Study on Removal of Heavy Metal Pollution from Water by Biochar and Its Composite Materials

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Abstract. Heavy metal pollution is a long-term pollution problem that is difficult to control. Water microorganisms cannot directly degrade heavy metals, and heavy metals can produce mutual transformation, dispersion and enrichment in various forms in water. Adsorption is the most effective techniques to remove harmful heavy metals from water. Biochar (BC) and its composite materials, because of their simple and abundant source, abundant pore structure and unique surface chemical properties, are a new type of efficient adsorption material. Their technical development offers a new idea for solving the heavy metal pollution condition in water and preparing adsorbent required by adsorption method. In this paper, the preparation method of biochar and its composite materials, the mechanism and principle of heavy metals adsorption in water are reviewed, also development prospect of the biochar for application composite materials in the heavy metal pollution for treatment in the future is discussed.

Keywords: Biochar, Composite material, Water pollution, Heavy metal, Adsorption.

1. Introduction

Biochar is an emerging adsorbent used for the adsorption of pollutants derived from various kinds raw materials like industrial and agricultural wastes and biomass materials. It can be produced in the environment of hypoxia and less oxygen through a series of processes such as depolymerization, isomerization, decarboxylation, carbonization and dehydration. Biochar is a refractory, stable, highly aromatic and high-carbonization material characterized with high porosity, large specific surface area, strong adsorption, abundant raw materials, rich in oxygen functional groups. Many researches show that biochar has great potential and has attracted much attention from the industry. At present, the research about the heavy metals removable from wastewater with biochar mainly focuses on the selection of raw materials and reaction conditions of preparation, and has achieved a certain degree of development. Affected by material sources and pyrolysis conditions, the particle diameter of biochar can be as small as nanometer [1]. Compared with bulk biochar, nano-biochar has smaller pore size and larger specific surface area [2]. Nano-biochar as a new material has been used more and more in environmental governance.

Heavy metal pollution is a serious global problem, mainly caused by human factors such as wastewater irrigation and waste gas discharge. Heavy metal pollution is different from organic pollution. Heavy metals are enriched and cannot be degraded naturally in many environments. The harms of heavy metals in water not only depend on the types, physical and chemical properties of heavy metals, but also depend on the concentration, the valence state and form of heavy metals. Even when the concentration of some beneficial metal elements exceeds a certain extent value, it is absorbed by organisms and accumulates in the body to produce serious toxicity, causing animal and plant poisoning and even death. The accumulation and intensification of heavy metal pollutants in water directly affect people's daily drinking water safety and food production safety, so the impact on people's health is serious and significant. Therefore, it is urgent to find a method to effectively remove heavy metal pollutants from water.

Ion exchange, physical or chemical precipitation, solidification, and electrochemical removal can all be used for remediation of heavy metal pollution in water. However, these methods have certain disadvantages. For example, partial remediation will produce sludge; the removal process is too complicated and time-consuming, or requires high maintenance and use costs, which is still challenging in many aspects. In recent years, adsorption has become the alternative treatment technologies for effluent containing heavy metals. Adsorption technology has many advantages for example, high efficiency, simple design and convenient operation in terms of capturing heavy metal ions. It is one of the most generally used practical technologies on heavy metal pollution remediation. Biochar is considered to be one of the most promising materials in the study of various adsorbents. It has remarkable adsorption effect on arsenic, chromium, cadmium and other heavy metals.

2. Biochar

Biochar is a solid material with chemical stability high, thermostability and biological inertness generated after thermal cracking of biomass raw materials under low temperature (<800 °C) hypoxic (or anaerobic) conditions, and is recognized as a good adsorption material because of its rich pore structure, super-high specific surface area and more oxygen-containing functional groups [3].

The ability of biochar removable heavy metals is mainly determined by its physical and chemical properties, which are subject to the selection of raw materials and pyrolysis conditions. Biochar prepared under high temperature conditions can obtain rich porous structure and high specific surface area, while inappropriate pyrolysis temperature will lead to under-carbonization or over-carbonization of biochar, reduce the number of functional groups on its surface, and thus reduce the metal ions's adsorption site and biochar surface's ionic compounds [4]. Also, biochar for application in effluent treatment is also faced with a major problem. Biochar in water is prone to solid-liquid separation difficulties. Therefore, more and more scholars began to improve the biochar's basic physical and chemical properties by loading different composite materials, and studied and prepared new biochar composite materials with higher performance, new structure, and able to meet different needs, giving biochar more surface active sites.

2.1. Preparation Method

At present, there are many kinds of biomass raw materials used for the preparation of BC, mainly sludge by-products, crops and shellfish. BC prepared from sludge by-product has a rich pore structure with high aroma and durability at the same time, which can stably fix heavy metals on the surface. Solid carbon containing abundant functional groups can be prepared by crop pyrolysis to prepare BC, which have excellent removal performance for heavy metals. There are a lot of pore structures in the preparation of BC from shells, which can acquire a bigger specific surface area and show greater advantages when loading nZVI. In addition to the abundant raw materials available, biochar can be prepared by a variety of pyrolysis methods, which include slow or fast pyrolysis, hydrothermal carbonization and gasification [5]. The yield of biochar is affected by biomass raw materials, pyrolysis temperature, residence time, heating rate and raw material size. Guo P et al. showed that the biochar's yield was greatly affected by pyrolysis temperature, which was related to the pyrolysis temperature of cellulose and lignin in biomass [6].

Brewer found that the pyrolysis process of biochar can be divided into four phases: (1) In water loss stage, biomass materials lose free water and bound water; (2) In the pyrolysis stage of cellulose and hemicellulose, combustibles in biomass are pyrolyzed; (3) In the pyrolysis stage of lignin, chemical bonds in some functional groups of biomass break, aromatization, cyclization and other reactions occur to form highly aromatic structures; (4) In the carbonization stage, the carbon network structure is formed inside the biochar [7].

3. Biochar Composite Materials

Highly aromatic structure and abundant functional groups are the key reasons on the removal of water pollutants by biochar. However, in the process of high temperature pyrolysis, although the degree of self-aromatization is increased, part of surface functional groups is inevitably lost. In the cause of solving this problem, a large number of scholars are still trying to build up the biochar's physical and chemical properties and enhance its adsorption performance by increasing the functional groups and active biochar's surface sites. Therefore, biochar composites have attracted the attention of many scholars.

Biochar composite material is based on biochar, through physical, chemical and other methods to modify biochar or load some inorganic or organic compounds, so as to improve its adsorption performance of the composite material. The common biochar composite materials include inorganic composite materials, organic composite materials, magnetic composite materials, biochar modified materials and nano composite materials.

Biochar loaded with nanoscale zero-valent iron (nZVI/BC) in biochar-nanocomposites. nZVI has the advantages of large specific surface area, strong reactivity, cheap and easy to obtain, easy to recycle, environmentally friendly, etc. It is a kind of environmental pollution remediation material with great application potential, and has been widely concerned in heavy metal pollution control.

Many studies have found that the combination of nZVI with activated carbon and other carriers cannot only maintain the strong reduction characteristics of nano zero-valent iron, but also enhance more stable, which is more suitable to engineer operations. Biochar has good pore structure and large specific surface area, and the use of biochar loaded with nano-zero-valent iron is conducive to the uniform dispersion of nano-zero-valent iron doping in biochar, and the raw materials for preparing biochar are easy to obtain, low cost, and have good adhesion properties, so it is an environmentally friendly material full of research value [8].

3.1. Preparation Method

Biochar composite material is prepared by modifying biochar or loading some inorganic or organic matter through different physical and chemical methods, so as to improve its adsorption performance. Table 1 outlines the common preparation methods of these composites.

Table 1. Biochar composites for preparation method

Biochar composites	Preparation method	References
Inorganic composite materials	Impregnation, coprecipitation method, extraction filtration	[9,10]
Organic composite materials	Impregnation	[11]
Magnetic composite materials	Impregnation, liquid precipitation and hydrothermal synthesis	[12]
Biochar modified materials	Physical activation and chemical activation	[9]
Nano composite materials	Impregnation, loading, carbonization, Ball mill method, centrifugal method and ball mill - centrifugal method	[13,14]

Li et al. found that ZVI/BC can be prepared using pyrolysis-liquid phase reduction or one-step pyrolysis [15]. In liquid phase reduction method, biomass is first pyrolyzed to obtain BC, and BC is soaked in iron salt solution. Then, reducing agents such as sodium borohydride are used to reduce Fe(II) and Fe(III) in the solution to nZVI, and finally nZVI/BC is obtained. The materials prepared by this method have excellent adsorption properties, but the preparation is relatively complex and the cost is high. The one-step pyrolysis method is to soak the biomass directly in the iron salt solution, and then it is pyrolyzed to obtain BC, and the iron salt is reduced to nZVI, thereby preparing nZVI/BC. Compared with the pyrolysis-liquid phase reduction method, the material properties obtained by the

one-step pyrolysis method are relatively poor, but its operation is simple and the cost is low, which is suitable for large-scale industrial production.

Wang Pei's research found that iron or zinc nanoparticles biochar was prepared by preimpregnation method and characterized by nitrogen adsorption desorption apparatus, scanning electron microscopy, Fourier infrared spectrometer, small angle X-ray diffraction and X-ray photoelectron spectroscopy [16]. The results show that P-biochar has a higher specific surface area, and the modified Fe/Zn-biochar has a larger specific surface area and void content. There are crystal ions uniformly attached to the surface of biochar loaded with iron and zinc nanoparticles, which may be formed iron oxides and zinc oxides, which are more favorable for removing Pb from water.

4. Governance Mechanism

The treatment processes of biochar and its composite materials on heavy metals are produced by the integrated action of various adsorption mechanisms [17,18]. Including a series of coupled removal mechanisms: (1) Co-precipitation, where metals precipitate to form insoluble compounds; (2) Complexation, the complexation of the functional groups on the biochar's surface with the π electron rich region on the aromatic structure; (3) Surface Adsorption, the surface and porous structure of biochar can absorb heavy metal ions and fix; (4) Electrostatic Adsorption, the interaction between biochar surface and electrostatic metal; And (5) Ion Exchange, cation exchange between metal ions and protons or other alkali metals on the surface of biochar [19,20].

The intrinsic oxygen-containing anions of biochar and its compounds can fix the heavy metal ions through coprecipitation, and through the negative charge and functional groups on the surface of biochar, electrostatic adsorption or through complexation. Biochar has reductive activity and can reduce heavy metal ions in fixed oxidation states by electron transfer. However, in the actual reaction process, multiple reactions are often carried out together [21].

Li et al. found in studying the adsorption mechanism of nZVI/BC that As exists in the form of As(III) and As(V) in water [22]. When removing As (III), nZVI mainly first complexed As (III) with the surface of the material to form a complex. At the same time, nZVI reacted with oxygen in water to produce hydroxyl radical. Then the pre-formed As(III) complex is oxidized by hydroxyl radicals to As(V) complex, which is finally coprecipitated with biochar to form a more stable and less toxic complex.

Besides, Liu et al. [23] and Xu et al. [24] found biochar can first reduce Cr(VI) to Cr(III), and then fix by functional groups on the composite material or electrostatic adsorption to form cationic Cr(III). Cr often exists in the form of Cr(III) (chromate) and Cr(VI) (dichromate) anions in water. Compared with cationic heavy metals, the anionic heavy metals are more difficult to electrostatic adsorption with negatively charged surface biochar.

Li et al. found biochar loaded iron oxide composite material (iron oxide /BC), loaded on the surface of the γ-Fe_2O_3 and α-Fe_2O_3 iron oxide, that these functional groups can adsorption Cr(VI) through electrostatic adsorption and complexation [25]. In addition, since the substrate of BC itself can directly reduce Cr(VI) to Cr(III) under acidic conditions, it can be removed from the water by chemical precipitation. The Fe_3O_4, Fe0 and organic matter on the biochar surface can afford electrons for the reduction of Cr(VI) and remove Cr(VI) in the form of CrOOH precipitation.

During the adsorption process, there are many factors affecting the adsorption efficiency of heavy metal ions in aqueous solution, including internal and external ones. For example, the pore structure and surface functional groups of biochar and its composite materials are important internal factors affecting its adsorption efficiency. External factors such as temperature, pH value of solution, adsorbent concentration, solution for initial concentration of heavy metals, and adsorption time should also be taken into consideration [26]. Pore structure of the composite material determines the whole biochar's specific surface area. The sizeable specific surface area with the composite material is, the better its adsorption performance will be. In addition, after the chemical modification of the biochar surface by the functional group surface of the composite material, the oxygen-containing

functional groups, for example, -OH, -CO, -O-, -COOH, etc. on the surface of the biochar are changed, thus increasing the adsorption sites for heavy gold ions and improving the adsorption performance of the material [27].

5. Conclusion

Biochar and its composite materials have the advantages of larger specific surface area, and developed pore structure, and their removal efficiency of heavy metals in water is also extremely excellent. The large specific surface area gives it many active sites that come into contact with various chemicals. This allows biochar and its composites not only to deal with a single type of heavy metal pollution, but also deal with multiple heavy metal combination pollution and organic pollution simultaneously.

However, in terms of practical application, biochar composites still face many challenges: (1) the preparation of some composites, especially the preparation process of nano-biochar composites, needs further research, and can only be effectively put into use from small batch production to mass production. However, the preparation of high-quality and stable nanomaterials is still a big challenge. (2) Removal of biochar and its composite materials after adsorption of heavy metals is another difficult problem to be promoted to practical application. (3) Most studies on biochar composites are carried out in the laboratory, and their adsorption mechanisms and effects in the actual environment still need to be supplemented by further studies.

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