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Preparation and Application Analysis of Iron-based Bimetallic Composite Materials Loaded on Waste Biomass Charcoal

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Abstract. In recent years, the problem of environmental pollution has become increasingly severe. This article analyzes the literature on waste-based carbon-loaded iron-copper (Fe-Cu) and iron-manganese (Fe-Mn) bimetallic composite materials in recent years, and discusses the current research status of recovering metals from waste and combining them with biomass. The analysis reveals that although the approach of "using waste to treat waste" for the preparation of catalytic or adsorption materials is theoretically very attractive, in practical applications, due to the complexity of the components of the experimental substances, the performance of the materials fluctuates significantly, and different metal composite materials exhibit different properties. After research, it was found that the Fe-Mn system demonstrated greater adaptability in the process of oxidation degradation, while the Fe-Cu system had a greater advantage in specific reduction reactions. This article summarizes the existing preparation methods and application fields, and focuses on comparing the properties of the composite materials made from Fe-Mn and Fe-Cu iron-based binary metals and waste biomass char. This article points out that although most current research is still at the laboratory stage, this system has remarkable practical applicability and a promising future.

Keywords: Waste biomass charcoal, Bimetallic composite material, Fe-Cu , Fe-Mn

1. Introduction

With the widespread adoption of the concept of circular economy, the recycling and reuse of agricultural and forestry waste and industrial waste metals has become a research hotspot in the field of environmental functional materials. Studies have shown that over 10 million hectares of farmland in China are contaminated by heavy metals, accounting for more than 8% of the total farmland area. As a result, the grain output has decreased by approximately 10 billion kilograms [1]. The concentration of heavy metals in the ocean, such as copper, has exceeded the natural level since 2500 BC. In recent years, with the rapid development of industry, the problems of water quality pollution by heavy metals and organic pollutants have become increasingly severe.

Biochar is a porous solid material obtained by pyrolyzing biomass. Due to its porous structure and active chemical properties, it possesses a variety of oxygen-containing functional groups and an

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extremely large specific surface area. This property usually has a very good adsorption capacity for heavy metals, and the numerous pores also make it an ideal carrier for loading metal active sites. Recent studies have no longer focused solely on the treatment of heavy metal and organic pollutant pollution through single biomass carbon. Instead, they have developed biomass carbon loaded with metals such as iron, copper, and manganese to form iron-based dual-metal complexes. The degradation ability of Fe-Cu for organic substances is better demonstrated in the combination with biomass charcoal. The Fe-Mn composite material also significantly enhances the adsorption capacity of heavy metals, thereby improving the treatment of heavy metal in wastewater. This type of biomass carbon composite material has been applied by many scholars in the treatment of heavy metal pollution adsorption and the degradation of organic pollutants in wastewater.

This study investigated the different preparation processes and methods of biomass carbon and Fe-Mn and Fe-Cu bimetallic composite materials. Firstly, it longitudinally compared the differences in the adsorption capacity of different biomass carbon and Fe-Mn metal composite materials obtained through different preparation methods. It also focused on comparing the advantages and disadvantages of the Fe-Cu composite materials obtained through different preparation methods in terms of organic pollutant degradation. Finally, a horizontal comparison was made between the Fe-Mn composite materials and the Fu-Cu materials in terms of their advantages and disadvantages in the treatment of heavy metal pollutants and organic pollutants. It was concluded that when these two systems work together in wastewater treatment, the effect will be enhanced to a great level which $1 + 1 > 2$.

2. Materials and manufacturing methods

In the preparation of Fe-Cu composite materials with biomass carbon, the most commonly used method nowadays is pyrolysis. In terms of raw material selection, this method mainly uses agricultural and forestry wastes (such as straw, sludge, fruit shells, etc.) as carbon sources. After drying and grinding, they are used as raw materials for the preparation of biochar from biomass. Subsequently, iron and copper salts (such as $FeSO_4$, $FeCl_3$, $CuSO_4$, etc.) were introduced. Through the impregnation method, the metal ions were fully adsorbed or complexed onto the surface of the biomass [2, 3]. Some studies further employed co-precipitation or bioleaching methods to enable Fe and Cu to deposit in situ on the carbon matrix, thereby enhancing the dispersion and bonding strength [4]. During the thermal conversion stage, the Fe-Cu-biomass carbon was subjected to pyrolysis under an inert atmosphere (such as nitrogen) at temperatures ranging from 300 to 800°C [2, 5]. During this process, the biomass was transformed into porous biochar, and at this time, the iron and copper salts underwent reduction or oxidation, forming zero-valent iron (Fe^0), iron oxides, or Fe-Cu bimetallic particles, which were uniformly loaded on the surface or pore structure of the carbon. Most researchers obtained the processed raw materials and adopted a one-step method, that is, mixing the biomass with metal salts and directly pyrolyzing them, which simplified the process flow and promoted the formation of the bimetallic cooperative structure [5]. This method has an extremely simple preparation process, but its drawbacks are also quite obvious. The extreme uncertainty in factors such as temperature and environment during the reaction process makes it difficult to fully demonstrate the catalytic and adsorption properties of the product. To optimize the material performance, various control methods have also been developed. Table 1 indicates that the hydrothermal method can achieve uniform loading at lower temperatures and enhance the dispersion of metals [6]; the ball milling method promotes the close combination of metals and carbon through mechanical force; acid washing or activation treatment (such as KOH activation) is used to increase

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the specific surface area and pore structure [4, 6]. Some studies also achieve synergistic enhancement of electron transfer and catalytic activity by controlling the ratio of Fe/Cu [1, 2].

Table 1. Preparation of biomass char Fe-Cu composite materials

Preparation method	Key steps	Method characteristics	Advantages	Limitations
Impregnation -Pyrolysis Method	Preparation of biomass carbon → Fe/Cu salt impregnation → High-temperature pyrolysis	Typical dual-metal loading process	Process mature; good catalytic performance of dual metals	Metal particles are prone to agglomeration, and dispersion is limited
Biological Leaching Method	Microbial leaching of metals → Loading onto biochar	Green synthesis method	High metal dispersion; environmentally friendly	Process complex; preparation cycle long
Impregnation -Activation Method	Fe salt impregnation → Pyrolysis → Activation treatment	Traditional preparation method	Simple operation; low cost	Only single metal, limited catalytic performance
One-step Pyrolysis Method	Combination of biomass and metal salt direct pyrolysis	Process integration	Flow simple; suitable for large-scale production	Uniformity of metal distribution difficult to control

In the preparation of Fe-Mn composite materials with biomass carbon, the selection of raw materials also adopts agricultural and forestry wastes (such as mulberry branches, straw, etc.) as the carbon source. After drying and grinding, they are used to prepare biomass carbon [7, 8]. The metals used are Fe^{2+}/Fe^{3+} and Mn^{2+} salts (such as $FeCl_3$, $MnCl_2$ or $KMnO_4$, etc.), and are introduced into the system by the impregnation method [7, 9]. Among them, the traditional impregnation method can cause metal ions to be adsorbed on the surface of biomass. However, to improve the dispersibility, some studies have adopted the co-precipitation method, where Fe and Mn are in situ generated as hydroxides or oxides under alkaline conditions [6]. After processing the raw materials, the mixture is commonly formed into biomass char and Fe-Mn composites using pyrolysis and hydrothermal methods. Pyrolysis is a process in which the impregnated biomass is carbonized under an inert atmosphere (300–800°C), simultaneously converting Fe/Mn into oxides or forming structures such as $MnFe_2O_4$ (crystalline spinel) to enhance the stability and magnetism of the material [6]. In contrast, the hydrothermal method is carried out at a lower temperature (<200°C), allowing Fe–Mn oxides to grow in situ on the surface of the biomass carbon, which is beneficial for maintaining the surface functional groups of the carbon material and improving structural homogeneity [10].Unlike the traditional pyrolysis method, the ball milling method promotes the close combination of Fe–Mn oxides and biochar through mechanical force, thereby significantly increasing the specific surface area and the number of active sites [8]; the chemical activation method (such as $KMnO_4$ oxidation or the introduction of cross-linking agents) can construct abundant oxygen-containing functional groups on the surface of the carbon, enhancing adsorption and catalytic performance [9]. Some of the latest studies have also incorporated methods such as sol-gel to achieve precise control of nano-scale structures [11].

3. Performance comparison

The Fe-Mn composite materials prepared by different methods have different adsorption properties. Table 2 compares the adsorption performance of Fe-Mn biomass carbon composite materials obtained by different preparation methods for heavy metals. It can be seen that the preparation method has a significant impact on the adsorption capacity of the materials. The material prepared

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by the traditional impregnation-thermal decomposition method has the maximum adsorption capacity of Cd^{2+} of 95.23 mg/g, which is at a relatively low level. [7, 9]. However, after adjusting the Fe/Mn ratio and optimizing the pyrolysis conditions, the adsorption capacity of the material for Pb^{2+} could be significantly increased to 180.7 mg/g. This result indicates that the metal ratio and structural regulation play a crucial role in performance [10]. The adsorption capacity of the $KMnO_4$ chemically modified material was 88.49 mg/g, although it was slightly higher than the basic method, it was still lower than the system with optimized structure. [8, 11] This shows that simply introducing surface functional groups has limited effect on the improvement of adsorption performance, while the construction of the crystal structure (such as $MnFe_2O_4$) plays a dominant role in enhancing the adsorption capacity.

Table 2. Comparison of adsorption performance of Fe–Mn biomass carbon prepared by different methods

Preparation method	Material type	Heavy metal	Maximum adsorption capacity (mg/g)
Impregnation - pyrolysis method	FMBC	Cd^{2+}	95.23
Optimization of pyrolysis (proportion regulation)	FMBC60	Pb^{2+}	180.7
Optimization of pyrolysis (proportion regulation)	FMBC60	Cd^{2+}	83.4
$KMnO_4$ chemical modification	Mn/Fe-BC	Pb^{2+}	88.49
Oxide modification	BC-FM	Cd^{2+}	141.1

In the research on the composite material system of Fe-Cu and biomass carbon, we found that its catalytic properties exhibited outstanding performance. Its ability to adsorb heavy metals was relatively weaker than its catalytic ability, but it still had research value. The adsorption capacity of heavy metals was generally in the range of 50-120mg/g. Because Cu mainly participates in the transfer of electrons and does not form a stable precipitation structure, the Fe-Cu system is often focused on studying its degradation ability rather than adsorption ability. From Table 3, we can see that different preparation methods resulted in Fe-Cu that is applicable for the degradation of different organic pollutants. Especially in the treatment of corresponding organic pollutants, this material can often achieve a 100% degradation of the pollutant.

Table 3. Comparison of the ability of Fe-Cu/biomass carbon to degrade organic pollutants by different methods

Preparation method	Material type	Contaminant type	Degradation efficiency/capacity	Reaction time	Key performance indicators
MOF-derived pyrolysis method	Fe–Cu@biochar	Tetracycline (TC)	>99%	20 min	Adsorption capacity 192.3 mg/g; k = 0.291 min^{-1}
Solvothermal-gel method	Cu–Fe@CS aerogel	Formic acid (FA)	Highly efficient degradation (superior to single metal)	—	Activation energy reduction (synergistic catalysis)
Single-step impregnation-pyrolysis method	Fe–Cu/BC	Dye (MB)	Significant removal	—	High Fe^{2+} content → Enhanced Fenton activity
Metal loading + Fenton system	Fe/Cu-BC + H_2O_2	Pesticide (2,4-D)	Removal rate close to complete	60 min	Reaction rate increased 3-5 times
Adsorption-catalysis coupling construction	Fe–Cu dual-site material	Antibiotic (TC)	98.5% (cyclic stable)	300 min	Energy consumption reduced by 70.8%

Figure 1 shows a horizontal comparison of the heavy metal adsorption capabilities of the Fe-Mn composite material and the Fe-Cu biomass carbon, as well as the Fe-Mn composite material and the

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Fe-Cu biomass carbon. In general, the adsorption capacity of the Fe-Mn system is significantly superior to that of the Fe-Cu system, and its maximum adsorption capacity can reach over 180 mg/g.

This difference mainly stems from the different mechanisms of action of the two systems. The Fe-Mn material can achieve multiple functions such as surface complexation, ion exchange, and precipitation by forming stable structures like $MnFe_2O_4$, thereby significantly enhancing the ability to fix heavy metals; while the Fe-Cu system mainly relies on Fenton-like reactions and electron transfer processes, and is more suitable for the degradation of organic pollutants. Its adsorption capacity for heavy metals is relatively limited. Therefore, in applications aimed at controlling heavy metal pollution, the Fe-Mn system has a greater advantage.

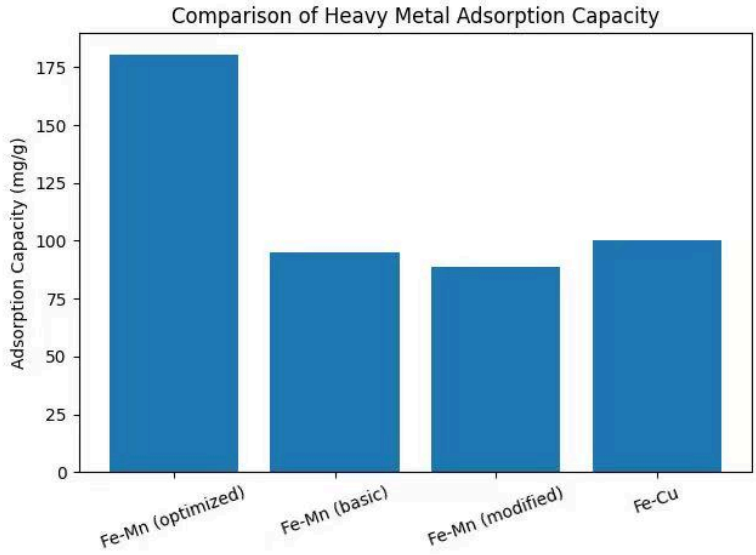

Figure 1. Comparison of adsorption capabilities of different material systems for heavy metals(picture credit : original)

4. Mechanism and application scenarios of biomass char-loaded iron-based bimetallic composites

The properties of the Fe-Cu composite material with biomass carbon mainly lie in its ability to adsorb and treat heavy metals. The main mechanism is that Mn-OH, Fe-OH combine with heavy metals to form internal coordination bonds on the surface, then undergo precipitation to form Mn/Fe hydroxides or metal precipitates, and finally, Mn^{2+}/Fe^{3+} exchange with the pollutant ions. The strong adsorption and stable fixation properties of this material make it widely used for the removal of heavy metals. Its essence is an "adsorption-dominated" material. The core mechanism of Fe-Cu in the biomass carbon composite material is to generate free radicals through the Fenton reaction and the similar Fenton reaction($Fe^{2+} + H_2O_2 \rightarrow \cdot OH$). The addition of Cu promotes the electron cycle, leading to the formation of multiple active oxygen species, thereby degrading organic pollutants in wastewater. Essentially, it is a "catalyst-driven type" material. Furthermore, the Fe-Cu system also exhibits surface adsorption properties, although it is slightly weaker than the Fe-Mn system. However, it still makes significant contributions to the enrichment of pollutants by biomass carbon. In practical applications, these two types of materials have their own advantages and disadvantages, and their applications in environmental remediation have a distinct complementary nature. Table 4 is the comparison of Fe-Mn and Fe-Cu systems.

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Table 4. Comparison of Fe-Mn and Fe-Cu systems

Comparison	DimensionFe–Mn/Biochar	Fe–Cu/Biochar
Dominant Mechanism	Adsorption + Precipitation + Complexation	Catalytic Oxidation (Fenton)
Pollutant Type	Heavy Metals	Organic Pollutants
Key Active Species	Mn–OH, Fe–OH	·OH, O_2^-, $^1O_2$
pH Adaptability	Neutral is better	Acidic is better
Stability	High	Medium
Reaction Rate	Moderate	Fast
Renewability	Difficult	Easy to Regenerate

The iron-copper system is commonly used in the treatment of organic pollutants, such as antibiotic wastewater, dyeing wastewater, and pesticide residue. In practical engineering, it can rapidly mineralize difficult-to-degrade organic substances like tetracycline and methylene blue. It is suitable for pharmaceutical wastewater treatment plants and deep treatment units in industrial parks, and has the advantages of a fast reaction rate and continuous operation. In contrast, the iron-manganese system is more suitable for the remediation of heavy metal pollution, such as the remediation of water and soil contaminated by Cd^{2+} and Pb^{2+}. In applications, this material is often used in adsorption reactors, permeable reactive barriers (PRB), or soil passivators. For example, in the remediation of heavy metal pollution in mine wastewater and farmland, iron-manganese biomass charcoal can significantly reduce the bioavailability of heavy metals and has the characteristics of high stability and environmental friendliness.

5. Existing issues and challenges

Although current research has revealed that waste biomass carbon and iron-based bimetallic composite materials possess many favorable properties, this system still has shortcomings and deficiencies. For instance, the stability and metal leaching issues of the Fe-Cu and biomass carbon composite materials remain significant factors restricting their application. During the Fenton-like reaction process, this system is prone to the release of metal ions (such as Cu^{2+} and Fe^{3+}), which may cause secondary pollution. In acidic or complex water bodies, the Fe-Mn system may also release Mn^{2+}, which affects environmental safety. Therefore, improving the stability and structural robustness of metal loading remains an important research direction. Regarding reaction conditions, this system is highly dependent. The Fe-Cu system usually requires acidic conditions (pH 3–5) to maintain efficient Fenton reactions, but the actual wastewater pH fluctuates greatly, and the instability of the actual situation increases the operating costs and control difficulty. The insufficient material regeneration and long-term operational performance are also bottlenecks in practical applications. The regeneration efficiency of Fe-Mn materials is low after adsorption saturation, which affects economic and sustainable aspects. The Fe-Mn system may also release Mn^{2+} in acidic or complex water bodies, affecting environmental safety. Therefore, improving the stability of metal loading and structural firmness remains an important research direction. In terms of reaction conditions, this system is highly dependent. The Fe-Cu system usually requires acidic conditions (pH 3–5) to maintain efficient Fenton reactions, but the actual wastewater pH fluctuates greatly, and the instability of the actual situation increases the operation cost and control difficulty.

Therefore, how to enhance performance while maintaining stability, environmental safety and engineering applicability is the core challenge for the further development of iron-copper and iron-

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manganese biomass carbon composite materials. Developing low-cost, green and scalable production technologies, and achieving a balance between performance and economy, is an important future direction.

6. Conclusion

This paper conducts a study on the preparation process, performance differences, and application scenarios of Fe-Cu and Fe-Mn dual-metal composite materials loaded on waste biomass carbon. Both of these composite materials use agricultural and forestry waste as the carbon source and are obtained through different composite methods. The Fe-Mn system focuses on adsorbing heavy metals and is suitable for the remediation of heavy metal pollution in water bodies and soils. The Fe-Cu system utilizes the Fenton reaction to achieve efficient degradation of organic pollutants, with fast reaction rate and recyclability, making it suitable for the treatment of organic wastewater. It is not difficult to observe that due to issues such as metal leaching, strong dependence on reaction conditions, and low regeneration efficiency, current research is still limited to the laboratory stage. However, looking to the future, by focusing on green large-scale production technologies, improving the stability and engineering applicability of the materials, and then applying them in practical scenarios, this system will maximize its ability to control environmental pollution and achieve the practical application value of "treating waste with waste".

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