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KYIV NATIONAL UNIVERSITY OF TECHNOLOGIES AND DESIGN  
Faculty of Chemical and Biopharmaceutical Technologies  
Department of Biotechnology, Leather and Fur

## QUALIFICATION THESIS

on the topic **Adsorption of cadmium by iron-modified cassava residue biochar**

First (Bachelor's) level of higher education

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**ASSIGNMENTS  
FOR THE QUALIFICATION THESIS  
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## SUMMARY

**Xiaoyu Liu. Adsorption of cadmium by iron-modified cassava residue biochar. – Manuscript.**

Qualification thesis on the specialty 162 «Biotechnology and Bioengineering». – Kyiv National University of Technologies and Design, Kyiv, 2024.

Soil is the foundation of human development, but with more and more development activities, a large number of heavy metal elements are deposited in the soil, which destroys the ecological environment balance. Heavy metal is an important factor causing soil pollution in China. Among them, cadmium (Cd), as one of the most toxic heavy metal elements, is easily absorbed by plants and has strong mobility, so it is difficult to degrade in the environment. Under the sustained development of industry and agriculture, some areas of China's land have been polluted by Cd. Currently, in situ remediation of Cd in soil using BC can reduce the bioavailability of such heavy metals, showing a good development trend in heavy metal remediation.

In this study, cassava residue was used as raw material to produce BC at 400 °C, and then modified with nanoscale  $\text{Fe}(\text{NO}_3)_3$  to produce five types of iron modified BC (BC-Fe) with a carbon iron mass ratio of 1:0.05, 1:0.075, 1:0.1, 1:0.125, and 1:0.15. Finally,  $\text{Cd}^{2+}$  adsorption experiments and characterization analysis were conducted. The following results were obtained: When the conditions were consistent, BC-Fe had a higher ability to adsorb Cd compared to the original BC, especially BC-Fe (1:0.125) performed the best, achieving adsorption equilibrium after 240 minutes, while BC needed 480 minutes to achieve. At the same time, its adsorption rate was significantly lower than BC-Fe (1:0.125). The characterization analysis results show that BC-Fe (1:0.125) exhibits a rough layered structure, and the surface of BC gradually loses regularity, which helps to fully volatilize the organic substances contained in BC; In terms of pH value, BC-Fe (1:0.125) is higher than BC, and an increase in pH value is helpful for adsorbing Cd; In terms of ash content, BC and BC-Fe (1:0.125) each account for 42% and 49%, respectively. The latter belongs to high ash BC and is beneficial for adsorbing heavy metals.

*Key words: Cassava residue; Biochar; Iron modification; cadmium (Cd)Chinese abstract; graduation thesis; achievement*

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## INTRODUCTION

The raw material used in this study is cassava residue. The original BC was prepared at 400°C by pyrolysis technology, and BC-Fe with different carbon-iron ratios (0.050: 1, 0.075: 1, 0.100: 1, 0.125: 1, 0.150: 1) was prepared at the same time. The physical and chemical properties of BC and BC-Fe(1:0.125) were analyzed, and the adsorption of  $\text{Cd}^{2+}$  in solution by these two materials was studied.

The conclusions are as follows:

(1) Five kinds of BC-Fe with the ratio of carbon to iron of 1: 0.05, 1: 0.075, 1: 0.1, 1: 0.125 and 1:0.15 all have advantages over BC in Cd adsorption. When the conditions are the same, the highest adsorption capacity for  $\text{Cd}^{2+}$  is BC-Fe(1:0.125), which can achieve the adsorption equilibrium after 240 minutes, and BC can achieve the adsorption equilibrium after 480 minutes. At the same time, the removal rate and adsorption capacity are lower than BC-Fe(1:0.125).

(2) The results of characterization analysis of BC and BC-Fe(1:0.125) show that the surface porosity, specific surface area and ash content of modified BC are all increased, but the H/C ratio has not changed significantly. It can be seen that iron modification has no effect on the aromaticity of BC, and the (N+O)/C ratio is greatly increased. It can be seen that the polarity of modified BC is increased. All of them can promote the improvement of  $\text{Cd}^{2+}$  adsorption performance of BC-Fe(1:0.125).

**The relevance** of the topic is Removal rate, adsorption capacity and characterization analysis.

**The purpose of the study** is the adsorption efficiency of Cd(II) was effectively improved by iron modification of original biochar.

**The objectives** of the study is the adsorption efficiency of Cd(II) was effectively improved by iron modification of original biochar.

**The object of the study** iron-modified cassava residue biochar

**The subject of the study** This study focuses on introducing iron into cassava residue biochar by a specific method to improve or enhance its original physical, chemical and biological properties. This topic covers the collection and pretreatment

of cassava residue, the selection of iron introduction methods, the optimization of carbonization conditions, and the performance characterization and potential applications of the resulting iron-modified cassava residue biochar.

Therefore, the theme of iron-modified cassava residue biochar mainly focuses on the effective use of biomass resources, the development of environmentally friendly materials and the innovative application of multi-functional materials.

**Research methods** Biochar was modified by chemical method.

**The scientific novelty** Iron-modified biochar with the best ratio of carbon to iron was selected according to the conditional experiment (different ratio of carbon to iron), and then the adsorption effect of cassava residue biochar on Cd in solution before and after modification was studied by  $\text{Cd}^{2+}$  adsorption experiment.

**The practical** significance of the results obtained is to improve the comprehensive utilization efficiency of biomass resources and promote environmental protection, resource conservation and sustainable development.



## CHAPTER 1

### LITERATURE REVIEW

#### 1.1 Cadmium pollution status and its harm

No matter in soil, water and air, there are potential heavy metal pollution, which has great influence on people's health and quality of life. In terms of environmental pollution, heavy metals are irreversible, long-term, latent and cumulative, which endanger the ecosystem, natural environment and food chain to a great extent, and the treatment cost is large and takes a long time. Heavy metal pollution is a kind of pollution caused by excessive accumulation of heavy metals, which is a general cause of environmental deterioration. Even if heavy metal pollutants are at trace levels, invading human bodies can also cause significant harm <sup>[1]</sup>. Yaning Li <sup>[2]</sup> et al. evaluated the effects of cadmium (Cd) exposure on the passive and active lethal efficiency of *Beauveria bassiana* (Bb) to gypsy moth larvae, and analyzed the corresponding mechanism. The results showed that the passive lethal efficiency of Bb to the larvae of gypsy moth exposed to Cd was significantly higher than that of the larvae not exposed to Cd. Cd exposure destroyed the mycelium structure and inhibited the mycelium growth and spore production. Cd exposure at low concentration promoted spore germination, but inhibited the hydrophobicity and adhesion of spores at high concentration. To sum up, Cd can be regarded as an abiotic environmental factor, which directly affects the lethal efficiency of Bb to pests.

Among the components of ecosystem, soil is the most basic part, which provides basic guarantee for human survival and development. The problem of Cd pollution is very extensive, which is extremely harmful to the sustainable utilization of soil resources and the safe cultivation of grain. Heavy metal ion Cd can easily lead to food pollution. Soluble Cd compounds have moderate toxicity, and all metal poisons including them can inhibit all kinds of sulfhydryl enzyme systems in human body, hinder tissue metabolism, and damage local tissues and cells, leading to edema and inflammation. After research, Guo Jian <sup>[1]</sup> and other scholars have observed that most of the Cd absorbed into the blood will bind to hemoglobin (Hb) and distribute in red

blood cells (RBC). Then slowly transfer to liver, kidney and other tissues, and then combine with metallolipoproteins (MT) contained in such tissues. Cd often accumulates in human eyes, bone tissues, kidneys and other organs and tissues, mainly bone tissues and kidneys, which will lead to related diseases, such as fragile fractures and renal failure, and do harm to human health. Cd will also affect the metabolism of trace elements such as zinc (Zn), copper (Cu) and cobalt (Co), and hinder the synthesis of Hb. Invasion of Cd into respiratory tract can lead to lung diseases such as pneumonia and emphysema (PE), and invasion of digestive system can lead to gastroenteritis. In vivo, it will damage blood vessels, cause tissue ischemia and involve multiple systems. Most Cd poisoning patients have anemia. Excessive accumulation of Cd in human bones can lead to bone softening, deformation and fracture, and even more serious, it can shrink. Cd poisoning can also lead to cancer.

## **1.2 Cadmium pollution control methods**

At present, chemical precipitation, membrane separation, ion exchange and electrolysis are commonly used to treat heavy metal polluted wastewater. Such technologies are costly, inefficient, will bring secondary pollution and other shortcomings, limiting their large-scale application. Adsorption is a common, efficient, environmentally friendly and reusable adsorbent method to effectively remove heavy metals from wastewater. The adsorption performance of adsorbents is a key factor in the treatment of heavy metals in wastewater. Common sorbents include activated ferric algal soil, activated sludge and carbon materials. The means of treating heavy metals in soil include chemical, biological, physical and physicochemical technologies, etc. Adsorption fixation belongs to a kind of physicochemical technology, which has attracted much attention in the research field due to its advantages of easy operation, simultaneous production and remediation. In the adsorption technology, the core lies in the selection of adsorbent, biochar as an adsorbent by virtue of its large specific surface area, low cost, environmentally friendly advantages, but in terms of adsorption performance, selectivity is not good,

so in order to improve performance need to be modified. Nowadays, chemical modification methods such as metal load modification, acid modification, organic modification and alkali modification are most commonly used<sup>[3]</sup>. Bon Ivan Carralero<sup>[4]</sup> et al. used free-living vibratory algae to remove Cd. The results showed that when the concentration of Cd was 5.0 or 25.0 mg/L, the removal efficiency of Cd by cyanobacteria culture reached the maximum (~ 60%) within 12-24 h. The adsorption of metals by negatively charged functional groups in the biomass of cyanobacteria is the main mechanism of metal removal in water medium by vibratory algae, followed by the bioaccumulation of Cd in living cells. In other words, the beneficial and sustainable management of industrial metal-contaminated wastewater can be achieved by maximizing metal removal performance through active cyanobacteria metabolism.

### **1.3 Overview of biochar**

#### **1.3.1 Properties of biochar**

Biochar is an environmentally friendly material with low repair cost. It has large porosity, high negative charge density, and a large number of oxygen-containing functional groups and mineral elements, which can improve the physical and chemical properties of soil, provide nutrients for soil, and absorb pollutants<sup>[5]</sup>. At the same time, it is also a kind of porous carbon generated by high temperature pyrolysis of biomass in an oxygen-restricted or oxygen-free environment. Due to its characteristics of large specific surface area, aromatization structure, developed pore structure and rich functional group structure, it can be used for wastewater pollutant removal, greenhouse gas emission control and soil improvement. The advantage of biochar (BC) is that the preparation of raw materials are wide, green and non-polluting, and can be effectively adsorbent, so it is used as an adsorbent in the treatment of wastewater pollution. In addition, Zang Jinqiu<sup>[6]</sup> and other scholars found that BC, with its advantages of large specific surface area, developed pore structure, and large number of surface functional groups, will release higher value in future wastewater treatment.

Because BC is different in raw material preparation and pyrolysis process, diversity can be seen in many physical and chemical properties, including functional group type, specific surface area, element content, pore structure, etc., resulting in significant differences in adsorption properties <sup>[7]</sup>.

The representative properties of biochar are its porous structure and large specific surface area. Generally speaking, the higher the pyrolysis temperature of biochar, the more pores on its surface and the larger the specific surface area, which can provide more adsorption sites. Jian Minfei et al. <sup>[8]</sup> have shown that biochar has abundant pore structure. With the increase of temperature, pore number increases and pore structure develops more completely. The pore structure of rice straw biochar is mainly mesoporous, and with the increase of pyrolysis temperature, the average pore size decreases and the specific surface area increases, reaching the maximum at 600. The results of infrared spectrum showed that with the increase of pyrolysis temperature, the rice straw lost alkane group, methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) disappeared slowly, but the aromatic substances increased and the aromatizing level increased. There are many functional groups distributed on the surface of BC, including ketone group, carbonyl group, hydroxyl group, lactone group and carboxyl group, which are mainly alkaline or oxygen-containing functional groups, so BC has good ion exchange, hydrophobic or hydrophilic, adsorption and other properties. After the use of biochar can have a high recycling rate, and the restoration of water pollution will not appear secondary pollution. Li Li et al. <sup>[9]</sup> confirmed that BC produced under 700 has higher aromatization degree, stronger hydrophobicity, larger specific surface area and more complete pore structure development.

### **1.3.2 Use of biochar**

As early as the 19th century, Indians found a kind of "black soil", this soil is actually biochar, this material has wide internal pores, has strong adsorption capacity and physical and chemical properties, can remove various pollutants in water and soil, used to improve the physical and chemical properties of soil, improve soil activity, is an excellent material in the background of high pollution and high consumption.

There are many researches on the removal of pollutants in water bodies. At present, relatively mature methods include membrane filtration technology, ion exchange, etc. These technologies have the advantages of energy saving and environmental protection and will not produce secondary pollution. Biochar, as one of them, uses adsorption to remove pollutants in wastewater and has a wide range of applications in water pollution treatment. In recent years, scholars have conducted related research on biochar prepared from different raw materials. For example, treatment of dye wastewater, treatment of pesticide wastewater and treatment of petroleum wastewater<sup>[10]</sup>.

In the constructed wetland system, biochar can be used as a substrate to improve the operation performance of the constructed wetland, effectively enhance the permeability of the constructed wetland, and alleviate the problem that the vertical flow constructed wetland substrate is easily blocked<sup>[11]</sup>.

At the same time, the application of biochar can not only inhibit the loss of nitrogen in farmland soil, but also realize the resource utilization of agricultural waste: alleviate the loss of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3\text{-N}$ , inhibit the escape of  $\text{N}_2\text{O}$ , and improve the ability of plants to absorb nitrogen. Biochar not only has a strong  $\text{NH}_4^+\text{-N}$  adsorption capacity, but also has the ability to increase soil carbon content, p H value and soil water content, so as to reduce the loss of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3\text{-N}$  caused by surface runoff and water infiltration. In addition, the application of biochar is helpful to reduce root growth resistance, promote plant root growth and development, improve plant nitrogen absorption ability, and further reduce  $\text{NO}_3\text{-N}$  concentration in soil solution<sup>[12]</sup>.

Cao Jianhua et al.<sup>[13]</sup> prepared biochar on a small fluidized bed with rice straw, rice husk and wood chips as raw materials. The effects of raw material type and pyrolysis temperature (400, 500, 600) on the physicochemical properties and  $\text{Cd}^{2+}$  adsorption performance of biochar were analyzed, and the mechanism of adsorption was qualitatively and quantitatively analyzed. The experimental results showed that the adsorption contribution of inorganic minerals in rice straw carbon and rice husk carbon increased first and then decreased, and reached the maximum value at 500

pyrolysis temperature, and the equilibrium adsorption capacity reached 30.19mg/g. Meng Qingmei <sup>[14]</sup> et al. prepared kelp biochar with kelp scraps as raw materials and explored its adsorption effect on heavy metal  $\text{Cd}^{2+}$ . The adsorption of  $\text{Cd}^{2+}$  was studied at 500, 600 and 700 pyrolysis temperatures. The optimum preparation temperature of  $\text{Cd}^{2+}$  was 700, and the maximum adsorption capacity of  $\text{Cd}^{2+}$  was 271.93mg/g. Luo Xin<sup>[15]</sup> et al. used sunflower seed shell as raw material to produce sunflower seed shell biochar by pyrolysis at 700 °C, and studied its adsorption of  $\text{Cd}^{2+}$  in water. The results show that the mesoporous structure is present and the surface contains many functional groups, such as C-OH and CO. When the pH of the solution is 2-7, the adsorption capacity of the biochar for  $\text{Cd}^{2+}$  gradually increases with the increase of pH, and the adsorption rate of  $\text{Cd}^{2+}$  is faster, and the adsorption equilibrium can be reached in 30min. When the adsorption temperature is 25-45, the adsorption capacity of  $\text{Cd}^{2+}$  is 3067-4082mg/g.

To sum up, biochar is a substance of high value to society. It has good economic and social benefits.

### **1.3.3 Modification of biochar**

In a long period of time, adsorption method has been widely used in the removal of heavy metals in the environment by virtue of its advantages of easy operation and efficiency. However, due to the shortcomings of traditional BC materials in adsorption efficiency, lack of good reproducibility and high cost, its practical application is limited. Therefore, mining a new type of adsorption material that is not only cheap but also efficient has gradually become the mainstream research in adsorption.

The adsorption performance of unmodified biochar for pollutants is not ideal, and its adsorption performance can be improved through modification<sup>[4]</sup>. In order to enhance the adsorption capacity of BC, it can be modified by many physicochemical technologies, and composite materials can be produced at the same time, so as to obtain BC materials with high reactivity, which can better adsorb heavy metals in water <sup>[16]</sup>. The modification technology of BC is mainly based on chemical and

physical means, the former mainly involves acid/alkali modification, nanomaterials composite, organic modification, aging modification, etc., the latter mainly involves ball milling modification, steam modification, etc. Compared with the physical technology, the surface area of BC modified by chemical technology is larger, and the micropore structure distribution is more uniform and more developed. When implementing acid-base modification, the main used modifiers are ammonia, HCl, KOH, HNO<sub>3</sub>, NaOH, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>. The acid-washed BC will increase the specific surface area, have a more obvious pore structure, and distribute a large number of oxygen-containing functional groups on the surface, which can remove the ash on the surface of BC and expose more adsorption sites<sup>[6]</sup>. Jiang Hui et al. used wheat straw as raw material, slowly pyrolysis in nitrogen (N<sub>2</sub>) environment, combined with HNO<sub>3</sub> modification technology, to prepare wheat straw BC, and analyzed the adsorption performance and mechanism of wheat straw BC on chromium (Cr) in aqueous solution before and after modification<sup>[17]</sup>.

Modification of BC by metal salts or metal oxides can enhance the ability of BC to treat pollutants. Since iron salts can provide iron ions, the magnetic properties of BC are enhanced, and the iron-based substances or mixtures are used as modifiers to modify BC materials, and the iron-modified biochar (BC-Fe) prepared has received much attention. Zhang<sup>[18]</sup> et al. modified banana peel biomass by using FeSO<sub>4</sub>, and the resulting modified BC showed good adsorption capacity for methylene blue (MB) (up to 862mg/g adsorption capacity), and was also magnetic. Zhao Qingrui<sup>[19]</sup> et al. used wetland plant cattails as raw materials to compound Fe and BC by hydrothermal method, and obtained that BC-Fe had good performance in magnetic properties. The results show that the magnetic properties of BC-Fe are good, and the removal rate of 99.6% can be achieved when the concentration of Cr is 100mg/L, the input of BC-Fe is 40 mg, the solution is 3 pH, the adsorption time is 1.5 hours, and the reaction temperature is 25 degrees Celsius. After three times of adsorption and desorption of BC-Fe, BC-Fe still showed good adsorbability for Cr in water, indicating that magnetic BC-Fe had a good performance in cycle stability. Shirong Zhang et al.<sup>[20]</sup> studied the simultaneous removal of Cr, Cu, Zn and Cd by modifying sludge

biochar with nano zero-valent iron (nZVI@SBC). The results show that nZVI@SBC can significantly improve the removal efficiency of four heavy metals from high-salinity wastewater.  $\text{NO}_3^-$  (N- $\text{NO}_3^-$ ) and humic acid (HA) can promote the removal of Cr, Cu, Zn and Cd, and  $\text{PO}_4^{3-}$  (P- $\text{PO}_4^{3-}$ ) can enhance the removal of Cd. The structure and composition of nZVI@SBC were characterized by SEM-EDS, XRD, BET and XPS. Chromium and copper are removed by adsorption and co-precipitation after nZVI reduction, while cadmium and zinc are removed by alkali precipitation and complexation. This work improves the understanding of nZVI@SBC simultaneous removal of HMs and provides a cost-effective method for the treatment of electroplating wastewater. Bhatia Drishti<sup>[21]</sup> et al. obtained iron-modified biochar by chemical modification and pyrolysis of rice straw. Three adsorption parameters such as contact time, amount of adsorbent and initial arsenic concentration were optimized by response surface method. When the dosage of adsorbent was 3.25 g/L, iron modified biochar could remove 99% of arsenic in 989 $\mu\text{g/L}$  arsenic water.

## **Conclusions to chapter 1**

This paper focuses on the application and mechanism of biochar in the treatment of cadmium pollution. Cadmium, as a toxic heavy metal, will seriously harm human health and destroy ecological balance if it exceeds the standard in the environment. For cadmium pollution, biochar, as a highly efficient adsorption material, shows great potential in environmental remediation due to its unique pore structure and chemical properties. The adsorption properties of biochar can be further optimized by modifying biochar by physical, chemical and biological methods. The purpose of this study is to prepare and characterize iron-modified biochar, study its adsorption effect and action mechanism on cadmium, and provide a new solution for environmental remediation of cadmium pollution, which is of great significance for ensuring ecological environment safety and sustainable development.



## CHAPTER 2

### Object, Purpose and Methods Of The Study

#### 2.1 Object of study

##### 2.1.1 Research background

Biochar, as a unique solid product, is prepared by a process that involves thermal cracking of the biomass under hypoxic or anaerobic conditions. This biomass comes from a wide range of sources, including wood, crop waste, plant tissue and animal bone, which are converted to biochar with significant adsorption properties and stability after being treated at high temperatures. The preparation of biochar not only makes full use of these biomass resources that might otherwise be regarded as waste, but also its preparation cost is relatively low, which makes biochar has great socio-economic significance in environmental governance and resource recycling.

Cassava residue, a typical agricultural waste in the tropics, is a large by-product of ethanol and starch processing. Because of its huge production, how to effectively treat and utilize the cassava residue has been an urgent problem to be solved. Converting cassava residue into biochar not only realizes its resource utilization, effectively alleviates the problem of its stacking, but also gives it new value. Cassava residue biochar has two significant advantages of low cost and resource utilization, which makes it a potential environmentally friendly functional material.

However, although tapioca residue biochar has many advantages, its natural form has some limitations. Natural cassava residue is actively lower than the surface, which means that the number of active sites on its surface that can be used for adsorption is limited. At the same time, the number of functional groups is relatively small, which further limits its adsorption capacity. In addition, the stability of natural cassava residue biochar is poor, and the performance may decline during long-term use. These problems may limit the efficiency of biochar in adsorbing heavy metal ions such as Cd.

Therefore, in order to give full play to the adsorption potential of cassava residue biochar, we need to improve its adsorption capacity through modification treatment.

This modification process can be achieved by introducing new functional groups, increasing specific surface area and improving pore structure. Through these modification methods, we can significantly improve the adsorption efficiency and stability of cassava residue biochar, making it a more efficient and reliable adsorbent, and making greater contributions to environmental governance and resource recycling.

### **2.1.2 Origin and definition of biochar**

Artificial black soil, also known as biochar, is a soil with a deep historical and cultural heritage. According to historical records, as early as 2,500 years ago, and possibly as far back as 6,000 years ago, ancient civilizations living in the Amazon River basin were already making and using this unique soil. Although the soil in the local environment is poor, it is this artificial soil that nourishes the life of the land, allowing ancient civilizations to continue and agriculture to flourish.

It is assumed that the raw materials used by these ancient peoples to make black earth included dung, fish, animal bones, and rich plant waste. However, among these materials, charcoal is undoubtedly the most critical ingredient, because it not only provides the nutrients needed by the soil, but also gives the soil its unique black appearance. The soil is affectionately known locally as "terra preta do indio," which means "black Indian soil."

This black soil is dense, productive and fertile, in sharp contrast to the surrounding loose and barren natural soil. In some areas, the reserves of black soil even stretch for several hectares, bringing huge benefits to local agricultural production and ecological environment.

From an ecological point of view, the formation of biochar is closely related to plant growth and carbon cycle. Plants absorb large amounts of carbon dioxide as they grow, but when they are cut down or burned, this absorbed carbon is released back into the atmosphere. However, if plants are cut down and burned in a controlled, low-oxygen environment, they are converted into charcoal, known as biochar. Charcoal is

a very stable solid form of carbon, which can fix carbon for a long time, thus slowing down the trend of global warming.

According to a new study in *Nature Geoscience*, biochar plays an important role in the fight against global climate change. The study found that through large-scale production and use of biochar, humanity could offset about 12% of global carbon emissions. This discovery undoubtedly provides a new way and possibility to deal with global climate change.

Biochar is a kind of black carbonaceous material prepared by high temperature pyrolysis or oxidation of biomass. It has a porous structure and a large surface area, which make it have strong adsorption properties. Different from ordinary coal or charcoal, biochar is rich in microorganisms and organic matter after a special preparation process, which has a good effect on soil improvement.

In the process of preparing biochar, about a third of the feedstock is converted into biochar, a third into substances that can be used to generate electricity, and the remaining third is formed into crude oil. This efficient conversion process allows biochar to help us address not only the climate change crisis, but also the energy crisis and the food and water crisis. Therefore, scientists generally agree that biochar is one of the important tools we have to deal with the three current global crises.

### **2.1.3The basic situation of cassava**

Cassava, a member of the cassava genus in the Euphorbiaceae family, is a unique woody plant. Its distinguishing feature is its cylindrical tuber root, which gives it its name, as this root is rich in starch and is widely used as a food source. Cassava's unique paper-shaped, nearly round leaf structure provides the plant with efficient photosynthesis, helping it thrive in the tropics.

Cassava flowers are also distinctive, with purplish red sepals and a layer of white frost on the surface, adding a mysterious and fascinating color to the flowers. White hairs are attached to the top of the anthers, a feature that makes the flowers even more striking. When cassava blossoms and bears fruit, the fruit takes on a cotton-round appearance that is both cute and interesting.

The seeds of cassava are also unique. The seed coat is crusty, with beautiful markings on the surface, smooth and glossy. These seeds are not only an important part of cassava reproduction, but also have a certain ornamental value because of their unique appearance. Cassava flowers are usually between September and November each year, and this time is the most gorgeous time of cassava.

Cassava is native to Brazil, but is now widely cultivated in tropical regions around the world due to its extreme adaptability. In China, cassava is cultivated in Fujian, Taiwan, Guangxi, Hainan, Yunnangui and other provinces and regions, and even wild cassava can be found in some places. Cassava is not only drought-tolerant, but also less pests and diseases, and the soil is not high requirements, which makes it a very valuable crop to promote. However, in order to achieve high yields, it is best to choose deep, loose soil when planting cassava.

The main way of cassava reproduction is to cut the stem propagation, which is simple and easy, the survival rate is high, and it is a commonly used method in cassava cultivation. By cutting stems, people can easily expand the area of cassava cultivation to meet the growing demand for food and industry.

#### **2.1.4 Research status of cassava residue**

In recent years, the Ministry of Agriculture and Rural Affairs and the Ministry of Ecological Environment have made remarkable efforts in promoting the transformation of agricultural development mode and strengthening the prevention and control of agricultural non-point source pollution. They are committed to promoting the use of waste resources and strengthening the treatment of non-point source pollution in rural areas to reduce environmental impact and promote sustainable agricultural development.

Under this background, the treatment and reuse of cassava residue, an agricultural waste, is particularly prominent. Cassava residue is a large amount of waste generated during the production of cassava starch, which has long brought great pressure to the environment due to its large output and high disposal cost. Improper treatment will not only lead to the occupation of land resources, but also may produce

toxic gases in the process of deterioration and decay, resulting in air pollution; At the same time, high concentrations of organic compounds in cassava wastewater, if discharged into the environment without proper treatment, also pose a potential threat to vegetation, soil, water bodies and human health.

Therefore, finding effective and environmentally friendly degradation and reuse methods of cassava residue has become one of the urgent problems in the field of solid waste management. Fortunately, through research and practical exploration, people have found that cassava residue actually contains great value. This waste is rich in carbohydrates, including lignocellulose, soluble sugars, and small amounts of protein, which can be converted into valuable resources.

At present, the use of cassava residue as animal feed is a major way of utilization. Cassava waste water is rich in carbohydrates, which makes cassava residue a good feed material. In addition, cassava residue can also be used to produce energy products such as biogas or bioethanol, which not only helps reduce greenhouse gas emissions, but also provides sustainable energy support for agricultural production.

In addition to the above uses, cassava residue also has the potential as a chemical raw material. About 38% of the starch contained in it can be effectively utilized and has similar functions to cationic starch. It is worth mentioning that cassava residue is also an effective organic adsorbent. By converting it into biochar materials, it can play an important role in soil remediation, carbon sequestration, heavy metal adsorption and so on. Compared with traditional water treatment methods, the use of cassava residue biochar adsorption to treat antibiotic wastewater has higher efficiency and better environmental performance.

In summary, by actively promoting the resource utilization and technological innovation of agricultural waste, we can effectively solve the environmental problems caused by agricultural waste such as cassava residue, and achieve a win-win situation of economic and environmental benefits.

## 2.2 Purpose of the study

This paper discusses the effective utilization of cassava residue, a typical agricultural waste in tropical areas. As a by-product in the production of starch and ethanol (ET), cassava residue has a huge output, which will cause serious stacking problems if it is not properly treated. However, it is this seemingly useless waste that, by converting it into biochar (BC), can realize the efficient application of its resources and solve its storage problems at the same time.

Tapioca residue has significant advantages such as low cost and abundant resources, which makes it an ideal choice for preparing environmentally friendly functional materials. However, due to its small specific surface area and limited number of functional groups, the adsorption performance of natural cassava residue is not ideal, and it lacks the necessary stability. This deficiency is particularly evident when used as an adsorbent and may significantly reduce its adsorption efficiency for heavy metal ions, especially harmful heavy metals like cadmium (Cd).

Cadmium is a heavy metal prevalent in industrial wastewater and agricultural pollution, and its long-term exposure poses a serious threat to human health and ecosystems. In order to effectively treat these cadmium-containing wastewater, we need to find an efficient and sustainable adsorbent. Cassava residue is an ideal raw material for preparing biochar because of its high fiber and organic content. Through high temperature carbonization, cassava residue can be converted into biochar with high specific surface area and rich functional groups, thus significantly improving its adsorption performance.

In order to further improve the adsorption capacity of cassava residue biochar for cadmium, an innovative modification method, iron modification, was adopted in this study. By introducing different proportions of iron, we prepared iron-modified cassava residue biochar with different ratios of carbon and iron, and investigated its adsorption performance and mechanism of Cd. This modification method aims to increase the adsorption capacity and selectivity of cadmium by increasing the active sites on the surface of biochar and improving its surface properties.

This study not only provides a new idea for the resource utilization of cassava residue, but also provides a low-cost, efficient and sustainable technical approach for the treatment of heavy metal wastewater. By preparing iron-modified cassava residue biochar, we can effectively fix cadmium ions in wastewater, reduce its harm to the environment and organisms, and realize the recycling of resources. This environmentally friendly, economical and effective treatment will play an important role in environmental protection and sustainable development in the future.

### **2.3 Research significance**

After extensive research, it has been proved that the modification of biochar can significantly improve its pore structure, specific surface area and functional group types. These improvements not only enhance the adsorption performance of biochar, but also show stronger environmental benefits than unmodified biochar in terms of cation exchange capacity and in-situ remediation of heavy metal pollution.

At present, when scholars explore the modification methods of biochar, most of them focus on acid-base modification methods, such as nitric acid, sulfuric acid, phosphoric acid, potassium hydroxide and sodium hydroxide and other common acid-base reagents. These methods improve the adsorption capacity of biochar by adjusting its acid-base properties, affecting its surface charge and functional groups.

However, in addition to acid-base modification, there are physical, chemical and biological modification methods to choose from. For example, the metal loading method can introduce new active sites by loading specific metal ions or metal oxides on biochar to enhance its adsorption capacity for specific pollutants. Biological methods use bioactive substances such as microorganisms or enzymes to modify the surface of biochar to improve its adsorption performance and biocompatibility. In addition, physical methods such as ball milling can also affect the adsorption properties of biochar by changing its particle size and morphology.

Among these modification methods, chemical method has attracted much attention because of its simple operation and remarkable effect. In particular, the use of iron, a substance with extensive sources and stable properties, has become a research hotspot.

Iron modification can not only increase the magnetic properties of biochar, but also effectively improve the adsorption efficiency of heavy metal ions. For example, the zero-valent nano-iron-chitosan modified biochar prepared by Tang Wenke et al., by introducing zero-valent nano-iron and chitosan, not only increased the adsorption site of biochar, but also improved its stability. This modified biochar has an excellent performance in soil remediation, which can significantly reduce the content of available heavy metal ions in soil and reduce the bioavailability of heavy metals, thereby reducing the harm to the environment and organisms.

As a new type of composite material, iron modified biochar has high application potential and research value. Its research significance is mainly reflected in the following aspects:

**Environmental protection:** The high adsorption capacity of iron-modified biochar enables it to effectively remove harmful substances in the environment, such as heavy metal ions and organic pollutants. It has broad application prospects in the fields of wastewater treatment and soil remediation.

**Resource utilization:** Through iron modification, biochar, a renewable resource, has been upgraded and utilized, increasing its added value and application fields. This not only promotes the industrialization of biochar, but also promotes resource conservation and sustainable development.

**Functional materials:** Iron modified biochar has excellent specific surface area and porosity, as well as unique physical and chemical properties. This makes it an ideal functional material such as adsorbent, catalyst and electrode material. It has wide application prospect in the fields of environmental treatment, chemical manufacturing, electrochemical energy and so on.

**Biomedicine:** The biocompatibility and bioactivity of iron-modified biochar make it a research hotspot in the medical field. It shows potential application value in drug delivery, tissue engineering, biosensing and so on.

In summary, the study of iron modified biochar is of great significance for improving the comprehensive utilization efficiency of biomass resources, promoting environmental protection and resource conservation. With the deepening of research



and technological progress, iron modified biochar is expected to be applied and popularized in more fields.

## 2.4 Methods of the study

In this paper, the process of preparing iron-modified biochar (BC-Fe) from cassava residue was discussed, and the performance and characterization of Cd adsorption were analyzed in detail. The following is a detailed description of the main aspects covered in this paper:

### 1. Preparation of BC-Fe

In this study, cassava residue was used as raw material to produce biochar (BC) by pyrolysis under high temperature. Specifically, we chose 400°C as the pyrolysis temperature, which is considered to be the appropriate temperature for the preparation of efficient biochar. After obtaining the original biochar, we further modified it with nanometer  $\text{Fe}(\text{NO}_3)_3$ . In the modification process, we set different mass ratios of carbon to iron, including 1:0.50, 1:0.75, 1:1.00, 1:0.125 and 1:0.150 (unit: g), to explore the effects of different ratios on the properties of biochar.

### 2. Analysis of adsorption performance of Cd by BC-Fe

After preparing BC-Fe with different mass ratios of carbon to iron, we carried out a series of experiments to analyze its adsorption performance to cadmium ion. First, we determined the optimum ratio of carbon to iron based on the experimental results of different mass ratios of carbon to iron. Subsequently, we used this optimal proportion of BC-Fe to carry out the  $\text{Cd}^{2+}$  adsorption experiment. By comparing the adsorption effect of cassava residue BC before and after modification on cadmium in solution, we further analyzed the influence of modification treatment on the adsorption performance of biochar. These experiments not only help us to understand the adsorption mechanism of BC-Fe, but also provide an important reference for the subsequent practical application.

### 3. BC-Fe characterization analysis

In order to further explore the physical and chemical properties of BC and BC-Fe, scanning electron microscopy (SEM) was used to characterize them. When sampling,

we specially selected BC-Fe with the best mass ratio of carbon to iron (1:0.125) and the original BC for comparative analysis. Through SEM images, we can clearly observe the surface morphology, pore structure and iron distribution of BC and BC-Fe. These characterization analyses not only help us to understand the microstructure characteristics of BC-Fe, but also provide strong support for further investigation of its adsorption properties and mechanisms. Through comprehensive analysis of these characterization data, we can understand the performance characteristics of BC-Fe more comprehensively, and provide scientific basis for its optimization and improvement in practical applications.

## **Conclusions to chapter 2**

This study focused on the preparation, modification and adsorption properties of cassava residue biochar (BC) in order to explore a new way of resource utilization of cassava residue to cope with global climate change and environmental pollution. BC was prepared by pyrolysis of cassava residue at high temperature and modified by nano-scale  $\text{Fe}(\text{NO}_3)_3$  (BC-Fe). The influence of different carbon-iron mass ratios on the  $\text{Cd}^{2+}$  quality of BC-Fe adsorption was studied. In addition, scanning electron microscopy (SEM) was used to analyze the morphology of BC and BC-Fe under the optimal ratio of carbon to iron, which provided theoretical basis and technical support for the utilization of biochar resources in cassava residue, and further promoted the development and progress of environmental protection industry.

## CHAPTER 3

### EXPERIMENTAL PART

#### 3.1 Preparation of Original Biochar

Experimental instruments and equipment (Tab. 3.1).

Table 3.1 – Main instruments and equipment

Instrument name	Model
Multi-head magnetic heating agitator	HJ-6A
muffle furnace	TNX1100-30
Electronic balance	BSA224S
Ultra-pure water machine	Evo-S45UVF

The reagent used in this experiment is mainly nanometer  $\text{Fe}(\text{NO}_3)_3$  (ferric nitrate).

In this experiment, the cassava residue used was common cassava residue sold in the market. First, it is thoroughly washed by pure water, then washed 3 times by deionized water, moved to the oven, 2d drying treatment at  $50^\circ\text{C}$ , and then crushed with the help of high-speed universal crusher, while passing through the screen (aperture is 1 mm). The crushed cassava residue was transferred to the crucible (100mL), sealed with tin foil, and then transferred to the Muffle furnace for 2 hours of firing at  $400^\circ\text{C}$ . The original BC that has been fired is taken out and filtered through a filter line with a 0.5mm aperture and a 0.053mm aperture. The portion of the filtered BC with a size of 0.5-0.053mm is retained and stored for later use.

#### 3.2 Preparation of modified biochar

$\text{Cd}^{2+}$  solution (20 mg/L) was prepared. Weigh 0.04 g cadmium chloride ( $\text{CdCl}_2$ ) on an electronic scale, then transfer to a volumetric bottle (50mL), dilute to 50ml with deionized water, and shake well; Use an electronic balance to weigh 0.25g, 0.375g, 0.5g, 0.625g and 0.75g ferric nitrate 9-hydrate, respectively, and place them in a 200mL volumetric bottle. Ferric nitrate and the fired BC are proportional to 0.05:1, 0.075:1, 0.1:1, 0.155:1 (unit: g) The mixture was recorded as BC-Fe (1:0.05),

BC-Fe (1:0.05), BC-Fe (1:0.01), BC-Fe (1:0.01), BC-Fe (1:0.01), BC-Fe (1:0.05), and 150mL of deionized water was added. At room temperature, the above 5 volume bottles were moved to the multi-head magnetic agitator. After 0.5d of stirring treatment, the mixture is moved to a large glass tray and all residues in the volumetric bottle are rinsed off with deionized water. The large glass tray is moved to the oven, dried at 50 ° C, and then re-placed in the Muffle oven, fired at 400 ° C for half an hour, the resulting BC-Fe, stored for use.

### **3.3 Adsorption effect of iron modified biochar on Cd<sup>2+</sup>**

#### **3.3.1 Introduction**

Cd pollution is the most serious heavy metal pollution in our country. The United Nations Environment Programme has identified Cd as the number one hazardous chemical in the world. The pollution can not only cause the imbalance of soil function and the deterioration of soil quality, but also cause certain harm to the physiological development of plants and affect the growth and metabolism of plants. Cd is absorbed, aggregated and transferred to the food chain by plants, which causes serious harm to human health and life.

Non-ferrous metal mineral development and smelting, as well as other industrial fields discharge of waste slag, wastewater and exhaust gas, can lead to Cd pollution. The amount of phosphate fertilizer used in arable land in China is very large, and this kind of chemical fertilizer contains a lot of Cd, and the application of this kind of phosphate fertilizer into the soil will also increase the content of Cd in the soil. In addition, incineration of municipal sludge and garbage will also increase the level of Cd in the soil.

The adsorption method has the following principles: organic improvement technologies such as biosolid composting and BC can stabilize soil Cd in situ, and the Cd ion mobility can be removed from the shelf by transforming the effective state Cd into a stable state Cd precipitation pathway. At the same time, this technology has good agricultural compatibility and high cost-effectiveness advantages, and has a good application prospect.

### 3.3.2 Experimental materials

Experimental instruments and equipment (Tab. 3.2).

Table 3.2 – **Main instruments and equipment**

Instrument name	Model
Multi-head magnetic heating agitator	HJ-6A
Constant temperature oscillator	THZ-82
Manual single channel adjustable pipette	M200
Ultra-pure water machine	Evo-S45UVF
Electronic balance	BSA224S
PH acidimeter	PB-10

The main reagents used in this experiment are: HCl (hydrochloric acid),  $\text{CdCl}_2$  and NaOH (sodium hydroxide).

### 3.3.3 Experimental methods

#### 3.3.3.1 Experiment on the Effect of Different Carbon-Iron Ratios on the Adsorption of $\text{Cd}^{2+}$

The concentration of  $\text{Cd}^{2+}$  in the solution used in this experiment was 20 mg/L. Weigh 0.5 g of different carbon and iron ratios one by one (0.050:1, 0.075:1, 0.100:1, 0.125:1, 0.150: 1) BC-Fe, and weigh 0.5 grams of the original BC, move the weighed BC to a conical bottle (100mL), put 50 ml of deionized water, and then extract 0.05 ml of  $\text{Cd}^{2+}$  solution to the conical bottle, adjust the pH of the solution to about 7. The conical bottle of the prepared mixture was moved to the constant temperature shaker, treated with 1d shock, removed, and then filtered the solution to determine the  $\text{Cd}^{2+}$  concentration in the supernatant.

#### 3.3.3.2 Experiment on the Effect of Different Reaction Time on the Adsorption of $\text{Cd}^{2+}$

The concentration of  $\text{Cd}^{2+}$  in the solution used in this experiment was 20 mg/L. The ratio of carbon to iron with the best adsorption properties obtained by first

weighing 1 g 3.3.1 partial sifting (1: 0.125), and weigh 1 gram of BC, and the weighed BC were moved into the conical bottle (100mL), put 100 ml of deionized water, and then put 0.1 ml  $\text{Cd}^{2+}$  solution and 0.1 ml sodium nitrate ( $\text{NaNO}_3$ ) solution into the conical bottle, moved to the thermostat oscillator and accepted oscillation treatment. Samples were taken at different time points (10, 30, 60, 120, 240, 480 and 720 min) and filtered to determine the residual  $\text{Cd}^{2+}$  concentration in the solution.

Three parallel samples were set for each of the above experimental groups, and the mean of the three samples was taken as the final value.

### 3.3.3.3 Calculation of Adsorption Capacity and Removal Rate

The adsorption effect of BC and BC-Fe on heavy metal Cd was analyzed by adsorption test. A certain amount of BC/BC-Fe was put into the solution with a  $\text{Cd}^{2+}$  concentration of 20 mg/L, and after a period of adsorption, the supernatant was collected and filtered with the filter head (0.45 $\mu\text{m}$ ), and then the  $\text{Cd}^{2+}$  concentration in the filtrate was detected with the atomic absorption spectrophotometer. Three parallel samples were arranged in the experiment.

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

In the above equation,  $Q_e$ 、 $C_0$ 、 $C_e$ 、 $V$ 、 $m$ , in turn, represents the amount of  $\text{Cd}^{2+}$  adsorbed by BC at adsorption equilibrium (unit: mg/g), the initial concentration of  $\text{Cd}^{2+}$  at adsorption equilibrium (unit: mg/L), the concentration of  $\text{Cd}^{2+}$  at adsorption equilibrium (unit: mg/L), the volume of solution (unit: L), and the mass of BC (unit: g). The adsorption capacity of BC and BC-Fe for  $\text{Cd}^{2+}$  in solution can be calculated by this formula.

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\%$$

In the above equation,  $\eta$ 、 $C_0$ 、 $C_e$ , and, in turn, represent the removal rate of  $\text{Cd}^{2+}$  (unit: %), the initial concentration of  $\text{Cd}^{2+}$  (unit: mg/L), and the concentration of  $\text{Cd}^{2+}$  at adsorption equilibrium (unit: mg/L). The removal rate of  $\text{Cd}^{2+}$  in the solution by BC and BC-Fe can be calculated by this formula.

### 3.3.4 Results and Analysis

#### 3.3.4.1 Effect of Different Carbon-Iron Ratios on Adsorption of $\text{Cd}^{2+}$

Through the adsorption results (Fig. 3.1), it can be found that the strongest adsorption performance is BC-Fe (1:0.125). In addition, the adsorption capacity of the five types of BC-Fe is stronger than that of BC. It can be seen that the modification treatment can enhance the adsorption performance of BC to heavy metal ions to a certain extent.

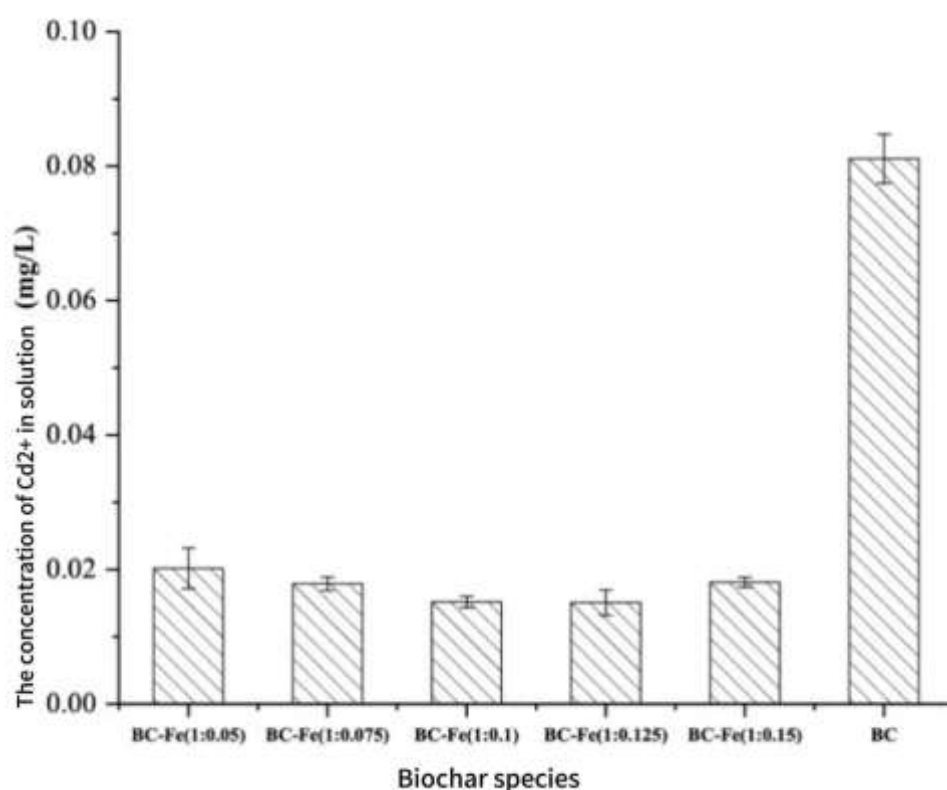


Figure 3.1 – The concentration of  $\text{Cd}^{2+}$  in solution after 24 h adsorption of BC-Fe and BC with different ratio of carbon to silicon

Among the 5 types of BC-Fe, the strongest adsorption property is BC-Fe (1:0.125), and the concentration of Cd in its solution is about 0.04 mg/L. In terms of adsorption properties, BC-Fe (1:0.1) was slightly weaker than BC-Fe (1:0.125), and the concentration of Cd in the solution was about 0.08 mg/L. The weakest adsorption property is BC-Fe (1:0.05), and the concentration of Cd in its solution is about 0.1 mg/L. The adsorption capacity of 5 types of BC-Fe is positively related to the ratio of carbon to iron.

### 3.3.4.2 Influence of different reaction time on $\text{Cd}^{2+}$ adsorption effect

It can be seen from Fig. 3.2 and Fig. 3.3 that the highest adsorption rate of BC-Fe (1:0.125) is observed at 0-120 minutes, and the adsorption rate slowly drops to the reaction equilibrium at 120-240 minutes, and reaches the reaction equilibrium point at 240 minutes. The highest adsorption rate of BC also appeared at 0-120 minutes, different from BC-Fe (1:0.125), when at 120-480 minutes, BC slowly fell to adsorption equilibrium, and reached the reaction equilibrium point at 480 minutes.

In terms of adsorption rate, BC-Fe (1:0.125) is higher than BC. When at the adsorption equilibrium point, compared with the removal rate and adsorption capacity of BC, the adsorption rate of BC-Fe (1:0.125) is also higher, and the adsorption rate of BC is about 96.58% and that of BC-Fe (1:0.125) is about 99.47%. The adsorption capacity of BC-Fe (1:0.125) is also slightly higher than that of BC, so it can be clear that the best adsorption capacity is BC-Fe (1:0.125).

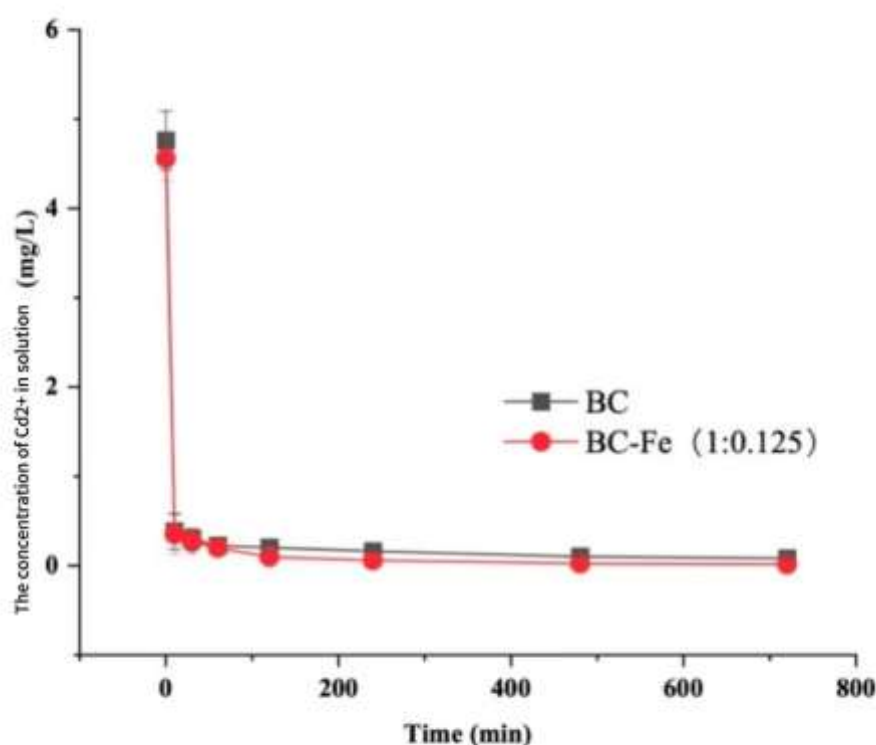


Figure 3.2 – The concentration of  $\text{Cd}^{2+}$  in solution after adsorption time of BC and BC-Fe (1 : 0.125)



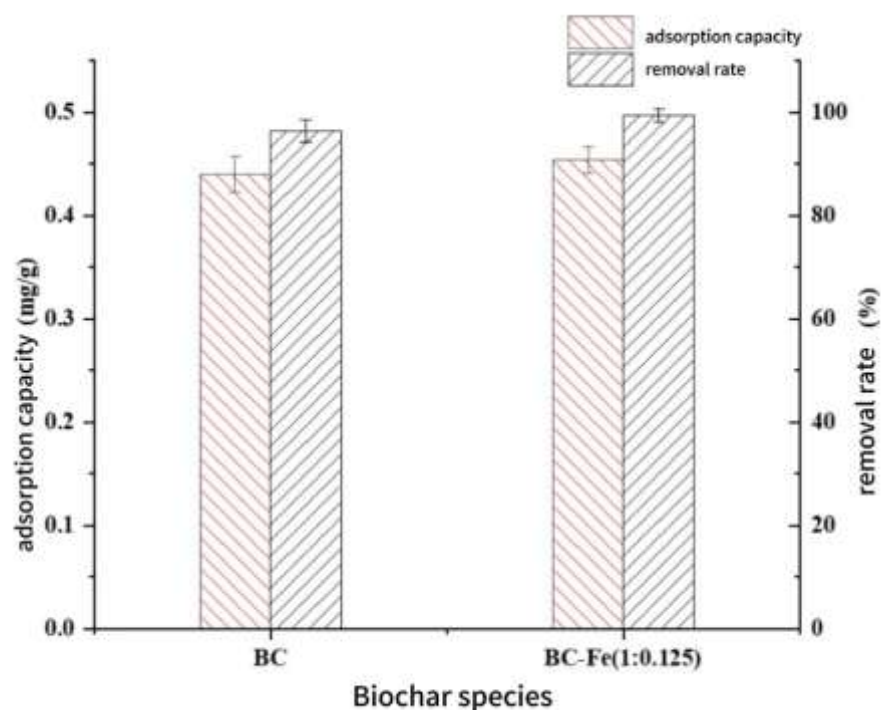


Figure 3.3 – Adsorption rate and adsorption capacity of BC and BC-Fe (1 : 0.125) at adsorption equilibrium

### 3.4 Characterization and Analysis of Iron Modified Biochar

Experimental materials (Tab. 3.3).

Table 3.3 – Main instruments and equipment

Instrument name	Model
Constant temperature oscillator	THZ-82
Ultra-pure water machine	Evo-S45UVF
PH acidimeter	PB-10
Electronic balance	BSA224S
scanning electron microscope	Hitachi-S4800
Manual single-channel adjustable pipette	M200

### **3.4.1 Characterization method of materials**

#### **Scanning electron microscope analysis**

Prepare dry BC and BC-Fe (1:0.125), weigh a little, evenly apply to the sampler, and then place in the instrument for determination. The surface morphology of the sample can be determined by the instrument.

#### **Determination method of pH value**

First weigh 1 gram of BC-Fe (1:0.125) and BC respectively, and then transfer them into a conical bottle (50mL), add 20 ml of deionized water, first implement shock treatment for 5 minutes, and then stand for half an hour to determine the pH value.

Measurement operation: The electrode probe that has been accurately calibrated pH meter is thoroughly washed by deionized water, and then all the water at the probe is absorbed by filter paper, and it is moved to the solution to be measured and immersed, and at the same time, the pH value of the solution to be tested is recorded after the pH meter reading becomes stable.

#### **Determination method of ash content of biochar**

First, 1 gram of BC-Fe (1:0.125) and BC were weighed respectively and transferred into the crucible respectively. Then the two crucibles were placed in the Muffle furnace, and the ashing treatment was carried out at 800°C for 4 hours. The ash content was calculated by the mass difference before and after burning.

#### **Characterization and analysis of biochar materials**

Because the adsorption experiment results show that the highest adsorption capacity is BC-Fe (1:0.125), this paper only explores BC-Fe with the highest adsorption capacity, so the following objects of characterization analysis are BC and BC-Fe (1:0.125).

### **3.4.2 Characterization of iron modified biochar**

pH value analysis of biochar (Tab. 3.4).

Table 3.4 – **Biochar pH**

Biochar type	pH value
BC	10.33
BC-Fe (1:0.125)	10.91

It can be found from the above table that in pH value, BC-Fe (1:0.125) is higher than BC. The pH value of BC is in the range of 5 ~ 12, with an average value of 9.15, and the pH value of straw BC is usually in the range of 8 ~ 11. The researchers' previous work also suggests that BC's pH is slightly alkaline.

Because  $\text{Cd}^{2+}$  is more likely to precipitate in alkaline environment, it is thus removed. It can be seen that BC-Fe (1:0.125) has an advantage over BC in terms of heavy metal removal ability.

### **Ash analysis**

The two types of BCS shown in Table 4-4 belong to high ash BCS, which are favorable for the adsorption of heavy metals. The ash content of BC-Fe (1:0.125) is higher than that of BC, and it also reflects that there is iron complex attached to BC modified by  $\text{Fe}(\text{NO}_3)_3$ , which proves that the modification in this experiment is effective (Tab. 3.5).

Table 3.5 – **Biochar ash**

Biochar type	Ash content	Ash ratio
BC	0.42 g	42 %
BC-Fe (1:0.125)	0.49 g	49 %

### **SEM analysis**

Fig. 4.1 shows the SEM images of BC and BC-Fe (1:0.125) at different magnifications. AB two illustrations BC, CD two illustrations BC-Fe (1:0.125).

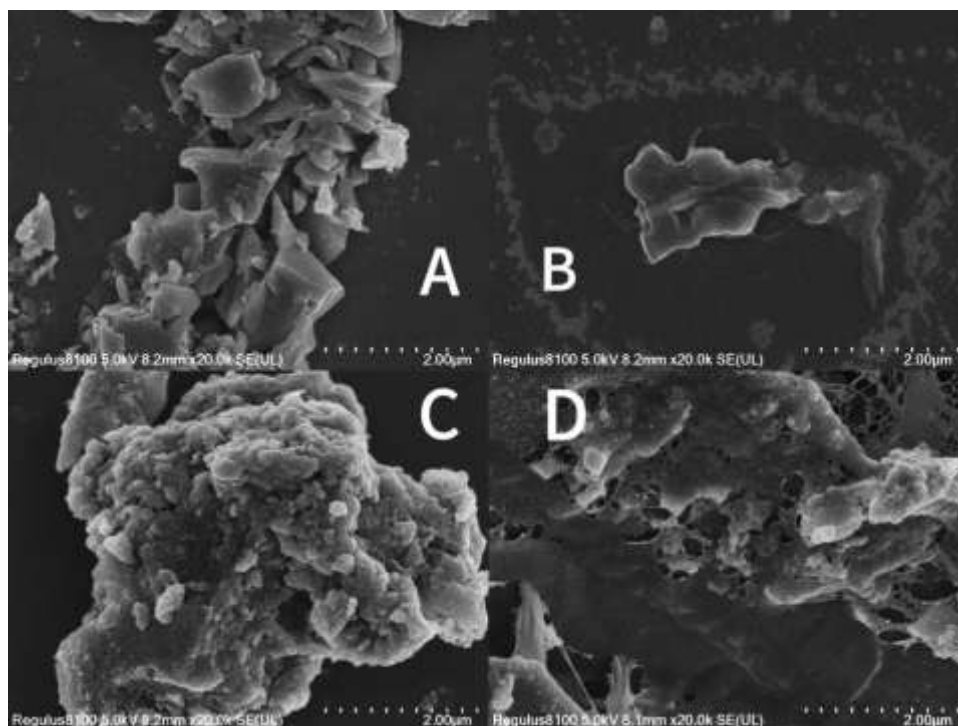


Figure 4.1 – BC (A、B) and BC-Fe (1:0.125) (C、D)

The layered structure of BC was relatively flat at the beginning, and after the modification of nano-scale  $\text{Fe}(\text{NO}_3)_3$ , it was transformed into a rough state. The surface of BC gradually lost its regularization, and the organic substances in BC realized more fully volatilization. With large specific surface area and rough surface, BC can obtain more active adsorption sites for adsorbing pollutants.

### Conclusions to chapter 3

This chapter describes in detail the preparation process of iron modified biochar, the adsorption effect of  $\text{Cd}^{2+}$  and the characterization and analysis of the modified biochar. Through the systematic experimental design and method, the application potential of iron modified biochar in heavy metal adsorption was evaluated comprehensively, and it provided a valuable reference for the subsequent research.

## CONCLUSIONS

In this study, the raw material is cassava residue, and the original BC is prepared at 400°C by pyrolysis technology. At the same time, BC-Fe with different carbon to iron ratios (0.050:1, 0.075:1, 0.100:1, 0.125:1, 0.150:1) is prepared. The physical and chemical properties of the original BC and BC-Fe (1:0.125) materials were analyzed, and the adsorption of  $\text{Cd}^{2+}$  in the solution by these materials was studied.

The conclusion is as follows:

- (1) The five kinds of BC-Fe with the ratio of carbon and iron of 1:0.05, 1:0.075, 1:0.1, 1:0.125 and 1:0.15 have advantages in the adsorption performance of Cd compared with BC. When the conditions are consistent, the highest adsorption capacity for  $\text{Cd}^{2+}$  is BC-Fe (1:0.125), which can achieve adsorption equilibrium after 240 minutes, while BC can achieve adsorption equilibrium after 480 minutes. Meanwhile, the removal rate and adsorption capacity are lower than that of BC-Fe (1:0.125).
- (2) The results of characterization analysis of BC and BC-Fe (1:0.125) showed that the modified BC showed up-adjustment in surface porosity, specific surface area and ash content, but the H/C ratio did not change significantly, indicating that the iron modification had no effect on the aromatics of BC, and the (N+O) /C was significantly increased, indicating that the polarity of BC was improved after modification. All of them can improve the adsorption performance of  $\text{Cd}^{2+}$  by BC-Fe (1:0.125).

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