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Effects of stabilizing materials on soil Cd bioavailability, uptake, transport, and rice growth

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Cadmium, a widespread toxic heavy metal in farmland soils, is harmful to human health. A field experiment was conducted to investigate the effects of biochar and biochar-based fertilizers on soil pH, organic matter, and available Cd, as well as rice Cd uptake and translocation. The results showed that rice biomass was significantly increased after both the application of biochar and high rate of biochar-based fertilizers at the tillering stage. The biomass and plant height of rice were improved at filling and maturity stages. Soil pH was significantly increased with the application of biochar but not with the biochar-based fertilizer. The amendments of biochar and biochar-based fertilizers had no significant ($p < 0.05$) influence on soil organic matter content. The concentration of available Cd in soil and the concentration of Cd in rice were decreased with the application of different amounts of biochar and biochar-based fertilizers in the mature stage. However, this effect was much greater under biochar amendment. Compared to the control, the concentration of available Cd in soil was reduced by 33.09% with the low application rate of biochar, while that was reduced by 18.06% with the high application rate of biochar. The lowest bioaccumulation factor was due to the high concentration of biochar and biochar-based fertilizers. It is concluded that biochar and biochar-based fertilizers particularly at a high addition rate are appropriate for decreasing Cd mobility and improve soil quality for contaminated paddy soils. The study showed a method for the safe production of rice in Cd-polluted farmlands by using a high application rate of biochar or carbon-based fertilizers.

KEYWORDS

biochar, biochar-based fertilizer, Cd, rice, farmland soils

1 Introduction

Heavy metal pollution of agricultural soil can be due to industrial wastes and the application of agricultural chemicals, such as fertilizers and pesticides (Jin et al., 2019). This seriously affects quality and yield of agricultural products, which further poses a threat to human health (Yan et al., 2016; Shang et al., 2019). The major heavy metals in

contaminated soils are Cd, Pb, Cu, and As, among which Cd is the most common heavy metal in agricultural soils. Rice, one of the main food crops in China, accounts for 55% of the annual grain consumption in China (Ye et al., 2012). Rice planted in Cd-contaminated soils can result in Cd accumulation in rice grains (Cai et al., 2019; Huang et al., 2019) and further enter into the human body through the food chain (Long et al., 2019). Accumulation of Cd in the human body can lead to a series of diseases, such as anemia, organ damage, and progression of cancer in humans (Zhong et al., 2017). Therefore, soil Cd pollution is a critical issue in the rice-growing area of China.

The *in situ* remediation technology of Cd is one of the most widely used agricultural soil remediation technologies (Xu et al., 2019). The amendments currently used widely for remediating Cd-contaminated soils can promote plant growth and reduce risk of soil pollution (Beesley and Marmiroli 2011; Bolan et al., 2014). However, different amendments derived from different materials can immobilize soil Cd to reduce its environmental risk in various ways (Abad-Valle et al., 2016; Kai et al., 2017). Among the passivators, biochar is a commonly used amendment to reduce Cd in agricultural soils to ensure safe production of rice (Hamid et al., 2020; Yang et al., 2021). Biochar-based fertilizers are also an eco-friendly fertilizer that are based on biochar in addition to the organic or inorganic fertilizers (Nyambishi et al., 2017). The application of biochar in the soil can improve soil's physical structure, improve soil's acidity by increasing soil pH, and enhances the water-holding capability and soil fertility, thus ultimately increasing the crop yield (Mansoor et al., 2021; Mohamed et al., 2021). Biochar has a large specific surface area and a strong adsorption capacity for heavy metals, which can be used to reduce the bioavailability of heavy metals (Tian et al., 2021). Previous research showed that biochar could significantly reduce the concentration of acid-soluble Cd in soils by increasing soil pH, thus consequently increasing the Cd immobilization (Xu et al., 2022). Meanwhile, the biochar is effective for promoting plant growth and reducing Cd accumulation (Albert et al., 2021; Wang et al., 2022), showing that the 1% application rate of biochar reduced the Cd concentrations of rice grains by 29.3–35.2%. Biochar derived from different raw materials and produced under different conditions can affect the remediation efficiency of Cd-contaminated agricultural soils (El-Naggar et al., 2021; El-Naggar et al., 2022).

The application of biochar and biochar-based fertilizers to polluted agricultural soils displayed a great practical significance for preventing soil nutrient loss and alleviating agricultural non-point source pollution (Lv et al., 2021). We hypothesized that the application of biochar and biochar-based fertilizers can reduce the transport of Cd from the soil to plant and the accumulation of Cd in rice grains through decreasing the bioavailability of Cd in soil. In this study, a field experiment was conducted to study the effects of the application rate of biochar and biochar-based fertilizers on chemical properties of soil, soil Cd availability, and its uptake by rice, as well as the growth of rice in a Cd-contaminated rice-growing soil. This study aims to search for an

effective method for decreasing Cd uptake and clarify the effects of biochar and biochar-based fertilizers on heavy metal immobilization and rice growth.

2 Materials and methods

2.1 Test materials

The tested soil was the paddy soil, with a pH of 5.56, organic matter of 2.3%, available N of 126 mg kg⁻¹, available P of 4.58 mg kg⁻¹, available K of 110 mg kg⁻¹, and total Cd of 0.42 mg kg⁻¹.

Biochar was produced from wood chips under an oxygen-limited condition; the material was heated to 450°C at a heating rate of 20°C/min with a retention time of 2 h in a muffle furnace and then taken out and left until the oven temperature dropped to room temperature. A biochar-based fertilizer was produced by mixing biochar and calcium magnesium phosphate fertilizer (P₂O₅≥12%) at a 1:9 ratio. The properties of biochar and biochar-based fertilizer are presented in Table 1.

2.2 Experimental design

The experiment was conducted in the Jinhua Economic Development Zone (119°21'26", 29°3'33"). Five treatments were set for this experiment: CK, soil without amendment (control); T1, low biochar (4500 kg hm⁻¹); T2, high biochar (9000 kg hm⁻¹); T3, low biochar-based fertilizer (2250 kg hm⁻¹); and T4, high biochar-based fertilizer (4500 kg hm⁻¹). Each treatment had three replicates. In the field experiment, the random block arrangement design was adopted with a plot area of 5m × 8m each. The ridge covered by a plastic film served as spacing between plots.

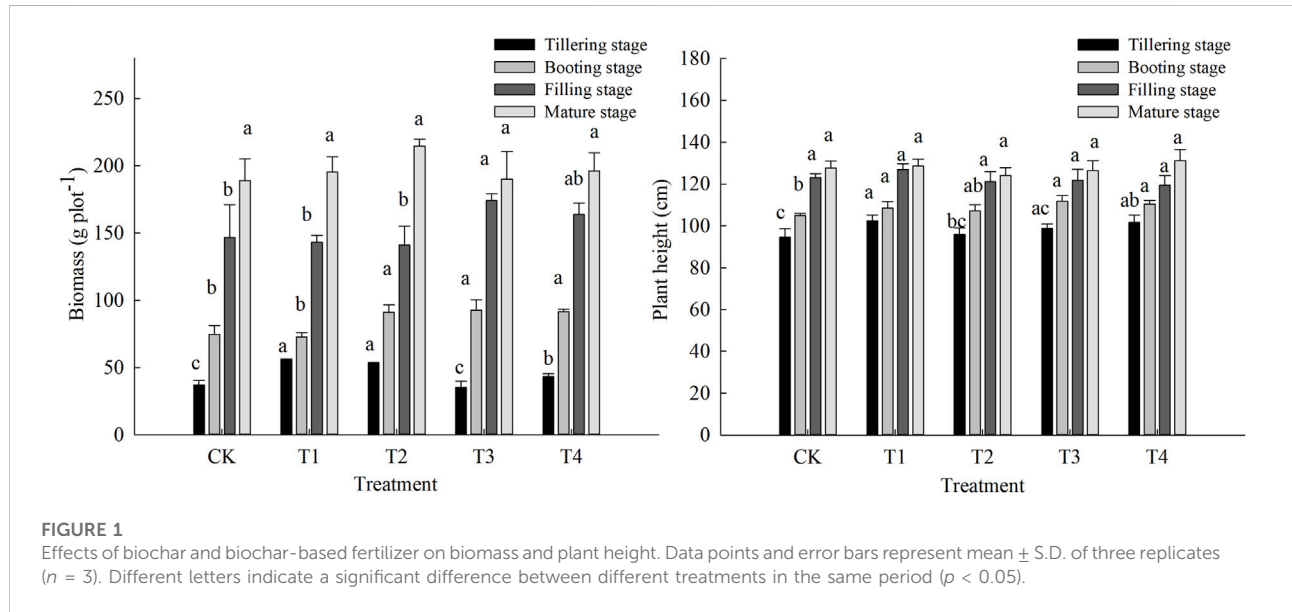
The rice variety (Yongyou 1540) at the three-leaf stage was transplanted to the field on 2 July 2020 and was harvested on 25 October 2020. The method of base fertilizer + top dressing was used for rice fertilization in all treatments. The base fertilizer was a compound fertilizer (with the contents of N, P, and K of 15-15-15), which was applied at the rate of 450 kg hm⁻², and the fertilizer was applied with top dressing (300 kg hm⁻²) at the tillering stage.

2.3 Sample collection and analysis

The samples of both rice plants and soils were collected at tillering, booting, filling, and maturity stages, respectively. Five samples were collected as a mixed sample from each plot with a depth of 0–20 cm. The harvested plants were washed three times with deionized water, heated at 105°C for 30 min, and then dried at 65°C to be of constant weight. Rice plants were divided into roots, stems, leaves, and brown rice, as well as carrying out the

TABLE 1 Characteristics of biochar and biochar-based fertilizer.

Property	Biochar	Biochar-based fertilizer
pH	10.42	8.27
Organic matter (%)	42.5	38.4
Ash (%)	12.9	11.2
Electrical conductivity (ds m ⁻¹)	0.38	0.31
Total Cd (mg kg ⁻¹)	Not detected (<0.05)	0.03



determination of dry weight of each part and plant height. The Cd content of each part was determined with digestion of 0.3 g sample with a mixture of HNO₃ and HClO₄.

The harvested soils were air-dried and passed through 2-mm and 0.149-mm sieves for chemical analysis. We determined their chemical properties such as pH value (soil/water ratio of 1:2.5), organic matter (potassium dichromate volumetric method), available N (alkaline diffusion method), available P (molybdenum antimony anti-colorimetric method), available K (flame photometer), and total Cd content (Xu et al., 2021). Available Cd contents in soils (extracted by 0.1 M CaCl₂ after shaking for 4 h at 1:20 w/v) were determined according to Xu et al. (2021). The soil and plant Cd contents were analyzed by atomic absorption spectroscopy (Shimadzu AA-7000, Japan). The number of certified reference material was GBW 07405 (GSS-5) for verification of soil analysis. The quality control showed the spiked recoveries of Cd between 90% and 110%. The Cd accumulation in terms of bioaccumulation factor (BCF) and translocation factor (TF) were determined as follows: BCF = [Cd concentration in rice tissues]/[Cd total concentration in

soil]; TF = [Cd concentration in the stem (leaf, husk, and brown rice)]/[Cd concentration in the root].

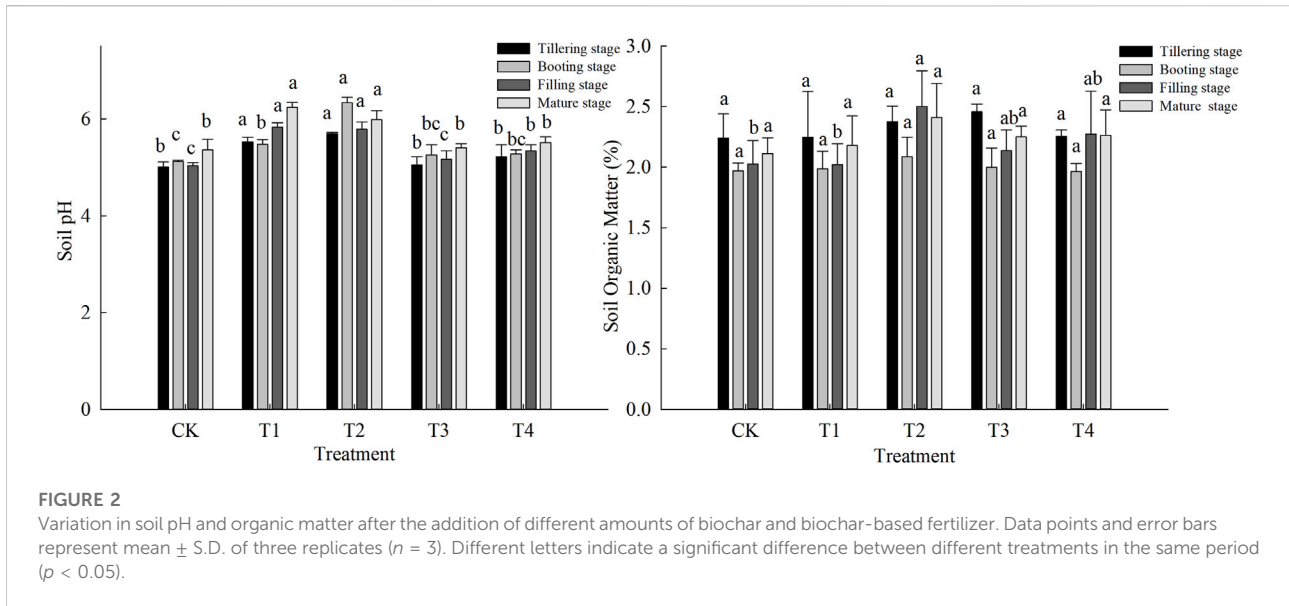
2.4 Statistical analysis of data

Statistical analysis was conducted using SPSS 21.0. The values were reported as mean and standard deviation of three independent replicates. The difference was statistically significant at p < 0.05 using one-way ANOVA and LSD. The graphical work was carried out using SigmaPlot software v.12.5.

3 Results

3.1 Plant height and the biomass of rice tissues

Figure 1 displays that the biomass of rice at the tillering stage was significantly increased by 50.63%, 42.57%, and 17.13% after



the application of low and high biochar and high biochar-based fertilizer compared to the control, respectively. The biomass of rice at booting and filling stages was increased by 24.30%, 18.63%, 22.86%, and 11.59% with different amounts of the biochar-based fertilizer compared to the control, respectively. The biomass of rice at maturity stages did not exhibit a significant increase with biochar and biochar-based fertilizer treatments compared to the control (Figure 1). The height of the rice plant was enhanced after the addition of biochar and biochar-based fertilizer at tillering and booting stages. There was no significant variation in plant height during filling and maturity stages.

3.2 Dynamic changes of soil properties

Figure 2 indicates that biochar treatment significantly increased soil pH by 0.49 unit compared to CK (p < 0.05) at the maturity stage. There was no change in soil pH after the application of the biochar-based fertilizer. The higher pH value was found in biochar-treated soils than those treated with the biochar-based fertilizer. The treatments of biochar and biochar-based fertilizer showed no significant improvement in soil organic matter (OM) compared to the control (Figure 2).

3.3 Effects of different stabilizing materials on available Cd in soil

The concentration of available Cd in soil was reduced by biochar and biochar-based fertilizer, except for the low

biochar-based fertilizer at the booting stage (Figure 3). The low application of biochar significantly reduced the concentrations of available Cd in soil by 26.26% compared to those in the control at the tillering stage. The available Cd concentrations in T1, T2, T3, and T4 were reduced by 33.09%, 21.12%, 11.94%, and 19.94% in comparison with those in the control at the maturity stage, respectively. The biochar showed more significant effects on Cd immobilization in soils than the biochar-based fertilizer.

3.4 Effects of different stabilizing materials on Cd uptake and translocation in rice

The concentrations of Cd in rice were decreased with the application of stabilizing materials (Figure 4). The concentrations of Cd in roots, stems, and brown rice were significantly decreased by 19.45%, 24.95%, and 18.06% in T2 treatment and 11.78%, 25.15%, and 14.45% in T4 treatment compared to those in the control. There was no significant difference in Cd concentration of roots with low application amendment (T1 and T3 treatments) in comparison with the control.

The bioconcentration factors and translocation factors of Cd in rice were reduced by different stabilizing materials (Table 2). The BCF size of Cd in rice was $BCF_{root} > BCF_{stem} > BCF_{leaf} > BCF_{husk} > BCF_{brown\ rice}$ in all treatments. The BCF of Cd in rice in all treatments was in the sequence of: CK > low biochar > low biochar-based fertilizer > high biochar-based fertilizer > high biochar. The TF of Cd in rice was $TF_{root-shoot} > TF_{root-leaf} > TF_{root-husk} > TF_{root-brown\ rice}$.

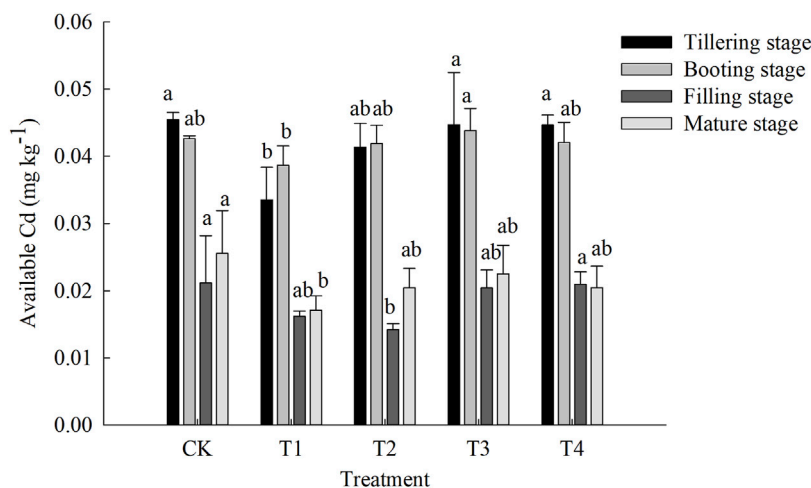


FIGURE 3 Concentrations of available Cd in soil with different stabilizing materials. Data points and error bars represent mean ± S.D. of three replicates ($n = 3$). Different letters indicate a significant difference between different treatments in the same period ($p < 0.05$).

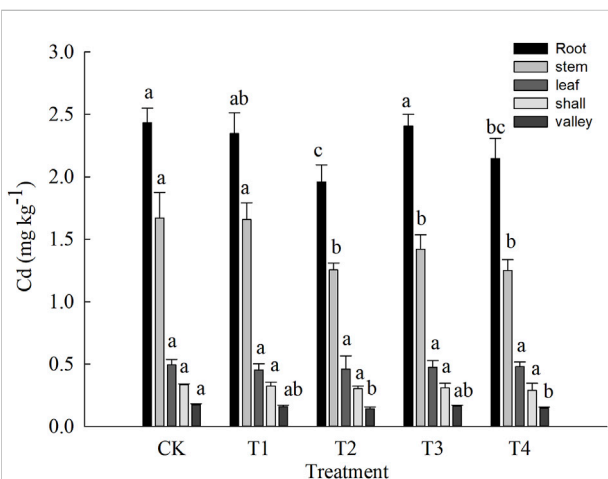


FIGURE 4 Concentrations of Cd in rice with different stabilizing materials. Data points and error bars represent mean ± S.D. of three replicates ($n = 3$). Different letters indicate a significant difference between different treatments in the same period ($p < 0.05$).

4 Discussion

Figure 2 exhibits the increase in soil pH and organic matter with the application of different stabilizing materials, and the highest pH value was recorded by treatments of biochar compared to the biochar-based fertilizer. This may be due to the higher pH of biochar (10.42) than that of the biochar-based fertilizer (8.27). The increase in soil pH and organic carbon may affect the bioavailability of Cd. The activated functional groups of

stabilizing materials (such as -OH, C-O, and CO_3^{2-}) might immobilize Cd ions in soil by precipitation, adsorption, ion exchange, or electrostatic methods (Ahmad et al., 2014; Liu et al., 2020). Previous research showed that the amendment of biochar could release free radical ions such as OH^- , HPO_4^{2-} , and CO_3^{2-} , which may precipitate with Cd and form compounds such as $\text{Cd}(\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2)$, CdCO_3 , $\text{Cd}_3(\text{PO}_4)_2$, and K_4CdCl_6 , thus reducing the bioavailability of Cd (Lei et al., 2019). In addition, the oxygen-containing functional groups (such as -OH, -COOH, and C=O) on the biochar surface could also complex with Cd in soil, increasing the Cd immobilization (Rocco et al., 2018). In this study, the decrease in available Cd concentrations in stabilizing materials may be explained by the increase in soil pH. The immobilization of Cd in soil with the amendments further decreased the translocation of Cd from soil to plants. Previous research also reported that the application of biochar (5%) to soil contaminated by heavy metals reduced Cd, Pb, and Zn mobility and availability and hence decreasing the accumulation of metals in different parts of *Phaseolus vulgaris* L (Lomaglio et al., 2018).

The results showed that Cd mainly accumulated in roots, followed by stems and leaves. The transportation route is root–stem–leaf–grain, and the application of stabilizing materials reduced the Cd accumulation in plant roots and rice grains. This suggests that the reduction of Cd transfer from the root to stem in biochar treatment may lead to the decrease in Cd accumulation in grains (Chen et al., 2016). Root–stem translocation is the main factor determining Cd accumulation in grains of rice (Yu and Zhou 2009). In this study, the transport factors from the above ground to grain of rice under high-biochar treatment increased, but the Cd concentration in rice still decreased significantly. This can be explained that the Cd

TABLE 2 Translocation factors and bioconcentration factors of Cd in rice.

Treatment	BCF					TF			
	Root	Stem	Leaf	Husk	Brown rice	Root-stem	Root-leaf	Root-husk	Root-brown rice
CK	5.40 ± 0.26a	3.71 ± 0.45a	1.09 ± 0.10a	0.76 ± 0.01a	0.40 ± 0.02a	0.687 ± 0.078a	0.204 ± 0.028a	0.139 ± 0.008a	0.072 ± 0.006a
T1	5.22 ± 0.37ab	3.69 ± 0.30a	1.00 ± 0.11a	0.71 ± 0.07a	0.36 ± 0.02ab	0.708 ± 0.071ab	0.194 ± 0.034a	0.138 ± 0.006a	0.069 ± 0.005a
T2	4.36 ± 0.30c	2.78 ± 0.12b	1.02 ± 0.24a	0.67 ± 0.05a	0.31 ± 0.03b	0.643 ± 0.072abc	0.234 ± 0.041a	0.155 ± 0.017a	0.073 ± 0.004a
T3	5.36 ± 0.21a	3.16 ± 0.26b	1.04 ± 0.12a	0.69 ± 0.08a	0.36 ± 0.02ab	0.59 ± 0.033bc	0.197 ± 0.022a	0.129 ± 0.02a	0.068 ± 0.002a
T4	4.78 ± 0.36bc	2.78 ± 0.19b	1.07 ± 0.08a	0.64 ± 0.12a	0.33 ± 0.01b	0.583 ± 0.021c	0.224 ± 0.003a	0.135 ± 0.024a	0.07 ± 0.003a

mobilization in the soil was reduced, and the transfer rate of Cd from soil to the part of the plant above the ground will be reduced (Rizwan et al., 2012). Our results were in accordance with the previous research studies (Bian et al., 2013; Yao et al., 2021). Since the reduction in Cd concentration in edible parts of plants is the key to produce safe food in Cd-contaminated soils (Rizwan et al., 2016), the amendments in this study showed potential effect on remediation of heavy metal-contaminated soil.

The biomass of rice was increased significantly after the application of biochar as stabilizing materials at the tillering stage (Figure 1). This may be due to the increase in soil organic carbon which can control the bioavailability of Cd through forming organic matter–metal complexes (Chiang et al., 2006). Meanwhile, the results showed that the soil organic matter was higher in the biochar treatment than that in the biochar-based fertilizer treatment, which may be due to the higher C storage of biochar than that of the biochar-based fertilizer (Albert et al., 2021). It has been reported that the increase in soil organic carbon with the amendment of biochar and biochar-based fertilizer also provided the carbon resource to microorganisms, promoting the soil microorganism abundance and stimulating soil enzyme activity (Yan et al., 2019). Some studies also show that biochar can improve nitrogen efficiency and promote rice growth by adsorbing and slowly releasing nitrogen (Spokas et al., 2012). This further improved the soil fertility and enhanced the growth of rice (Mansoor et al., 2021). In addition, Cd may reduce the plant cell-wall constituents, inhibit mitosis, and damage the Golgi apparatus of plants which reduced the plant growth (Kachout et al., 2010), while biochar can decrease the detrimental influence of heavy metals, for example, increasing the plant chlorophyll content (Abbas et al., 2017b). In addition, plants could also mediate the transformation, mobility, and bioavailability of heavy metals, which may be due to the interactions of plant, soil, and microbes (Park et al., 2011). Thus, the amendment of biochar not only promoted the plant growth through increasing organic carbon content or nitrogen efficiency which enhanced the interactions of plant and soils but also increased the Cd immobilization in soil through reducing the Cd accumulation and transport of

cadmium in plants, increasing the rice yield and food safety (Zhang et al., 2013; Abbas et al., 2017a).

5 Conclusion

The biomass of rice increased with the application of different amounts of biochar and carbon-based fertilizers, while the height of the rice plant increased with the application of low biochar and high carbon-based fertilizer at the mature stage. The concentration of available Cd in soil was reduced with the application of biochar and biochar-based fertilizer. This may be due to the improvement of soil properties, like the increase in soil pH and organic carbon content, which further reduced the BCF of Cd at the high application rate of soil amendments. Although the translocation of Cd from the root to stem showed no significant difference with the addition of biochar, the decrease in Cd accumulation in the root still decreased the Cd accumulation in grains. It is concluded that biochar and biochar-based fertilizer with a high application rate in this study not only improve Cd-contaminated soils but also provide practical significance for future field experiments.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

MX and DL contributed to the conception and design of the study. FL and FT organized the database. ZR performed the statistical analysis. MX wrote the first draft of the manuscript. GR, ZY, DL, and MX wrote the sections of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of interest

Authors MX, FL, and FT were employed by the Chengbang Ecological Environment Co. Ltd.

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