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# Exploring the Application Status of Iron-Modified Biochar to Remove Heavy Metals from Wastewater

**Yanjie Cao**[1],

**Keqi Qin**[2,*]

**and Yueqi Tian**[3]

[1]College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an City, Shanxi Province ,710300, the People's Republic of China

[2]College of Environment and Ecology, Hunan Agricultural University, Changsha City, Hunan Province,410128, The People's Republic of China

[3]College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang City, Hebei Province, 050024, the People's Republic of China

*Corresponding author: qkq62418024@stu.hunau.edu.cn

**Abstract:**

With the rapid development of industrialization, the degree of heavy metal pollution in water bodies has continued to increase, seriously threatening the ecosystem, human health and social development. As an efficient heavy metal adsorption material, iron-modified biochar not only inherits the advantages of the original biochar such as wide sources and developed pore structure, but also enhances the adsorption active sites on the surface of the material through iron modification, effectively overcoming the shortcomings of the original biochar in terms of adsorption capacity and selectivity. Therefore, iron-modified biochar has attracted widespread attention in the field of wastewater treatment in recent years. This paper aims to analyze the preparation method and structural characteristics of iron-modified biochar, and deeply analyze its removal mechanism for heavy metals. At the same time, this paper also discusses the challenges faced by iron-modified biochar in practical applications and looks forward to its application prospects and research directions in heavy metal pollution control. The analysis of this paper can provide an important reference for the application of heavy metal pollution control in water bodies.

**Keywords:** iron-modified biochar, heavy metal pollution, adsorption mechanism, synergistic effect.

## 1. Introduction

Having a healthy living environment is an important foundation for human survival and development. However, with the rapid development of industrialization and urbanization, the discharge of a large amount of untreated or substandard industrial wastewater is increasing. At present, heavy metal pollution has become one of the serious problems facing the global environment. Its main pollutants include lead, mercury, cadmium, etc. Heavy metals are highly toxic and non-degradable. They can be enriched and bioaccumulated through the food chain, posing a serious threat to humans and the entire ecosystem[1]. Such environmental problems are becoming increasingly serious, triggering widespread attention to efficient governance methods. Therefore, it is of great significance to develop efficient and environmentally friendly wastewater heavy metal treatment technologies.

Although traditional heavy metal removal methods have certain effects, they generally have defects such as high cost, high energy consumption, easy-to-produce secondary pollution or insufficient selectivity. In recent years, biochar, as a green adsorption material, has the characteristics of wide raw material sources, simple operation and good adsorption performance, and has been widely used to remove heavy metals in wastewater[2]. However, the adsorption capacity and selectivity of raw biochar for heavy metals are still limited by the limitations of its surface chemical properties and pore structure[3]. In order to improve the treatment capacity of biochar materials, researchers have introduced modification methods, among which iron-modified biochar can not only enhance the adsorption active sites of the material but also achieve efficient recovery through magnetic separation. At the same time, the redox reaction between iron-based components and heavy metals further broadens its application potential[4][5]. Wei et al. found that iron-modified biochar can effectively remove metal-cyanide complexes in wastewater through chemical precipitation and hydrogen bonding between functional groups and complexes. The study showed that the maximum adsorption capacity of iron-modified biochar for [Fe(CN)6]3- and [Ni(CN)4]2- can reach 580.96 mg/g and 588.86 mg/g, respectively[6].

Therefore, based on the comprehensive research at home and abroad, this paper systematically analyzes the current research status, reviews the preparation method, structural characteristics and removal mechanism of heavy metals in wastewater by iron-modified biochar, and combines the main factors affecting the removal effect to explore the challenges of the current practical application of iron-modified biochar in wastewater, and looks forward to the application potential and research direction of biochar, which provides an important reference for the treatment and application of biochar for heavy metal pollution in water bodies.

## 2. Current status of research on heavy metal removal from wastewater

At present, the treatment technologies for heavy metal wastewater can be mainly divided into three categories: physical, chemical and biological. The physical method is represented by membrane separation, and its core is to separate pollutants through physical interception or surface adsorption, but due to the high treatment cost and poor selectivity, it limits large-scale application. Chemical methods are mainly chemical precipitation and oxidation-reduction, but they are prone to secondary pollution and have limited removal efficiency for low-concentration heavy metals. Biological methods rely on the metabolism of microorganisms or plants to fix or transform heavy metals. Although they are environmentally friendly, they have a long treatment cycle and poor tolerance to highly toxic wastewater. The many limitations of traditional technologies have led researchers to explore more efficient and environmentally friendly alternatives. In recent years, the rise of biochar technology has provided new ideas for the removal of heavy metals in wastewater.

Biochar has been applied to the removal of heavy metal pollutants from different polluted water bodies due to its advantages such as low cost, simple preparation process, rich pore structure and strong adsorption capacity. However, its native form has insufficient adsorption capacity and selectivity for heavy metals, so the relevant properties of biochar can be significantly improved through iron modification. On the one hand, the loading of iron oxides not only enhances the magnetic properties of the material and facilitates material recovery, but also strengthens chemical adsorption through the coordination of surface hydroxyl groups with heavy metals; on the other hand, the reducibility of iron species can reduce the more toxic Cr(VI) and As(V) to low-toxic states (such as Cr(III) and As(III)), and the $Fe^{2+}/Fe^{3+}$ hydrolysis products generated can further fix heavy metals through co-precipitation. Studies have shown that the adsorption capacity of iron-modified biochar for Cd(II) can reach 2.67 mg/g, and the removal rate reaches 66.86%, which is significantly improved compared to the removal efficiency of unmodified biochar[7].

## 3. Preparation and structural characteristics of iron-modified biochar materials

### 3.1 Preparation method

The preparation methods of iron-modified biochar mainly include the liquid phase reduction method, co-precipitation method, hydrothermal mixed carbonization method, etc.

#### 3.1.1 Liquid phase reduction method

The liquid phase reduction preparation method of iron-modified biochar is a method of loading iron species on a biochar carrier in a liquid phase system by chemical reduction.[8]

The advantages of the liquid phase reduction method are

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mild preparation conditions, simple operation, and high selectivity. Yan et al. prepared porous biochar by pyrolyzing rice husks under anoxic conditions and then added 5.0 g of ferrous sulfate heptahydrate solution and 1.0 g of biochar into a three-necked flask and stirred them thoroughly. A certain amount of potassium borohydride($KBH_4$)and sodium dithionite($Na_2S_2O_4$)were added dropwise to the solution using the co-sulfurization method. The solution was stirred vigorously for 2 hours, and then washed with deoxygenated ultrapure water and deoxygenated ethanol and vacuum dried to obtain the S-nZVI/BC composite material[9].Wang et al. also used the liquid phase reduction method to add hexahydrated ferrous sulfate, sodium borohydride aqueous solution, hexahydrated nickel nitrate, and palladium dichloride to the basic biochar made of coconut shell particles under anoxic conditions, and prepared innovative biochar particles containing nanocrystalline NZVI, Fe/Ni, and Fe/Pd, respectively, which improved the enrichment and adsorption capacity of the material[10].These studies show that the liquid phase reduction method can effectively achieve nanoscale dispersion and composite modification of iron species and improve the adsorption and catalytic properties of biochar. However, the liquid phase reduction method also has its shortcomings. It causes serious environmental pollution and some reagents are toxic. For example, the decomposition of sodium borohydride may produce borate pollution.

#### 3.1.2 Coprecipitation

The chemical co-precipitation method is to mix a metal salt solution with a precipitant (such as NaOH, $NH_4OH$) to generate a composite oxide, which is used for biochar modification to enhance its adsorption and catalytic functions.

This method can evenly load metals and their oxides on the surface of biochar, thereby increasing the specific surface area and the number of active sites of the material. For example, Feng et al. used the chemical coprecipitation method to construct a new double-layer biocarrier, reacting $Mn^{2+}$ with an oxidant under alkaline conditions to generate manganese oxide nanoparticles that were loaded on the surface of biochar, increasing the specific surface area and active sites[11]. Similarly, Ye et al. used $Fe^{2+}$ and $Na_2S$ to react to generate $FeS_2$ for biochar modification, evenly loading iron and sulfur on the biochar surface, increasing the reaction sites and enhancing the arsenic removal capacity[12].

#### 3.1.3 Hydrothermal mixed carbonization method

Hydrothermal carbonization (HTC) is an integrated technology that combines biomass raw materials with the iron salt solution in a high-temperature and high-pressure hydrothermal environment to simultaneously complete biomass carbonization and iron species loading. This method has the advantages of simple process, low energy consumption, and good iron dispersion, and is particularly suitable for the fields of environmental remediation and resource utilization.

As a green and efficient biomass conversion method, it has shown broad prospects in the fields of environmental remediation and energy recovery in recent years. The process regulation and reaction mechanism analysis of hydrothermal mixed carbonization technology are the key to improving the performance of biochar. Tan et al. hydrothermally mediated in situ nitrogen doping of lees biochar increased its oxygen reduction reaction activity by 2.3 times, which was attributed to the synergistic enhancement of electronic conductivity by pyridine-N/graphite-N[13]. Wu et al. treated wine lees by a one-step hydrothermal method and found that increasing the temperature (180–250°C) can increase the yield of carbon quantum dots and biochar, but exceeding 220°C will reduce the fluorescence performance of carbon quantum dots due to excessive carbonization, proving that the process parameters need to be precisely controlled[14]. Although HTC technology has broad prospects, current research still faces challenges such as poor product uniformity and high process energy consumption, and its sustainability remains controversial. For example, Seo et al. pointed out that the ash content (8-25%) of crop residue charcoal will irreversibly reduce the life of fuel cell catalysts[15]. Future research can focus on the development of green modifiers, the synergy of multiple technologies (such as HTC-gasification co-production of hydrogen energy and high value-added carbon materials), and the construction of a full life cycle sustainability assessment system based on machine learning.

### 3.2 Structural characteristics

The structural properties of iron-modified biochar include pore structure, surface morphology and surface functional groups.

Iron-modified biochar is mainly optimized through chemical activation or physical pore formation to optimize the pore structure. For example, Guo Qi et al. used a scanning electron microscope (SEM, GeminiSEM 500, Carl Zeiss, Germany) to observe the surface morphology and microstructure of the material and found that with the increase of pyrolysis temperature and iron loading, the surface of biochar changed from smooth to wrinkled, which increased the specific surface area and promoted the formation of micropores and mesopores[16]. However, through SEM characterization of the morphological characteristics of the original biochar and iron-modified biochar, it can be seen that if the iron loading is too high, the specific surface area will decrease due to iron compounds entering the pores and blocking them[17].

Through iron modification, its performance can be further optimized, and the surface morphology changes significantly at the physical and chemical levels. From a physical point of view, SEM analysis shows that iron-modified biochar has a significant pore structure at the nanoscale. Some small pores may merge to form large pores, increasing the pore size, and the number of some micropores increases. The pore size distribution is at the nanoscale, with a large specific surface area. These characteristics are conducive to the generation of adsorption sites, thereby improving the adsorption performance of iron-modified biochar.

In terms of chemical properties, TEM analysis reveals the dispersion and crystallization state of the modifier iron in the carbon matrix. There are iron-enriched areas inside the iron-modified biochar. The iron element on the surface promotes the formation of oxygen-containing functional groups on the surface of the biochar, enhances the surface polarity, improves the affinity for polar pollutants, and gives the biochar higher reactivity and adsorption selectivity. The formation of these areas affects the overall redox properties and catalytic activity of the biochar, expanding its application in wastewater heavy metal treatment. For example, the green iron-modified calcium-based biochar developed by Jiao Xiangfei (2024) significantly reduces the mobility of Cu, Zn, and Pb in mining soils through ion exchange and surface complexation[18].

Through iron modification, the surface chemical environment of biochar can be reconstructed, and its surface functional groups will undergo significant changes, increasing the adsorption and catalytic capabilities of biochar and improving the removal efficiency of heavy metal ions. Chen Lei et al. found that when Fe3O4 was used to modify biochar, Fe3+ reacted with the oxygen-containing groups of carbonized wood, and a certain amount of hydroxide ions were formed around it, which improved the hydrophilicity of the material[19]. In addition, it was found through research that the iron element in iron-modified biochar mainly exists in the form of Fe3+ and Fe2+, and the number and types of oxidizing functional groups on its surface increased significantly, allowing the material to adsorb more heavy metal ions while strengthening the fixation of heavy metal ions through complexation, precipitation and other effects[8,20].

# 4. Removal mechanism

In wastewater, the removal mechanisms of heavy metals include the adsorption mechanism, reduction mechanism, and adsorption-reduction synergy.

## 4.1 Adsorption mechanism

Biochar itself has a rich pore structure and a large specific surface area, which provides adsorption sites for heavy metals and can intercept heavy metal ions through physical adsorption. The iron and its oxides introduced during the modification process further optimize the pore distribution of biochar and enhance the physical adsorption capacity of the material. Cill et al. used nano-zero-valent iron to modify orange peel powder biochar to treat hexavalent chromium in water. Characterization found that the surface of biochar modified with nZVI was rougher than that of unmodified biochar, and the porosity and effective surface area were significantly increased[21]. The surface charge of iron-modified biochar in solution is regulated by pH, and heavy metal ions can be adsorbed electrostatically. Hu et al. found that under acidic conditions, Cr(VI) mainly exists in the form of negatively charged HCrO4- and is adsorbed on the surface of the material by electrostatic attraction[22]. The surface of iron-modified biochar is rich in oxygen-containing functional groups, such as carboxyl and hydroxyl groups. These functional groups can exchange with heavy metal ions and undergo complexation or form hydrogen bonds to achieve large-scale adsorption, thereby reducing the heavy metal content[23].

## 4.2 Reduction mechanism

The conversion of Fe(II) and Fe(III) valence states in iron oxides in iron-modified biochar triggers redox reactions, reducing high-valent heavy metals to low-toxic or stable valence states through electron transfer, and then complexing with surface oxygen-containing functional groups to fix the reduction products through coprecipitation. For example, nano-zero-valent iron (nZVI)-loaded biochar can reduce highly toxic Cr(VI) to low-toxic Cr(III) through direct electron transfer, while $Fe^{2+}$ generated by $Fe^0$ oxidation further participates in the reduction reaction to form $Fe^{3+}$-$Cr^{3+}$ hydroxide coprecipitation[24]. Under acidic conditions, the dissolution of $Fe^{2+}$ and the pore adsorption of biochar synergistically broaden the pH adaptability of the reaction. Iron modification can also achieve material recycling through magnetic recovery, taking into account both economic efficiency and environmental friendliness. In the future, it is necessary to further explore the valence state distribution of iron species, the interfacial electron transfer pathway, and the influence mechanism of competing ions in complex water bodies to promote engineering applications.

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### 4.3 Adsorption-reduction synergistic effect

Adsorption-reduction synergistic effect refers to the simultaneous adsorption and redox reactions when biochar removes heavy metal pollutants, forming a synergistic effect.

First, heavy metal ions are enriched on the surface of the material or enter the pores through electrostatic attraction, and some are intercepted. The heavy metal ions on the surface undergo valence transformation at the active sites of $Fe^{2+}$ and $Fe^{3+}$. The low-valent metals (such as $Cr^{3+}$ and $As^{3+}$) produced by reduction are more likely to form stable complexes with oxygen-containing functional groups due to the increase in charge density, or to be stabilized by co-precipitation. For example, Wu et al. revealed that biochar composites remove methylene blue through the synergistic effect of adsorption and reduction, with a total removal rate of 96.5%, an increase of 37%[25].

## 5. Challenges and Prospects

### 5.1 Challenges

In practical applications, the performance of iron-modified biochar in removing heavy metals is affected by a variety of environmental and process parameters, including modification methods, solution pH, heavy metal ion concentration, and coexisting ions, as follows.

Different iron modification methods will affect the structure and properties of iron-modified biochar, thus affecting its removal effect on heavy metals. For example, the iron element in the iron-modified biochar prepared by the impregnation method is mainly present in the form of load, while the iron element in the iron-modified biochar prepared by the co-precipitation method may be more evenly distributed on the biochar surface in the form of iron oxides. Therefore, the iron-modified biochar prepared by the co-precipitation method may have better adsorption and reduction properties.

The pH value of the solution has an important influence on the effect of iron-modified biochar in removing heavy metals. Under acidic conditions, the functional groups on the surface of iron-modified biochar are easily protonated and positively charged, which is conducive to the adsorption of negatively charged heavy metal ions; at the same time, acidic conditions are also conducive to the reduction reaction of iron oxides. Under alkaline conditions, the functional groups on the surface of iron-modified biochar are easily deprotonated and negatively charged, which is not conducive to the adsorption of heavy metal ions; and alkaline conditions may cause iron oxides to precipitate, reducing their reduction activity.

The concentration of heavy metal ions affects the adsorption and reduction process of iron-modified biochar. When the concentration of heavy metal ions is low, the adsorption sites on the surface of iron-modified biochar and the reduction activity of iron oxides can meet the needs of heavy metal removal; when the concentration of heavy metal ions is high, the adsorption sites and reduction activity may reach saturation, resulting in a decrease in removal efficiency.

There are often multiple coexisting ions in wastewater, which may compete with heavy metal ions for adsorption sites on the surface of iron-modified biochar, thereby affecting the removal of heavy metals. For example, divalent cations such as calcium ions and magnesium ions may compete with heavy metal ions for adsorption sites, reducing the adsorption of heavy metals.

The stability and activity regulation mechanism of iron species is not yet clear. Although iron oxides can impart magnetic and reducible properties to biochar through chemical precipitation or pyrolysis loading, iron is easily dissolved or passivated in complex water, resulting in a decrease in adsorption capacity after recycling.

Large-scale application faces technical and economic bottlenecks. The iron modification process has high preparation costs, high energy consumption (pyrolysis temperature needs to be 500-700℃), high recycling and regeneration costs, and capacity decreases after multiple cycles. The regeneration method may destroy the material structure, and low-cost iron sources need to be developed.

### 5.2 Outlook

In the future, the study of iron-modified biochar can use in-situ characterization techniques (such as XANES and EXAFS) to reveal the dynamic coupling relationship between the evolution of iron species valence and heavy metal adsorption/reduction, especially the influence of $Fe^{2+}/Fe^{3+}$ cycles on electron transfer efficiency. And it is necessary to leap from laboratory to engineering and clarify the applicable boundaries under different water quality conditions by establishing a standardized performance evaluation system (such as ISO/TC 282). At the same time, expand its application in emerging scenarios such as soil-water complex pollution remediation and heavy metal resource recovery, and truly achieve the sustainable development goal of “waste treatment with waste”. In addition, it is necessary to strengthen life cycle assessment (LCA) research. Listing Hao et al. analyzed the resource utilization path of tea residue biochar, established a “raw material-modification-application-regeneration” full-chain carbon footprint model, and promoted its inclusion in the carbon neutrality strategy[26]. Quantify the carbon emissions and resource consumption of the entire process from biomass raw material acquisition, and modification preparation to waste disposal, and promote the development of green preparation processes (such as solar-assisted pyrolysis) and regeneration technologies (such as acid washing-magnetic separation combined regeneration).

## 6. Conclusion

This paper mainly studies how to use iron-modified biochar to remove heavy metals from wastewater, three methods for preparing iron-modified biochar, the removal mechanism of heavy metals in wastewater, and the influencing factors of iron modification methods. There are many advantages to modifying biochar using liquid phase reduction, chemical coprecipitation and hydrothermal mixed carbonization. On the basis of adsorption mechanism and reduction mechanism, the adsorption-reduction synergy is established to greatly improve the efficiency of heavy metal removal. Iron-modified biochar also faces many challenges, and many factors will affect its effect on removing heavy metals. Large-scale application faces economic bottlenecks, and economical iron sources need to be developed in the future. In the future, with the help of in-situ characterization technology and strengthening life cycle assessment, the transition from laboratory to engineering and green preparation technology can be achieved.

Authors Contribution
All the authors contributed equally and their names were listed in alphabetical order.

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