Effects of Modified Biochar Application on Cd Speciation Transformation in Soil

Zhigen Li*, Yuchen Lin

School of Life and Environmental Sciences, Shaoxing University, Shaoxing, 312000, China

Abstract. This study investigated the preparation of iron/manganese-modified rice husk biochar (Fe/Mn@BC) and its application for cadmium (Cd) immobilization in contaminated acidic soils. The biochar was synthesized via pyrolysis at 450°C, followed by chemical modification with $FeCl_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$. SEM and BET analyses confirmed that modification significantly increased specific surface area and introduced abundant active adsorption sites. The modified biochar was applied to acidic paddy soils (pH 4.94–5.31) at 1% and 5% (w/w) dosage rates. BCR sequential extraction results demonstrated that 5% Fe/Mn@BC effectively reduced acid-soluble Cd from 55.1% to 13.2-17.4% and increased residual Cd from 17.5% to 48.3-66.3% under anaerobic conditions. Notably, during aerobic incubation, 5% Fe/Mn@BC maintained stable Cd immobilization, whereas unmodified biochar showed significant Cd re-mobilization. The enhanced performance is attributed to Fe/Mn oxides acting as electron shuttles, facilitating iron transformation, elevating soil pH, and promoting Cd precipitation and surface complexation. These findings indicate that Fe/Mn modification effectively overcomes the limitations of pristine biochar in acidified soils, offering a sustainable and cost-effective strategy for remediating Cd-contaminated agricultural land.

1 Introduction

In China, with the continuous expansion of mining operations, unscientific and irrational application of pesticides and fertilizers, as well as increasingly serious problems regarding improper discharge of industrial waste and inadequate disposal of domestic garbage, the situation of soil contamination by heavy metal cadmium (Cd) has become increasingly severe[1]. Cd exhibits strong bioaccumulation properties, accumulating in crops and subsequently entering organisms through the food chain, ultimately posing serious threats to human health. Cd exists in various complex forms in soil, and different Cd species demonstrate significantly distinct biological effects. According to the 2022 China Ecological and Environmental Status Bulletin, Cd has become the primary pollutant affecting soil environmental quality in agricultural land. Consequently, due to its high bioaccumulation potential and widespread sources, Cd is considered one of the most toxic heavy metals[2].

Specifically, the hazards of Cd contamination in soil can be categorized into three aspects: detrimental effects on plants, human health, and ecosystems. Cd is not an essential element for plant growth. When plants absorb excessive Cd beyond a certain threshold, their metabolic activities such as respiration and photosynthesis are severely impaired. Additionally, the activity of various enzymes and coenzymes within plant tissues is diminished, ultimately compromising crop yield and quality[3]. Cd primarily enters the human body through the food chain, and prolonged consumption of Cd-contaminated food may lead to Itai-itai disease. More critically, the accumulation of Cd in soil alters microbial community structure and functionality, thereby disrupting the balance of soil ecosystems. Currently, the remediation of Cd-contaminated soil constitutes a critical component of comprehensive soil environmental management[4].

The severity of Cd pollution in soils is becoming more widely acknowledged as a result of societal development, technological advancements, increased industrialization, and the developing effects of environmental degradation. The main causes of Cd contamination have been found to be excessive pesticide use, mining operations, and industrial effluent. Conventional remediation techniques, such chemical leaching and soil replacement, are expensive and may harm the original soil structure, which restricts their broad use. Low initial investment, easy equipment operation and maintenance, and quick remediation times are just a few benefits of soil amendment technology. These approaches have been widely used to remediate heavy metal-contaminated soils, especially on agricultural land. Currently, the main soil amendments under investigation include lime, biochar, modified biochar, and sepiolite[5].

Common methods for preparing iron/manganese-modified biochar include impregnation and co-precipitation techniques. The formation of iron/manganese precipitates substantially increases specific surface area and porosity, providing greater adsorption space for Cd and considerably enhancing the adsorption capacity of biochar. Additionally, the types and quantities of functional groups on the modified

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* Corresponding author: zhigen.li@usx.edu.cn

biochar surface undergo considerable changes, with increased presence of oxygen-containing functional groups such as hydroxyl and carboxyl groups. These functional groups can undergo complexation, chelation, and ion exchange reactions with Cd ions, thereby strengthening Cd adsorption performance[6].

Biochar is produced through the pyrolysis of biomass under anaerobic or oxygen-limited conditions, yielding a carbon-rich solid material characterized by a large specific surface area, abundant pore structures, and diverse surface functional groups. It exhibits excellent biosorption performance under various environmental conditions, particularly demonstrating strong adsorption capacity for multiple contaminants in soil, and has therefore been widely applied in soil remediation engineering. However, unmodified biochar presents certain limitations in remediating cadmium-contaminated soils, with uncertainties arising from pyrolysis processes and environmental aging. Iron/manganese modification of biochar can further enhance its adsorption performance for cadmium. The primary mechanism involves the introduction of iron and manganese, which increases the number of active adsorption sites on the biochar surface, while the modification process may also induce structural alterations that optimize the adsorption properties of the modified biochar. Investigating the changes in soil cadmium speciation following the application of iron/manganese-modified biochar is of great significance for elucidating the mechanisms of biochar-mediated remediation of Cd-contaminated soils and for optimizing remediation technologies. Furthermore, this research can deepen the understanding of interaction mechanisms among soil, biochar, and cadmium, thereby providing practical and feasible technical approaches for the treatment and management of contaminated soils[5-6].

2 Materials and Methods

2.1 Preparation of iron/Manganese modified biochar

Take 1000 g of rice husks, rinse them with water, and dry them in an oven at 150°C until constant weight is achieved. Then crush the dried husks, pass them through a 100-mesh sieve, place them in a crucible, cover with a lid, and calcine in a muffle furnace at 450°C for 2 hours. After cooling to room temperature, remove the sample to obtain rice husk biochar. For the preparation of iron/manganese-modified biochar, mix the as-prepared biochar separately with $FeCl_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ solutions, and react at 60°C for 2 hours. Subsequently, filter, wash, and dry the products to obtain iron-modified biochar and manganese-modified biochar, respectively.

The microscopic morphology and surface elemental composition of the biochar samples were characterized using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS, JSM-6360LV, JEOL, Japan). After grinding, sieving, and vacuum drying, the samples were sputter-coated with gold using an ion sputtering instrument to improve electrical conductivity. The pore morphology of the biochar surface was observed at an accelerating voltage of 15 kV under high vacuum mode.

2.2 Soil collection and characterization

The tested soil was collected from an acidified agricultural field in southern China, with the sampling site located at 120.86° E longitude and 30.01° N latitude. Surface plow layer soil (0–20 cm) was sampled using a soil shovel. To meet the requirements of subsequent experiments, the soil samples were passed through a 100-mesh sieve to remove impurities such as stones, plant residues, and earthworms. Soil pH was determined using a pH meter with a soil-to-water ratio of 2.5:1 (w/v). Cation exchange capacity (CEC) was measured by the NH_4Cl–NH_4OAc extraction method. Total Cd content in the soil was determined by perchloric acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS): 0.3–0.5 g of air-dried soil sample sieved through a 100-mesh nylon sieve was weighed into a polytetrafluoroethylene (PTFE) crucible, followed by the addition of 10 mL of aqua regia, and the mixture was left to stand overnight. On the next day, the crucible was placed in a fume hood and heated at 140–170 °C until the solution volume was reduced to approximately 2 mL. After cooling to room temperature, 3 mL of perchloric acid was added, and heating was continued at 140–220°C until the residue turned grayish-white and the solution became clear. After cooling, the solution was diluted to a final volume of 10 mL, and the Cd concentration in the solution was determined using an inductively coupled plasma mass spectrometer (ICP-MS).

2.3 Determination of different components of Cd

The pristine biochar and modified biochar prepared in the aforementioned experiment were used as soil amendments, and were thoroughly mixed with the collected acidified soil at application rates of 1% and 5% (w/w), respectively. Each amendment treatment was performed in triplicate. The observation period for soil physicochemical properties was 30 days, while that for redox potential was 60 days. On the 30th day of incubation, mixed soil samples were collected and extracted with deionized water at a soil-to-water ratio of 1:5 (w/v).

The Community Bureau of Reference (BCR) sequential extraction procedure was employed to analyze cadmium speciation in soil. The procedure is briefly described as follows: Step 1: Acid-extractable fraction—0.5 g of soil was placed in a 50 mL polypropylene centrifuge tube, and 20 mL of 0.11 mol/L acetic acid was added. The mixture was oscillated for 16 h to reach equilibrium, then centrifuged at 4000 rpm for 20 min. The supernatant was stored at 4°C for analysis. The residue was washed with deionized water for the next extraction step. Step 2: Reducible fraction (Fe-Mn oxide-bound)—20 mL of 0.1 mol/L hydroxylamine hydrochloride (pH 2) was added to the residue from Step 1. After oscillation and centrifugation, the supernatant was collected and stored at 4 °C. The residue was again washed with deionized water.

Step 3: Oxidizable fraction (organically bound)—The washed residue from Step 2 was carefully transferred to a centrifuge tube, and 5 mL of 30% (m/v) H_2O_2 was added and allowed to stand in an 85 °C water bath for 1 h. An additional 5 mL of 30% H_2O_2 was added, and digestion continued at 85 °C. After cooling, 25 mL of 1 mol/L ammonium acetate (pH 2) was added. The mixture was oscillated and centrifuged under the same conditions as Step 1. The supernatant was collected and diluted to 25 mL for cadmium determination. Residual fraction—The residue from Step 3 was washed, air-dried, and digested with a 3:1 (v/v) HCl–HNO_3 mixed acid to extract the residual Cd.

3 Results and Discussion

In this study, scanning electron microscopy (SEM) was employed to obtain high-resolution microscopic images of biochar, which clearly revealed its pore structure, particle morphology, and surface characteristics. As observed from the biochar morphologies shown in Fig.1 , the microstructural features of biochar can be clearly distinguished. The biochar surface exhibited a porous structure, and the presence of these pores endowed it with a large specific surface area, which is conducive to the adsorption and immobilization of heavy metal ions in soil. Meanwhile, the microscopic morphology of biochar also indicated its granular structure, which facilitates its uniform distribution in soil and further enhances its immobilization efficiency toward heavy metals in soil, such as cadmium as investigated in the present study. The microstructural characteristics of biochar verify its excellent adsorption performance.

Following iron-manganese modification, the biochar surface became noticeably rougher, with an increased number of pores and cracks. This structural alteration resulted from the incorporation of iron-manganese oxides, which induced changes in the internal architecture of the biochar. Additionally, granular substances were observed on the surface of the modified biochar, predominantly formed by the deposition of iron-manganese oxides. The presence of iron-manganese compounds not only increased the specific surface area of the biochar but also enabled complexation reactions with cadmium ions to form stable complexes, thereby enhancing the cadmium immobilization capacity of the biochar. This agglomeration phenomenon improves the stability of biochar in soil, contributing to more effective long-term soil remediation outcomes. Compared with pristine biochar, iron-manganese-modified biochar demonstrates superior adsorption and immobilization capabilities, proving more effective in reducing the bioavailability of cadmium in contaminated soils[7].

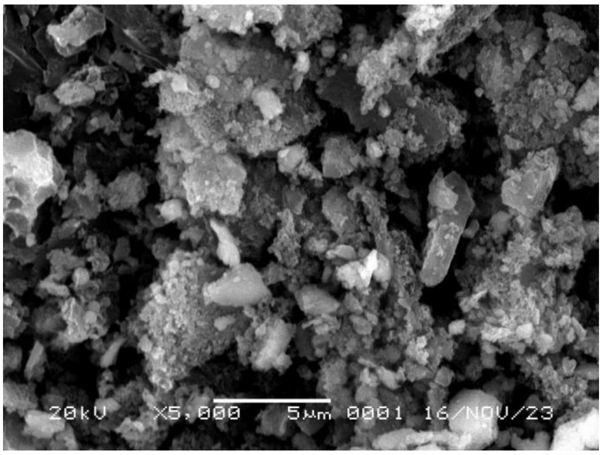

Fig.1 SEM detection results of Fe and Mn modified rice straw biochar.

Table 1: pH, Cd content, CEC of soil samples.

Soils	pH	Cd (mg/kg)	CEC (cmol/kg)
A	5.31	0.42	17.50
B	4.94	0.48	6.57
C	5.25	0.27	12.21

First, the characteristics of soil samples and their Cd concentrations were determined. Table 1 displays the findings: the pH of the collected paddy soils ranged from 4.94 to 5.31, making them generally acidic. Soil samples had Cd concentrations ranging from 0.27 to 0.48 mg/kg (Table 1). Eighty percent of the paddy soil samples had Cd concentrations above the danger limit (0.3 mg/kg) for soil pollution at pH <5.5, as per the China national standard GB 15618-2018. Soil samples taken from various places had a wide range of CEC values. In particular, the CEC ranged from 6.57 to 17.50 cmol/kg.

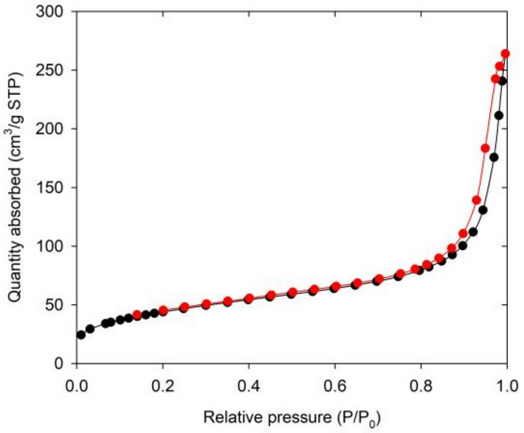

Fig.2 Nitrogen adsorption diagrams before modification of biochar.

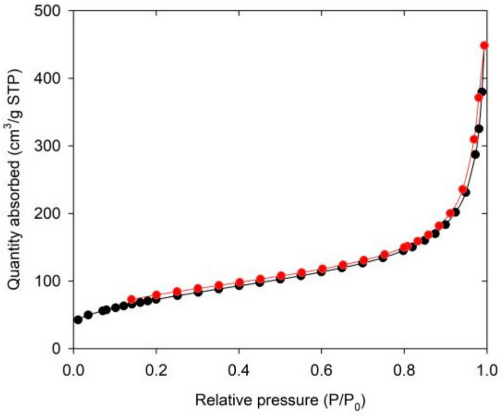

Fig.3 Nitrogen adsorption diagrams after modification of biochar.

Fig.2 and Fig.3 present the nitrogen adsorption-desorption isotherms (BET) of biochar before and after modification. Nitrogen adsorption experiments, commonly referred to as BET analysis, enable the determination of specific surface area, mesopore volume, and micropore volume of the samples through the adsorption-desorption process. As shown in the figure, modified biochar exhibited significant increases in both S_{bet} (total specific surface area) and S_{mic} (micropore surface area), whereas S_{mes} (mesopore surface area) remained relatively unchanged. These results indicate that the modification process substantially enhanced the specific surface area of the biochar.

Subsequently, dynamic variations in the four fractions of soil Cd were examined under varying biochar application rates. During anaerobic incubation, acid-soluble Cd decreased markedly while residual Cd increased substantially, with more pronounced changes over time. After 5 d of treatment, acid-soluble Cd declined significantly, whereas reducible and oxidizable Cd changed slightly, accompanied by an increased proportion of residual Cd. Relative to the control, unmodified biochar decreased acid-soluble Cd from 55.1% to 46.3%, and Fe/Mn-modified biochar exhibited stronger immobilization, reducing acid-soluble Cd to 40.2% and elevating residual Cd from 17.5% to 28.4%. At 30 d, modified biochar showed a clear dose effect: acid-soluble Cd was 26.3%–29.7% under BC treatment and only 13.2%–17.4% under Fe/Mn@BC treatment, with residual Cd increasing to 48.3%–66.3% (Fig.4). In the reduction phase, prolonged incubation increased reducible, oxidizable, and residual Cd, especially the residual fraction, which was enhanced by all biochar treatments (Fig.4). Upon switching to aerobic incubation, acid-soluble Cd rapidly rebounded toward the initial level, consistent with changes in soil redox potential. Notably, the 5% Fe/Mn@BC treatment maintained low Cd mobility throughout the oxidation period, likely due to the sustained stabilization of Fe/Mn oxide precipitates. After 20 d of oxidation, acid-soluble Cd returned to baseline in BC and 1% Fe/Mn@BC treatments, but was effectively suppressed by 5% Fe/Mn@BC, where residual Cd remained dominant and acid-soluble Cd stayed low, closely correlated with soil redox potential[8].

Based on the comprehensive evaluation of all treatment groups, the 5% iron/manganese-modified biochar demonstrated the optimal performance, achieving the highest conversion of cadmium to the residual fraction and exhibiting the maximum transformation efficiency. Soil possesses a buffering capacity for pollutants, and soil colloids exhibit a high adsorption capacity for heavy metals. Generally, heavy metal pollutants entering soil can be rapidly immobilized by soil colloids, thereby reducing their bioavailability to plants. However, in acidified soil environments, heavy metals are difficult to immobilize, leading to aggravated contamination. For instance, the amelioration effect of biochar on Cd immobilization is significant, with its pH value showing a significant negative correlation with extractable Cd concentration[9]. The addition of biochar can enhance the hydrolysis of Cd^{2+} and promote its precipitation in forms such as $CdCO_3$. Similar studies have demonstrated that the application of green manure and bamboo-derived biochar can reduce the exchangeable fraction of Cd in contaminated soils, as Cd is more prone to adsorption and precipitation in the form of $CdCO_3$. The significant decrease in Cd mobility can be primarily attributed to the enhanced precipitation and adsorption immobilization of Cd promoted by elevated soil pH following biochar amendment. Fe/Mn-modified biochar serves as an electron shuttle, facilitating iron transformation in soil and increasing soil pH, thereby suppressing Cd activation[10].

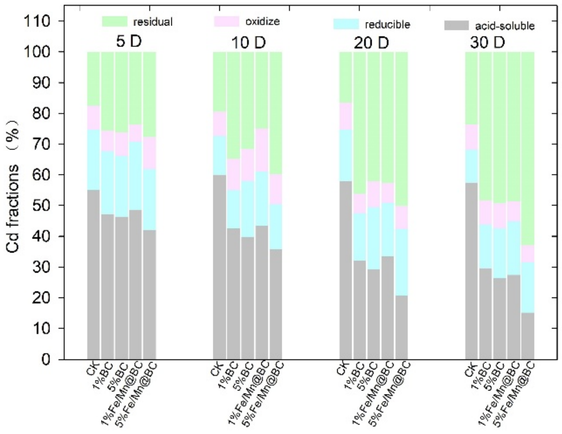

Fig.4 The influence of different biochar treatments on Cd forms in Cd-contaminated soil

4 Conclusion

This study successfully prepared iron/manganese-modified rice husk biochar (Fe/Mn@BC) and evaluated its effectiveness in immobilizing cadmium in contaminated acidic soils. SEM-EDS and BET analyses confirmed that the modification process significantly enhanced the specific surface area and introduced abundant active adsorption sites through iron-manganese oxide deposition. BCR sequential extraction results demonstrated that Fe/Mn@BC application substantially transformed Cd from bioavailable acid-soluble fractions to stable residual forms. Under anaerobic conditions, 5% Fe/Mn@BC reduced acid-soluble Cd from 55.1% to 13.2–17.4% while increasing residual Cd from 17.5% to

48.3–66.3%. Notably, during aerobic incubation, the 5% Fe/Mn@BC treatment maintained effective Cd immobilization, whereas unmodified biochar showed significant Cd re-mobilization. The superior performance of Fe/Mn@BC can be attributed to its electron shuttle function, which facilitates iron transformation, elevates soil pH, and promotes Cd precipitation and surface complexation. These findings indicate that Fe/Mn modification effectively overcomes the limitations of pristine biochar in acidified soils, providing a cost-effective and sustainable approach for remediating Cd-contaminated agricultural land. Future research should focus on long-term field trials, optimization of modification parameters, and mechanistic investigations at the molecular level to facilitate practical application of this promising soil amendment technology.

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