



The long-term effectiveness of ferromanganese biochar in soil Cd stabilization and reduction of Cd bioaccumulation in rice

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Received: 1 May 2021 / Accepted: 7 July 2021 / Published online: 27 July 2021
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Abstract

The application of Fe–Mn-modified biochar for the remediation of Cd-contaminated soil over long time periods has been little studied. In this paper, we describe the performance of coconut-shell-derived biochar modified with ferromanganese in relation to soil Cd stabilization and rice Cd bioaccumulation during a 3-year laboratory study. Different application dosages (0.05–0.5 wt%) and different rice varieties (the early and late rice) are also considered. The results show that ferromanganese is mainly loaded in biochar pores as MnFe_2O_4 , and that it decreases the specific surface area (SSA) and total pore volume of biochar. Ferromanganese biochar (0.5 wt%) applied to paddy soil is more effective than the same dose of pristine biochar in decreasing the soil-exchangeable Cd fraction (27.42–41.92% vs 22.56–33.85%), predominantly by decreasing soil Eh and increasing root Fe plaques. Ferromanganese biochar application helps to reduce Cd bioaccumulation in rice, especially in the grain (up to 48.6%–61.0%), and grain Cd levels (0.2 mg/kg) are all within the acceptable limit for food security in China. It is shown that ferromanganese modification and application can maintain soil at low redox status, keep root Fe plaques at a high level, and may also increase the stability of pristine biochar. All of these effects contribute to maintaining its high remediation efficiency over a 3-year inoculation period. The results presented in this paper demonstrate the potential applications of ferromanganese biochar in soil remediation and the improvement of food safety.

Keywords Biochar · Ferromanganese · Modification · Cadmium · Stabilization

1 Introduction

Contamination of soil and water with heavy metals, especially cadmium and arsenic, is becoming a major problem in developing countries, particularly those in the Asia-Pacific region (Arunakumara et al. 2013; Xue et al. 2019; Yang

et al. 2020; Zhao et al. 2015a). Cadmium is the most serious heavy metal pollutant in China, with ~7% of total soil having concentrations of Cd that exceed the environmental standard limit (Zhao et al. 2015a). The bioaccumulation of Cd in plants, especially in rice (*Oryza sativa* L.), is commonly high, and may decrease the uptake of essential nutrient elements and increase the exposure of Cd to human through food chain transfer. In China, the recently released Action Plan on Prevention and Control of Soil Pollution aims to halt the worsening situation (Zhang and Li 2016).

Technologies for remediation of contaminated soil can utilize physical, chemical, electrokinetic, thermal or biological methodologies, but in situ chemical stabilization is regarded as one of the most straightforward and cost-effective techniques (Du et al. 2020; Latif et al. 2020; Van Poucke et al. 2018; Yao et al. 2019). Biochar, which is a carbon-rich material with a porous structure, large surface area, high cation-exchange capacity (CEC) and abundant functional groups, has a high capacity for heavy metal sorption (Li et al. 2017; Chen et al. 2019). For this reason it has been widely used as a green and low-cost amendment for

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stabilizing heavy metals in soils (He et al. 2019; Liu et al. 2020b; Wu et al. 2017).

The underlying mechanisms for biochar application have been systematically reported in a number of review papers, including those by Ahmad et al. (2014), Bandara et al. (2019), Chen et al. (2019) and Inyang et al. (2015). In summary, biochar sorbs metals via electrostatic forces, cation exchange, surface complexation and precipitation (Thomas et al. 2020). In addition, biochar can alter soil pH, CEC, organic matter content and composition (Cooper et al. 2020), which in turn increase heavy metal stabilization by their indirect effects. However, the performance of biochar in soils is strongly dependent on synthesis conditions, such as pyrolysis temperature and feedstock type (Wei et al. 2019). Biochar dosage, equilibrium time, mixing depth, soil mineral composition and temperature may have complex effects (Chang et al. 2019; O'Connor et al. 2018; Zhao and Zhou 2019). In this case, the application of conventional biochar for contaminant immobilization requires further improvements, while biochar modified with novel structures and surface properties is a promising way.

To date, various organic (e.g., amino, polyethylenimine, chitosan and microbial) and inorganic (e.g., KMnO_4 , HNO_3 , NaOH , H_2O_2 , clay, silicate and Fe/Mn/Al) compounds have been used to modify the surface of biochar (Cai et al. 2021; Li et al. 2017; Rajapaksha et al. 2016; Zhu et al., 2020). Iron oxide is widespread in the environment as a low-cost sorbent, and manganese oxide is a very promising compound due to its high redox potential. Fe–Mn binary oxides, which are a combination of iron (hydr)oxides and manganese oxides, avoid the crystallinity problems of iron oxides and offer the beneficial characteristics of manganese oxides (Du et al. 2018; Xie and Zhao 2016), which have an excellent adsorption capacity for binding heavy metals. Ferromanganese is also the major component of root plaques (Fu et al. 2016), which could adsorb and/or co-precipitate metals, thus modulating the uptake and bioaccumulation of metals in plants (Zhang et al. 2019c). However, the modification of ferromanganese (Fe–Mn) and its application in contaminated soils have been little studied (Cui et al. 2019; Yu et al. 2016). In practice, Fe–Mn binary oxides could readily release Mn(II), which would limit their widespread application (Khan et al. 2012). The immobilization of Fe–Mn binary oxides on a host material such as biochar may reduce Mn(II) release, and the advantages of both materials could be exploited (Lin et al. 2017; Wang et al. 2015; Zhang et al. 2019a). For example, a recent study by Yin et al. (2020) showed that Fe–Mn-modified biochar sorbs much more Cd (~95 mg/g) than pristine biochar (~30 mg/g) in an aqueous solution. Lin et al. (2017) reported that Fe–Mn-modified biochar shows a higher adsorption of As ($Q_{\text{max}} = 8.25$ mg/g) than Fe–Mn binary oxide and pure biochar. To our knowledge, there have been very few studies of the application of

such materials in contaminated soils, with just one study reporting that the use of Fe–Mn-modified biochar could increase soil redox potential and reduce the soil content of available As (Lin et al. 2019). However, that study only monitored soil As speciation over a short period (100 days). Therefore, there is a need to explore the performance of this additive, especially with regard to the stabilization of soil heavy metals and the reduction of their bioaccumulation by plants, over a longer time period.

In the present study, a ferromanganese biochar was synthesized by co-pyrolysis of coconut shells with $\text{Fe}(\text{NO}_3)_3$ and KMnO_4 at 600 °C, and was then utilized in a three-year pot experiment accompanied by six rice (*Oryza sativa* L.) crop seasons. The aim was to determine the dynamic changes in soil Cd speciation and rice Cd accumulation, as well as in soil pH, Eh, and root Fe and Mn plaque content, over this long cultivation period with ferromanganese biochar amendments. It was hoped that by ascertaining the long-term performance of this material, new insights might be gained into the development of biochar-based materials for green remediation of Cd-contaminated paddy soils.

2 Materials and methods

2.1 Preparation and characterization of Fe–Mn-modified biochar

Coconut shells (CS) were obtained from Aigenisi Environmental Technology Co., Ltd (Jiangsu Province, China), and used to produce pristine biochar (CSB) by slow pyrolysis at 600 °C for 2 h in a muffle furnace under nitrogen flow (300 mL/min). Next, a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (200 mL, 0.672 M) and KMnO_4 (200 mL, 0.224 M) (Fe:Mn molar ratio, 3:1) was dripped in, and subjected to additional pyrolysis at 600 °C for 30 min to produce Fe–Mn-modified biochar (FM-CSB). Deionized (DI) water was used to wash resulting samples several times to eliminate any impurities, and the samples were then dried at 65 °C.

Elemental analyzer (Elementar Analysen Systeme GmbH, Hanau, Germany) was employed to calculate the C, N and H content of CSB and FM-CSB. pH meter (Sartorius PB-10, Germany) was used to measure pH at a ratio of 1:10 (w/w) biochar: water. Total pore volume and specific surface area (SSA) were calculated by BET- N_2 analyzer (JW-BK222, JWGB, China), and surface morphology and chemical composition were examined by a scanning electron microscope (SEM) combined with an energy-dispersive spectroscopy (EDS; JSM-5600LV, Japan). FT-IR spectrometer (Nexus 870, Nicolet, USA) was used to record the Fourier transform infrared (FT-IR) spectra. Powder X-ray diffraction (XRD) was measured using a Bruker D8 ADVANCE powder diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406$ Å).

2.2 Pot experiment design

Samples of Cd-contaminated paddy soil were collected from the plow layer (0–20 cm) in Zhuzhou City (113°19'E, 27°51'N), Hunan Province, China. Soil chemical properties were as follows: pH, 5.31; organic matter (OM) content, 36.32 g/kg; CEC, 12.10 cmol/kg; total N, 2.21 g/kg; total P, 0.66 g/kg; Fe, 38.30 g/kg; Mn, 255.42 mg/kg; Cd, 1.05 mg/kg. The soil that was sampled was moderately polluted with Cd following the Soil Environmental Quality Standards for China (GB 15,618–2018).

Pot experiments were performed in triplicate, and each pot was filled with 25 kg of soil. Biochar was pre-inoculated into the soil prior to rice cultivation. There were six different pre-inoculation treatments, namely control (no amendment), 0.05 wt% FM-CSB, 0.1 wt% FM-CSB, 0.2 wt% FM-CSB, 0.5 wt% FM-CSB and 0.5 wt% CSB. All additives were added only once, in April 2017. As rice is traditionally cultivated twice a year (the early and late rice) locally, the study design consisted of three annual cycles (from 2017 to 2019) with six crop-growing seasons. The soils were watered daily to maintain flooded status (~2 cm above the soil surface). The details of the procedures for cultivation and management were identical to those described in our two recent studies (Liu et al. 2018; 2020b).

2.3 Sampling and analysis

In situ soil redox potential and pH were measured using a redox electrode (TES-1381, Taiwan, China). Root Fe–Mn plaques at the mature stage were extracted using the dithionite–citrate–bicarbonate (DCB) method as described by Taylor and Crowder (1983), with DCB solution containing 0.03 M sodium citrate, 0.125 M sodium bicarbonate and 1 g of sodium dithionite. Plasma mass spectrometry (ICP-MS, Agilent-7500cx) was employed to measure the DCB-Fe, DCB-Mn and DCB-Cd levels in the extracts.

At the mature stage, we collected the topsoils (0–15 cm). Samples were air dried and ground so that they could be passed through a 0.147 mm sieve. Soil Cd fractionation (exchangeable fraction (F1), easily reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4)) were achieved using a sequential extraction procedure (BCR) proposed by the European Community Bureau of Reference (Ure et al. 1993). The Cd concentration was measured using ICP-MS.

Roots (after extraction of Fe and Mn plaques), stems, leaves, and grains were collected after harvest, air dried, and digested in a mixed solution of HNO₃ and HClO₄ (4:1, v/v). The total Cd concentration was measured using ICP-MS.

SPSS 21.0 software was used for the statistical analyses. Significant differences between treatments ($p < 0.05$) were calculated by One-way ANOVA.

3 Results and discussion

3.1 Characterization of ferromanganese biochar

The coarse surfaces and porous structures of pristine biochar are shown in the SEM images in Fig. 1. After modification, the pores were full of small particles that were shown by energy spectrum analysis to be rich in Fe and Mn elements (Fig. 1b). This indicates that ferromanganese is predominantly located in pores rather than on the rough surface, which may suggest the blockage of biochar pores, giving rise to a decreased SSA and total pore volume (especially micropore) (Table 1). XRD was further performed to determine the Fe–Mn mineral composition. Compared with pristine biochar, FM-CSB showed several *d*-spacings located at ~0.297, 0.253, 0.211, 0.162 and 0.149 nm (Fig. 1d), which is consistent with the structures for jacobsonite (MnFe₂O₄) (Wang et al. 2015). FT-IR analyses further revealed hydroxyl (–OH stretching vibrations, 3396 cm^{–1}), carboxylic (C=O and C=C stretching vibrations, 1635 cm^{–1}) and alcohol (C–O, 1422 cm^{–1}) functional groups on pristine biochar (Fig. 1c), consistent with previous observations for other biochars (Wei et al. 2019; Zhang et al. 2020). For FM-CSB, typical vibrations at around 550 cm^{–1} were assigned to the Fe/Mn–O bonds (Fig. 1c). Protonation of Fe/Mn–O functional groups may generate OH[–], creating a higher pH of FM-CSB (9.86) than CSB (9.54) (Table 1). For both pristine and modified biochar, C was the major element (76–80 wt%), followed by O, H and N (Table 1), consistent with biochar derived from other feedstocks, such as sesame straw and rice straw (Park et al. 2016; Tao et al. 2019). All of these findings demonstrate that ferromanganese is successfully loaded in mineral form into biochar pores. This structural feature may protect ferromanganese against soil aging (for a period of ~3 years), and help to maintain its long-term effectiveness after inoculation into soil.

3.2 Ferromanganese biochar changes soil pH, Eh and root Fe–Mn plaque contents

Biochar has been reported to have many significant effects on soil properties (Duan et al. 2020; Huang et al. 2020), among which soil pH, Eh, and root Fe–Mn plaques are the key geochemical factors that determine the bioavailability of heavy metals and their transport into plant roots (Shen et al. 2020; Zhang et al. 2019b; Zhu et al. 2016). In summary, our results show that biochar application significantly increases soil pH and reduces soil Eh ($p < 0.05$) (Fig. 2), consistent with previously reported findings (Yin et al. 2017). Moreover, the magnitude of these changes is

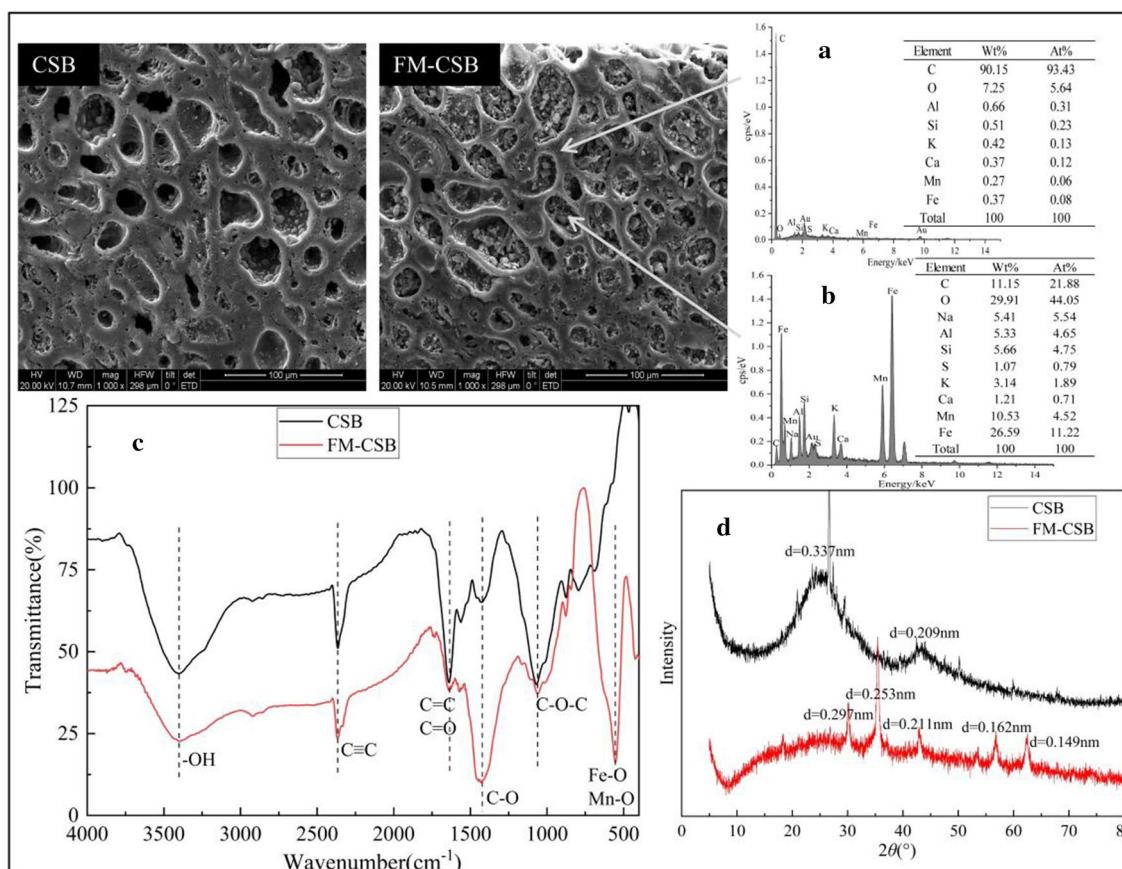


Fig. 1 SEM-EDS (a, b), FT-IR (c) and XRD (d) spectra for pristine (CSB) and ferromanganese biochar (FM-CSB)

Table 1 Basic properties of pristine (CSB) and ferromanganese biochar (FM-CSB)

	S_{BET} m ² /g	Pore volume (cm ³ /g)			Ash %	C	H	N	O	pH
		Total	Mesopore	Micropore						
CSB	511.26	0.50	0.32	0.18	20.37	80.00	3.90	0.31	13.14	9.54
FM-CSB	462.91	0.48	0.37	0.11	23.54	76.70	2.85	0.36	21.61	9.86

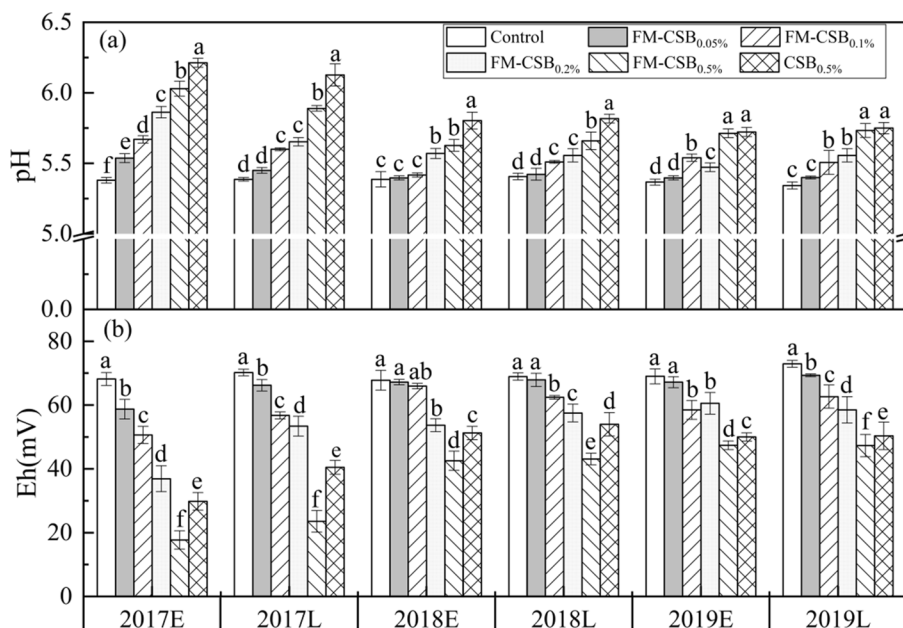
S_{BET} specific surface area (SSA)

positively correlated with the application dosage. For soil pH, in any single year CSB_{0.5%} was more effective than FM-CSB_{0.5%} in increasing soil pH (from 0.38 to 0.79). The most likely underlying mechanism is the hydration of dissolved Fe/Mn ions (Zhang et al. 2020; Yin et al. 2020) from ferromanganese, which results in an increase in acidity of the soil matrix, and partially neutralizes the alkaline effect of biochar. The increasing amplitude of pH slows down with inoculation time as a result of the strong buffering capacity of soil. For Eh, FM-CSB_{0.5%} treatment was most effective in reducing soil redox potential (21.60–50.47 mV), followed by the CSB_{0.5%} treatment (Fig. 2b). This is because, in the experimental flooded status (anoxic reducing condition), ferromanganese more readily releases Mn²⁺ which are a strong reductant that

can significantly lower Eh. Like the pattern of change in soil pH, the rate of Eh reduction slowed down over time because of the strong buffering capacity of the soil matrix. In summary, increasing soil pH and decreasing soil Eh promote heavy metals passivation (Latif et al. 2020; Zhou et al. 2018b), so ferromanganese biochar has a strong and durable capacity for long-term stabilization of soil Cd.

Fe constituted the majority (61.6–122.2 g/kg) of the plaques, in contrast to Mn (0.57–1.37 g/kg), consistent with previous observations for root plaques (Cao et al. 2018; Zhou et al. 2018b). The Fe content of root plaques remained almost unchanged, whereas the Mn content decreased after 1 year of inoculation. This is consistent with the results obtained by Wang et al. (2015), who reported that Fe is predominantly deposited as a coating on the root epidermis,

Fig. 2 Soil pH and Eh values after amendment with pristine (CSB) and ferromanganese biochar (FM-CSB) over the 3-year inoculation period. Error bars denote \pm standard deviation ($n = 3$). Lowercase letters represent significant difference using one-way ANOVA ($p < 0.05$)



whereas Mn is readily absorbed and transferred into rice roots. Increased production of DCB-Fe/Mn was observed after soil amendment with FM-CSB compared with the control and the CSB treatment ($p < 0.05$). In addition, DCB-Fe/Mn production was positively correlated with the dose of ferromanganese applied. These findings suggest that ferromanganese in biochar pores may release dissolved Fe/Mn ions during aging, and that this may contribute to the formation of amorphous Fe/Mn minerals on the root surface. It is also interesting that DCB-Mn had the similar variation tendency to the Eh reduction in Fig. 2, i.e., Eh reduction/DCB-Mn increment lasted only 1 year of inoculation, then alleviated in the 2nd year, and continued relatively constant until the 3rd year. It is possible that Mn is more responsible for Eh reduction than Fe, probably attributable to the higher reductive property of Mn^{2+} . The DCB-Cd fractions are regarded as those adsorbed by the Fe–Mn plaques (Hu et al. 2019; Huang et al. 2018), and are considered to be inactive with regard to bioaccumulation. The results shown in Fig. 3 demonstrate that DCB-Cd increases significantly ($p < 0.05$) after FM-CSB amendment compared with the control and the CSB treatment. Thus, the transfer of Cd from the soil to root tissue is significantly suppressed after ferromanganese biochar application. More importantly, the DCB-Cd content remains high throughout the 3-year experimental period, which demonstrates its long-lasting effect.

3.3 Ferromanganese biochar changes soil Cd fractionation

The results for soil Cd speciation over the 3-year inoculation period are shown in Fig. 4. The exchangeable fraction (F1)

was readily mobile and bioavailable, whereas the residual fraction (F4) was the most stable form and was unavailable to biota. The reducible fraction is thought to consist of Cd bound to amorphous Fe–Mn oxides and hydroxides, whereas the oxidizable Cd is predominantly associated with organic matter and sulfides (Wang et al. 2006). The bioavailability of these two fractions is dependent on soil properties (Jayarathne et al. 2018; Palleiro et al. 2016). For untreated soil (control), Cd fractionation remained almost unchanged over the 3-year period, with the exchangeable Cd being predominant, followed by the reducible, oxidizable and residual fraction. Biochar plays an important role in shaping soil Cd fractionation, as the exchangeable Cd decreases, whereas the residual Cd generally increases after the application of both pristine and ferromanganese biochar (Fig. 4). This suggests that biochar can stabilize soil Cd and decrease its bioavailability, consistent with previous observations (Cui et al. 2016; Li et al. 2016). Moreover, it seems that ferromanganese biochar is more effective in soil Cd stabilization than pristine biochar at the same dosage (0.5%).

Biochar and ferromanganese undergo many soil processes during aging, which result in a decrease in their stability (Quan et al. 2020), therefore influencing Cd speciation. For example, in 2017E and 2017L, all biochars were able to reduce the reducible fraction, but after 2018E to the end of incubation the reducible fraction did not change. This trend agrees with those of Eh/DCB-Mn in Figs. 2 and 3, suggesting that Mn hydroxides play a dominant role in changing the reducible Cd fraction. However, over the 3-year experimental period the levels of oxidizable Cd gradually increased, possibly due to that biochars provide more functional groups during aging, maintaining it high ability to

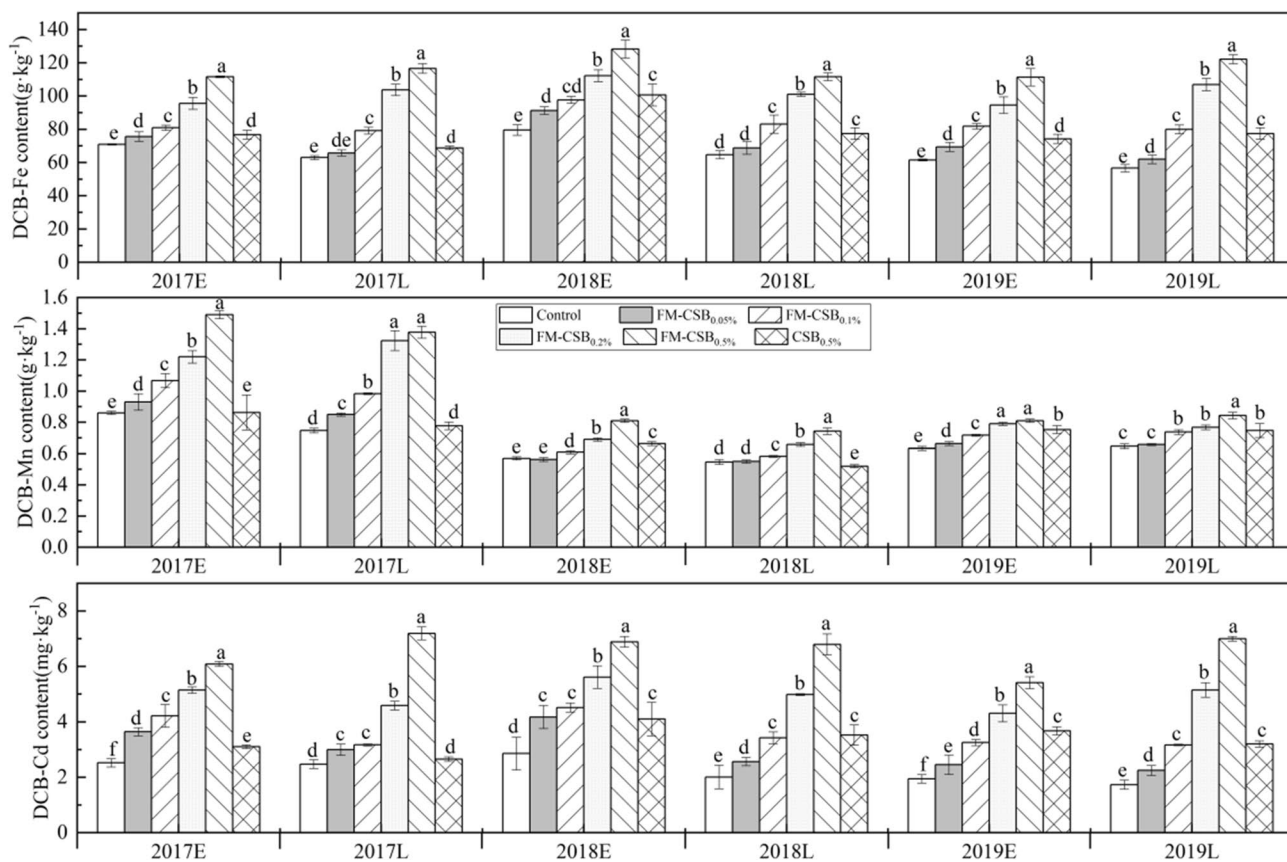


Fig. 3 DCB-Fe, Mn and Cd content in root plaques after amendment with pristine (CSB) and ferromanganese biochar (FM-CSB) over the 3-year inoculation period. Error bars denote \pm standard deviation

($n=3$). Lowercase letters represent significant difference using one-way ANOVA ($p < 0.05$)

capture heavy metals. These changes between the different Cd fractions reflect a dynamic change in the efficiency of biochars amendment over time. Overall, then, ferromanganese biochar can significantly stabilize Cd over a 3-year period, which provides further evidence for its long-term effectiveness.

3.4 Ferromanganese biochar reduces Cd uptake by rice tissues

The Cd levels in different tissues in rice are presented in Table 2. In general, both pristine and ferromanganese biochar applications resulted in a decrease in the Cd content of roots, leaves, stems and grains, compared with no amendment. Of the different treatments, FM-CSB_{0.5%} was the most effective in decreasing Cd accumulation in rice, followed by CSB_{0.5%} and FM-CSB_{0.2%}, followed in decreasing order by FM-CSB_{0.1%} and FM-CSB_{0.05%}. Root and grain Cd levels are commonly regarded as two of the most important indicators for assessing the efficiency of remediation. The results showed that amendment with FM-CSB_{0.5%} resulted in a 30–70% reduction in root Cd content and a 50–70%

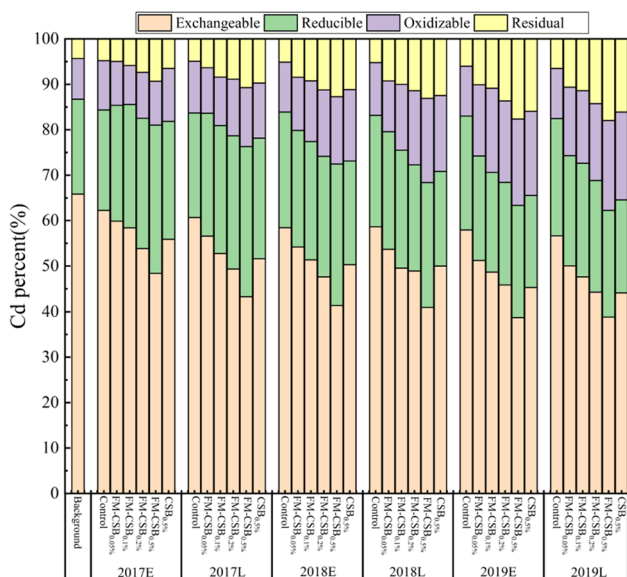


Fig. 4 Soil Cd fractionation after amendment with pristine (CSB) and ferromanganese biochar (FM-CSB) over the 3-year inoculation period

Table 2 The Cd concentration in different rice organs after amendment with pristine (CSB) and ferromanganese biochar (FM-CSB)

Years	Treatments	Early rice				Late rice			
		Roots	Stems	Leaves	Grains	Roots	Stems	Leaves	Grains
2017	Control	4.575 ± 0.108a*	2.846 ± 0.109a	1.683 ± 0.042a	0.225 ± 0.017a	4.460 ± 0.106a	2.326 ± 0.084a	1.660 ± 0.821a	0.122 ± 0.008a
	FM-CSB _{0.05%}	4.264 ± 0.140b	2.468 ± 0.046b	1.492 ± 0.010b	0.195 ± 0.008b	4.196 ± 0.223b	2.085 ± 0.094a	0.969 ± 0.552c	0.077 ± 0.004b
	FM-CSB _{0.1%}	3.742 ± 0.193c	2.068 ± 0.084c	1.373 ± 0.026c	0.176 ± 0.020bc	3.821 ± 0.069c	1.618 ± 0.108b	1.284 ± 0.722b	0.038 ± 0.008c
	FM-CSB _{0.2%}	3.319 ± 0.125d	1.752 ± 0.119d	1.213 ± 0.022d	0.151 ± 0.007c	3.715 ± 0.150c	1.351 ± 0.121c	1.018 ± 0.175bc	0.037 ± 0.006c
	FM-CSB _{0.5%}	2.802 ± 0.057e	1.315 ± 0.036f	0.881 ± 0.043e	0.109 ± 0.016d	2.662 ± 0.133d	1.032 ± 0.255d	1.032 ± 0.255bc	0.036 ± 0.010c
	CSB _{0.5%}	3.299 ± 0.046d	1.563 ± 0.090e	1.244 ± 0.058d	0.160 ± 0.008c	3.733 ± 0.116c	1.311 ± 0.123c	0.978 ± 0.876c	0.047 ± 0.024c
2018	Control	4.933 ± 0.160a	0.748 ± 0.097a	0.611 ± 0.032a	0.125 ± 0.018a	4.143 ± 0.359a	0.886 ± 0.168a	0.729 ± 0.066a	0.218 ± 0.030a
	FM-CSB _{0.05%}	4.283 ± 0.077b	0.538 ± 0.054b	0.547 ± 0.051b	0.103 ± 0.018ab	4.045 ± 0.125a	0.636 ± 0.026b	0.591 ± 0.044b	0.192 ± 0.013ab
	FM-CSB _{0.1%}	3.477 ± 0.094c	0.453 ± 0.039bc	0.386 ± 0.046c	0.086 ± 0.027bc	2.894 ± 0.122b	0.545 ± 0.066bc	0.532 ± 0.081b	0.183 ± 0.015b
	FM-CSB _{0.2%}	2.628 ± 0.281d	0.443 ± 0.045bc	0.332 ± 0.010d	0.070 ± 0.006c	1.856 ± 0.155d	0.408 ± 0.084 cd	0.407 ± 0.062 cd	0.124 ± 0.015c
	FM-CSB _{0.5%}	2.149 ± 0.117e	0.384 ± 0.005c	0.299 ± 0.018e	0.066 ± 0.005c	1.832 ± 0.118d	0.373 ± 0.037d	0.340 ± 0.036d	0.109 ± 0.018c
	CSB _{0.5%}	2.461 ± 0.174d	0.435 ± 0.065bc	0.382 ± 0.030d	0.08 ± 0.008bc	2.523 ± 0.064c	0.591 ± 0.039b	0.490 ± 0.043bc	0.130 ± 0.009c
2019	Control	4.405 ± 0.210a	0.689 ± 0.066a	0.588 ± 0.018a	0.112 ± 0.014a	5.938 ± 0.279a	0.940 ± 0.096a	0.888 ± 0.113a	0.223 ± 0.059a
	FM-CSB _{0.05%}	3.440 ± 0.117b	0.396 ± 0.034b	0.39 ± 0.107b	0.086 ± 0.009b	3.359 ± 0.160b	0.597 ± 0.088b	0.535 ± 0.089b	0.192 ± 0.030a
	FM-CSB _{0.1%}	2.902 ± 0.146c	0.367 ± 0.021b	0.382 ± 0.036b	0.067 ± 0.007c	3.050 ± 0.118c	0.577 ± 0.050bc	0.408 ± 0.071bc	0.171 ± 0.017ab
	FM-CSB _{0.2%}	2.782 ± 0.220c	0.334 ± 0.020bc	0.304 ± 0.038bc	0.050 ± 0.020c	2.697 ± 0.167d	0.469 ± 0.049 cd	0.446 ± 0.047bc	0.114 ± 0.060bc
	FM-CSB _{0.5%}	2.201 ± 0.413d	0.253 ± 0.053c	0.249 ± 0.013c	0.057 ± 0.011c	1.952 ± 0.145e	0.424 ± 0.036c	0.392 ± 0.201c	0.087 ± 0.017c
	CSB _{0.5%}	2.839 ± 0.234c	0.371 ± 0.087b	0.358 ± 0.010b	0.074 ± 0.012bc	3.015 ± 0.093c	0.520 ± 0.009c	0.383 ± 0.181c	0.155 ± 0.005abc

*Means average ± SE (n = 3), the same letter means no significant differences in column at 0.05 level

reduction in grain Cd levels during the 3-year inoculation period. In comparison, amendment with the same dose of CSB_{0.5%} resulted in a 16–50% reduction in root Cd content and a 30–40% reduction in grain Cd levels. This clearly demonstrates that, compared with pristine biochar, ferromanganese biochar has a greater ability to reduce Cd bioaccumulation. It is also noteworthy that grain Cd concentrations were all below the acceptable limit of 0.20 mg/kg (National Food Safety Standard for Maximum Levels of Contaminants in Foods, GB 2762–2017), and the remediation efficiency of FM-CSB remained high throughout the 3-year period.

3.5 Mechanisms and implications

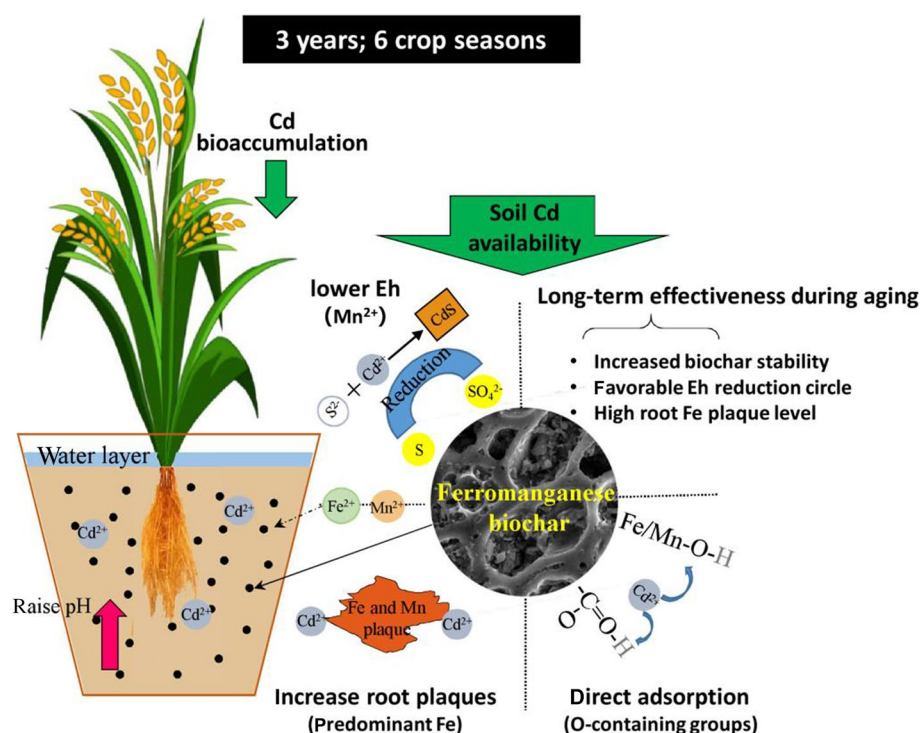
There is a lack of attention paid to the application of ferromanganese biochar for remediation of heavy metal-contaminated soil, especially over long time periods. Our findings indicate that ferromanganese biochar is more effective than the same dose of pristine biochar for the remediation of Cd-contaminated paddy soil. There are several possible explanations for this (Fig. 5).

First, although the physical structure (decreased SSA and total pore volumes) of ferromanganese biochar is not more favorable for Cd binding than that of pristine biochar, elemental analysis shows that ferromanganese biochar exhibits a higher O/C ratio (28.17%) than pristine biochar (16.43%). Li et al. (2016) proposed that Cd adsorption by biochar is positively correlated with the O/C ratio, with higher O/C ratios indicating the presence of more O-containing

functional groups that are able to form complexes with Cd (Liu et al. 2021). The newly formed Fe/Mn–OH bonds on the surface may also contribute to an increased O/C ratio, thereby the mineral fraction can also complex a great quantity of Cd (Liu et al. 2020a). Thus, ferromanganese biochar itself may have a strong binding capacity for Cd when introduced into soil.

Second, more Fe–Mn plaques are observed on root surfaces after soil amendment with ferromanganese biochar. This indicates that, under flooded conditions, ferromanganese minerals on biochar pores dissolve and release soluble Fe/Mn ions that subsequently contribute to the formation of root Fe–Mn plaques (Kashem and Singh 2006). However, previous studies report that Fe–Mn plaques can accelerate root uptake and transport heavy metals into rice tissues (Du et al. 2017; Zhang et al. 2020). This may be caused by the highly Cd depositing on plaques and then becoming the Cd source of roots through Fe–Mn transporters (*OsNRAMP5*) (Zhang et al. 2019c). However, as a general rule, Cd accumulation in root tissue increases when the DCB-Fe content is in the range of 15.0~22.5 g/kg, and decreases when DCB-Fe levels exceed 22.5 g/kg (Zhang et al. 2020). The DCB-Fe values in the present study (> 60 g/kg) greatly exceed 22.5 g/kg, which suggests that Fe–Mn plaques reduce Cd uptake by root tissue under experimental conditions. In addition, because ferromanganese biochar amendment increases the production of Fe–Mn plaques, more labile soil Cd can bind strongly to Fe–Mn plaques through inner-sphere complexes (Zhou et al. 2018a).

Fig. 5 Hypothesized reaction mechanisms that contribute to the immobilizing soil Cd and preventing its translocation to rice



Third, compared with pristine biochar, ferromanganese biochar shows a greater ability to decrease soil Eh. Decreased Eh is owing to the presence of dissolved Fe³⁺ and Mn²⁺ released from ferromanganese. And also because Mn²⁺ is a stronger reducing agent, the Eh variation tendency, therefore, more resembles that of Mn²⁺. This in return influences the dynamic changes in the reducible (F2) over the 3-year inoculation period, i.e., the reducible fraction did not change significantly after 1 year incubation. Under flooded conditions, soil is in a reducing state (low Eh). Sulfur and sulfate could be reduced to sulfide (S²⁻), generating a more stable Cd fraction as a result of sulfide precipitation, which is associated with the F3 fraction (Chen et al. 2020; Karimian et al. 2018; Rajendran et al. 2019). Overall, however, ferromanganese biochar can stabilize soil Cd by both direct and indirect means.

Long-term effectiveness is very important for stabilization-based remediation. The finding of current study shows that the remediation efficiency of ferromanganese biochar remains high over a 3-year period. Biochar itself can stabilize soil heavy metals by direct adsorption and/or precipitation, and by increasing soil pH and decreasing Eh (Sheng and Zhu 2018). After it has been introduced into soil, aged biochar has more carboxylic, carbonylic, phenolic and other O-containing functional groups, which maintain its strong ability to capture heavy metals over time (Bian et al. 2014; Li et al. 2016). In the current study, three additional processes may have contributed to the long-term effectiveness of the ferromanganese biochar. First, it is soil Eh after the

addition of FM-CSB_{0.5%} that is always lowest during the inoculation period. This is because, under reducing conditions, ferromanganese more readily releases Fe³⁺/Mn²⁺, which further increases the degree of reduction, creating a favorable cycle (Yin et al. 2017; Islam et al. 2021). Second, the results shown in Fig. 3 demonstrate that DCB-Fe maintains at a high level, presumably because of the fact that Fe ions are continuously released from ferromanganese biochar, and subsequently contribute to root plaque formation. Therefore Fe plaques can sequester Cd on the root surface and reduce Cd transport into rice root tissue over a period of years. Third, biochar-based materials undergo an aging process in soils, as their surface structures and properties show major changes over time. Soluble carbon produced as a result of biochar decomposition is utilized by microorganisms against biochar-stabilized Cd for long-term. However, biochar aging with minerals has been reported to increase biochar stability (Lai et al. 2019; Lu et al. 2020; Ren et al. 2018). For example, the interaction of biochar with minerals (such as kaolinite, FeCl₃, AlCl₃ or CaCO₃) increases the proportion of aromatic carbon, further reducing the loss of biodegradable carbon and increasing the stability of soluble and insoluble biochar (Li et al. 2014; Yang et al. 2018a, 2018b, 2016; Zhao et al. 2015b). Therefore, the ferromanganese coating in the present study may also enhance the long-term stability of biochar and the associated Cd, but further research is required to obtain more direct evidences. Furthermore, this study was conducted under flooded conditions; so, the behavior of ferromanganese biochar in unsaturated soil

needs to be investigated thoroughly to expand its already wide application.

4 Conclusions

Ferromanganese biochar was synthesized by co-pyrolysis of coconut shells with $\text{Fe}(\text{NO}_3)_3$ and KMnO_4 at 600 °C. Pot experiments showed that the application of ferromanganese biochar (0.5 wt%) to paddy soil was much more effective in stabilizing soil Cd than the same dose of pristine biochar. Its stabilizing effect was predominantly exerted by decreasing soil Eh and increasing root Fe plaques. Ferromanganese biochar application helps to reduce Cd bioaccumulation in rice plants, and the grain Cd levels are all below the acceptable limit for food security. We propose that ferromanganese itself can maintain a low soil redox status and high levels of root Fe plaques, and may also increase biochar stability, all of which can enable its high remediation efficiency over a long time period. In summary, the results of this study indicate that ferromanganese biochar has great potential for application in the chemical stabilization of Cd-contaminated paddy soils.

Acknowledgements This work was financially supported by the National Key Research and Development Program of China (2017YFD0801505), National Natural Science Foundation of China (NSFC) (No. 41907015), China Postdoctoral Science Foundation (2019M662782), and Scientific Research Fund of Hunan Provincial Education Department, China (18B120).

Author Contributions YL: Methodology, Formal analysis, Investigation, Data Curation, Writing—Original Draft, Visualization. HL: methodology, Formal analysis, Investigation, Visualization. BT: Conceptualization, Validation, Resources, Data Curation, Supervision, Project administration, Funding acquisition. DL: Methodology, Investigation. SL: Methodology, Investigation. ML: Validation, Supervision. HD: Validation, Formal analysis, Data Curation, Writing—Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

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