenic-containing minerals and the use of arsenic-containing substances. Arsenic released by human activities will eventually be carried by the soil, and arsenic -containing substances will continue to accumulate in the soil, and its content will eventually reach a threshold harmful to the human body, causing diseases of the human respiratory system, nervous system, immune system and so on. In severe cases, it can lead to paralysis. Or carcinogenic, some acute arsenic poisoning may also directly lead to death.

The content of arsenic in soil in China is about 11.2 mg kg^{-1} , which is 1.5 times the average arsenic content in soil in the world. With the release of arsenic-containing substances in the soil through human activities, the problem of arsenic pollution in some areas has gradually become prominent. According to the data of the National Pollution Survey (2005-2013), the rate of excess arsenic pollutants in the national soil is 2.7%, among the 8 inorganic pollutants of cadmium, mercury, arsenic, copper, lead, chromium, zinc, and nickel Ranked third. There have been soil arsenic pollution incidents in Dushan County of Guizhou, Chenxi County of Hunan, Shimen, Hechi City of Guangxi, and Yangzonghai of Yunnan in China. There are also related reports of soil arsenic pollution in Mexico, Poland, Chile, and the United States [1-3]. Groundwater pollution, which is closely related to human health, is also prominent in China. The area with an arsenic content exceeding $10 \mu\text{g}\cdot\text{L}^{-1}$ (WTO drinking water standard) covers an area of $150,000 \text{ km}^2$, and nearly 20 million people live in groundwater with high arsenic pollution area, and about 200 million people worldwide are threatened with high arsenic exposure. Therefore, it is necessary to develop reasonable and efficient arsenic pollution remediation technology to prevent and control arsenic pollution, which is of great significance for protecting human health, realizing the ecological circulation of land, and ensuring food security.

Biochar is a carbon skeleton polymer with a rich and complex pore structure and a large specific surface area, which is produced by high-temperature pyrolysis using biomass as a basic material under oxygen-free or low-oxygen conditions. Because of its wide sources of materials (trees, straw, grass, sludge, organic waste, etc.), low cost, and no secondary pollution, biochar is often used for pollution remediation.

2. Structure and functional groups of biochar

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The structure of biochar is formed after carbonization processes such as water loss and fracture based on the structure of biomass materials. The overall structure is composed of porous carbon frame, stable aromatic compounds and minerals. And the pore structure is constructed by pyrolysis and volatilization of aromatic compounds and other functional groups. The pores of biochar are mainly micropores ($< 2 \text{ nm}$), and the proportion of mesopores ($2 \sim 50 \text{ nm}$) and macropores ($> 50 \text{ nm}$) is relatively small. The structure of biochar is mainly affected by raw materials and pyrolysis temperature. Due to the differences in the structure and material composition of biomass, there are significant differences in the structural characteristics of biochar after pyrolysis and carbonization, such as crystallinity, crosslinking and branching. The macroporous structure of biochar made from raw materials with high lignin content increases, and the biochar made from raw materials with high cellulose content mainly has microporous structure. Pyrolysis temperature is another main factor affecting the structure of biochar. With the increase of pyrolysis temperature, the amorphous carbon structure gradually transformed into graphite microcrystalline structure, the amorphous carbon gradually decreased, and the turbine layered aromatic carbon gradually increased until it tended to graphitization. With the increase of pyrolysis temperature, the volatile substances contained in the raw materials are gradually pyrolysis and volatilized, resulting in a large number of pore structures. However, when the temperature is higher than $700 \text{ }^{\circ}\text{C}$, the microporous structure of biochar begins to be damaged. When the temperature is higher than $800 \text{ }^{\circ}\text{C}$, the carbon frame structure begins to be unstable and collapse. The residence time and change rate of pyrolysis temperature also affect the structure of biochar. Studies have shown that when the pyrolysis temperature stays at $500\text{-}700 \text{ }^{\circ}\text{C}$, the

porosity of biochar increases first and then decreases after 2 hours [4]. Slow temperature rise is more conducive to the formation of microcellular structure of biochar than rapid temperature rise. This is because rapid temperature rise will lead to incomplete pyrolysis of substances (such as tar) and can not volatilize completely, so as to block the pores. Functional groups such as hydroxyl, carboxyl, carbonyl and ester groups generally exist on the surface of biochar, most of which are oxygen-containing functional groups or basic functional groups. These functional groups are formed by pyrolysis of protein, cellulose or hemicellulose in carbon making materials. Therefore, the formation of functional groups is determined by the type of carbon making materials and pyrolysis temperature. The protein, cellulose or hemicellulose of monomer materials provide the basis for the formation of functional groups. For example, the N and S functional groups of biochar made of cellulose materials are more than those of non cellulose materials. The pyrolysis temperature further dominates the formation of functional groups. Taking 300 °C as the watershed, the carboxyl and carbonyl contents increase first and then decrease. With the gradual increase of temperature, the aliphatic functional groups gradually decrease (400 ~ 550°C), and then the alkyl functional groups gradually disappear (above 600 °C) [5].

3. Preparation of modified biochar

In order to further improve the adsorption performance of biochar, it is usually modified to improve the remediation efficiency. Common modification methods include physical modification such as steam modification, gas purging modification and UV modification, and chemical modification such as acid-base modification, oxidation modification and metal load modification.

Steam modification can promote the formation of crystalline carbon. In the modification process, oxygen atoms are exchanged to the free active point on the surface of biochar, hydrogen atoms can form complexes with carbon atoms, and the incomplete combustion products in the pyrolysis process can also be effectively removed. Some studies show that after steam modification, the specific surface area of biochar increases and the adsorption capacity of cadmium increases. Gas purging modification is a process of adding inert gases such as carbon dioxide, nitrogen or ammonia to increase the nitrogen-containing groups, specific surface area and pore volume on the surface of biochar during the pyrolysis of carbon making substrate. Ultraviolet modification uses the mechanism of free radical polymerization to initiate the graft polymerization of monomers on the surface of biochar with ultraviolet light to increase the surface functional groups of the biochar and enhance its adsorption performance. Research by Li Qiao et al. showed that the oxygen-containing functional groups on the surface of biochar and the specific surface area were greatly increased after 365nm ultraviolet light was used to irradiate the modified biochar, and its saturated adsorption capacity for benzene and toluene increased by about 16 times and 29 times, respectively. Acid modification is to modify biochar with sulfuric acid, hydrochloric acid and nitric acid, introduce acidic functional groups, and dissolve some impurities produced by pyrolysis, thereby increasing the total amount of biochar pores. Studies have shown that the modification of biochar with hydrochloric acid can increase the specific surface area by more than 60% [6]. Alkali modification is to use sodium hydroxide, potassium hydroxide, etc. to introduce carboxyl, carbonyl and other oxygen-containing functional groups on the surface of biochar to increase the specific surface area of the biochar and improve the adsorption performance. Oxidation modification is to add oxides during the firing process of biochar, so that oxygen-containing functional groups are attached to the surface of biochar, the specific surface area is increased, and the adsorption performance is enhanced. Common oxidants include hydrogen peroxide and potassium permanganate. The metal loading modification method is to use a metal ion solution or a metal salt solution to soak the carbon substrate before making carbon, and convert the metal ions or metal salt ions into metal oxides by pyrolysis. The cation charge of biochar can enhance the adsorption capacity of biochar to anions such as nitrate and fluoride.

In addition to the above-mentioned biochar modification methods, there are also various modification methods such as organic modification and composite modification according to different requirements for improving the capacity of biochar. The creation of the modification method has

greatly expanded the application fields of biochar and promoted the development of biochar related industries.

4. Application of modified biochar in remediation of arsenic pollution

As an adsorption material, biochar has been widely used in the field of arsenic pollution remediation and has achieved remarkable results. Studies have shown that the biochar fired with cow dung, pine needles and straw has an arsenic adsorption capacity of 16.9 mg kg^{-1} , 23.4 mg kg^{-1} , and 41.7 mg kg^{-1} in an aqueous solution with an arsenic concentration of 10 mg L^{-1} , respectively. In order to further improve the remediation performance of biochar for arsenic pollution, scholars have modified the biochar with metals, acids, alkalis, etc., and conducted a lot of research on the changes in its remediation ability. In terms of repairing arsenic-contaminated water, Cho et al. used CO_2 as the reaction medium to pyrolyze the papermaking sludge to convert iron into iron oxide, and at the same time generate syngas and magnetic biochar, which act as an adsorbent for As(V). The results show that the magnetic biochar containing iron and calcium solid minerals has a strong adsorption capacity for As(V), and the maximum adsorption capacity reaches 34.1 mg g^{-1} . In addition to powdered materials, magnetic biochar can also be prepared into gelatin microspheres, which can expand the specific surface area of biochar and increase the adsorption sites for heavy metals. It is an effective material for treating wastewater containing As(V). Wang et al. [7] modified pine wood biochar with hematite, and the modified biochar had an increased adsorption performance of As(V) by 0.62 times, and the adsorption capacity was 0.429 mg g^{-1} . Zhu et al. modified wheat straw biochar with potassium hydroxide and ferric nitrate. After the modification, the adsorption capacity of As(III) increased from 1.05 mg g^{-1} to 65.20 mg g^{-1} . He et al. modified corn stover biochar with ferric chloride[8]. After the modification, the adsorption performance of biochar on As(V) increased from 0.017 mg g^{-1} to 6.80 mg g^{-1} . Modified biochar can also be used to repair arsenic-contaminated soil. Studies have shown that the modification of porous materials with iron or aluminum improves the adsorption capacity of arsenic, cadmium, zinc, etc. The application of iron-modified biochar reduces the leaching loss of arsenic under acid rain leaching conditions and promotes the effectiveness of arsenic Sexual decrease. The iron-manganese modified biochar can significantly increase the redox potential of the soil, reduce the bioavailability of As, and promote the conversion of As that originally exhibits non-specific absorption and specific binding into residual amorphous hydrated oxide and crystalline hydrated oxide forms. It is more conducive to the growth of soil microorganisms. Lin et al. [9] analyzed the As fractionation, enzyme activity, and bacterial abundance to study the potential effects of iron-manganese modified biochar complexes (FMBCs) on the volatilization of toxic As in flooded rice fields. The results showed that FMBCs reduced the volatilization of toxic As from contaminated soil, and the effect was more pronounced at higher doses. Zhang et al. [10] used potassium phosphate (K_3PO_4) as raw materials to pyrolyze biomass materials such as wood, bamboo, corn stalks, and rice husks to prepare a new type of phosphorus-modified biochar, and studied the effects of modified biochar on soil heavy metals. The results show that the addition of phosphorus can increase the extraction rate and mobility of As(V). Ferric chloride loading can promote the formation of microporous structure of biochar and effectively increase the specific surface area of biochar. The specific surface area of iron-loaded biochar is $33.11 \text{ m}^2 \text{ g}^{-1}$, which is 10.6 times higher than that of unmodified biochar ($2.85 \text{ m}^2 \text{ g}^{-1}$). After the application of iron-loaded biochar (3% of the soil mass), the stability rates of As(III) and As(V) in polluted soil with an arsenic concentration of 150 mg kg^{-1} can reach 38.22% and 51.22%, respectively, and the stability rates of available as (III) and as (V) can reach 39.56% and 53.67% respectively.

5. Prospect

With industrial development and the development and application of chemical products, environmental pollution as a by-product has become more and more serious, which has become a key issue that hinders social and economic development and affects human health. As a typical and difficult environmental problem, arsenic pollution has attracted more and more scholars' attention. In

order to solve the problem of arsenic pollution, scholars have conducted a lot of research. Biochar remediation technology has attracted the attention of most scholars because of its high cost performance and no secondary pollution. Biochar and modified biochar products have been applied in the field of remediation of arsenic-contaminated water and have achieved satisfactory results. However, soil is a complex aggregate of substances and biochar has different characteristics. The use of biochar and modified biochar to treat arsenic-contaminated soil requires a lot of research to further explore the effect of biochar on soil arsenic in specific areas to obtain effective biochar products. On the other hand, biochar remediation technology can not remove arsenic pollutants from soil or water, but can only reduce their toxicity. The synergistic remediation of arsenic pollution by phytoremediation technology can make up for the shortcomings of biochar remediation technology. Therefore, it is necessary to carry out the research on the synergistic remediation of arsenic pollution by plants and biochar, and expand the application of biochar in the remediation of soil arsenic pollution.

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