Iron-modified biochar and water management regime-induced changes in plant growth, enzyme activities, and phytoavailability of arsenic, cadmium and lead in a paddy soil

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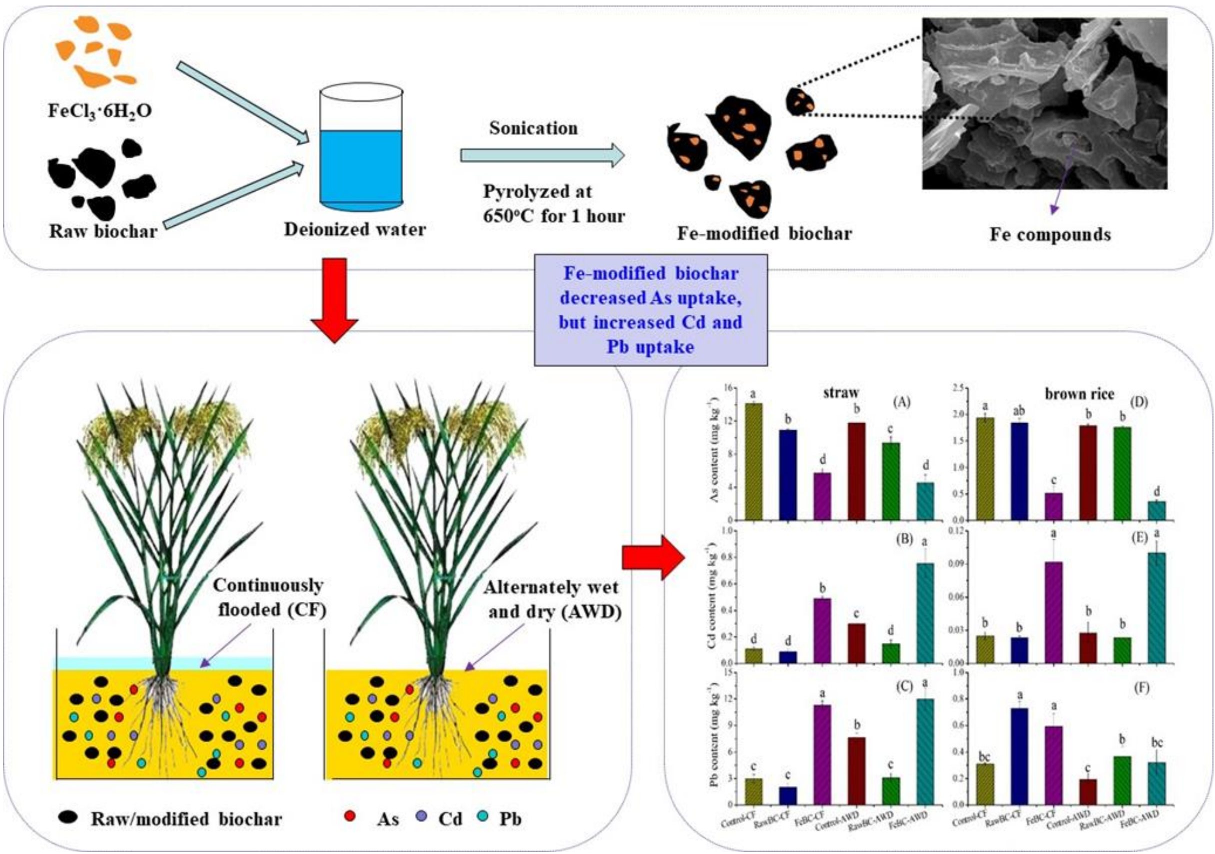
Highlights

- Fe altered the functions of biochar for PTE transformation in soil-plant system
- Soil water conditions affected the interactions between Fe, biochar and PTEs
- Fe-modified biochar mitigated the phytotoxicity of As more than raw biochar
- Raw biochar enhanced, but Fe-modified biochar inhibited the soil enzyme activities

Graphical abstract



Abstract

The aim of this study was to evaluate the effect of raw (RawBC) and iron (Fe)-modified biochar (FeBC) derived from *Platanus orientalis* Linn branches on the plant growth, enzyme activity, and bioavailability and uptake of As, Cd, and Pb by rice in a paddy soil with continuously flooded (CF) or alternately wet and dry (AWD) irrigation in a pot experiment. Application of RawBC (3%, w/w) significantly increased soil pH, while FeBC decreased it. The FeBC was more effective in reducing As and Pb bioavailability, particularly under the AWD water regime, while RawBC was more conducive in reducing Cd bioavailability under the CF water regime. The FeBC decreased As concentration, but increased concentrations of Cd and Pb in the straw and brown rice, as compared to the untreated soil. Soil catalase and urease activities were enhanced by RawBC, but decreased by FeBC treatment. The FeBC increased the grain yield by 60 and 32% in CF and AWD treatments, respectively. The FeBC can be recommended for immobilization of As in paddy soils, but a potential human health risk from Cd and Pb in FeBC-treated soils should be considered due to increased uptake and translocation of the metals to brown rice.

Keywords: Heavy metal; Bioavailability; Soil enzyme; Engineered biochar; Irrigation.

1. Introduction

Paddy soils have been contaminated with potentially toxic elements (PTEs) in large areas worldwide, which is mainly attributed to anthropogenic activities (Chen et al., 2019; Palansooriya et al. 2020). According to a National Survey, among others, arsenic (As), cadmium (Cd), and lead (Pb) are widely distributed pollutants in agricultural soils in China (Chinese Ministry of Environmental Protection and Ministry of Land and Resources, 2014). The PTEs in soils have increasingly gained attentions because of their ubiquitous distribution, bioavailability, and toxicity (Yang et al., 2019; Bandara et al., 2020). The PTEs can be taken up by crops, and subsequently accumulate in human bodies by going up in the food chain (Yang et al., 2016; Li et al., 2019; Antoniadis et al., 2019). Rice (*Oryza sativa* L.) is one of the most widely grown field crops and a staple food for millions of people in Asia (Sohn, 2014). Previous studies showed that rice was more effective than other crops in accumulating PTEs such as As, which could enter into human bodies through daily diet (Antoniadis et al., 2019). Appropriate management of risks posed by PTEs has become imperative to food safety and public health (Rizwan et al., 2016a; Rizwan et al., 2016b; O'Connor et al., 2020).

Recent studies found that soil amendments including biochar could be used to decrease the bioavailability and bioaccumulation of PTEs through adsorption, precipitation, complexation and other physicochemical mechanisms (e.g., Wei et al., 2019; Wu et al., 2020; Rinklebe et al., 2020), while maintaining or even increasing crop yields due to reduced phytotoxicity and improved soil physicochemical properties (Ye et al., 2020). Owing to high porosity and specific surface area, highly aromatic structure, and various functional groups (Wu et al., 2019), biochar has drawn particular attention as a potential remediation agent for PTE-contaminated soils (Qin et al., 2018; Bandara et al., 2020).

Biochar can be used to alleviate stress posed by PTEs, and improve the overall soil health, including soil fertility (Li et al., 2018; Feng et al., 2020; Matin et al., 2020) and microbial diversity (Lu et al., 2019; Chen et al., 2020), and facilitate plant growth (Nie et al., 2018; Chu et al., 2020). Furthermore, researchers suggested that iron (Fe) oxides could reduce the mobility of PTEs (especially As) in the soil, and thus mitigate PTE bioavailability and leaching potential (Qiao et al., 2019; Tang et al., 2020; Wang et al., 2020). Studies also suggested the feasibility of using biochar loaded Fe materials to remove As and other toxic elements from aqueous solutions (e.g., Niazi et al., 2018; Xia et al., 2019; Yin et al., 2020). Nevertheless, little information is available on the effect of Fe oxide-designed biochar on the bioavailability and transportation of PTEs in the soil-rice system.

Water management is another important factor that controls PTE bioavailability in paddy soils (Arao et al., 2009; Li et al., 2020). The growth of paddy rice responded differently to an anaerobic condition caused by continuous flooding, and an aerobic condition facilitated by alternative wetting and drying (Wu et al., 2018). Arsenic is more available as arsenite under anaerobic condition, whereas it can be readily transformed to arsenate under aerobic condition (Talukder et al., 2014). Divalent metal cations in soil, such as Cd^{2+} and Pb^{2+}, could also be stabilized with sulfur under anaerobic condition caused by continuous flooding, thereby reducing the accumulation of these PTEs in rice grains (Arao et al., 2009; Bandara et al., 2020).

A co-benefit of using biochar as a soil amendment is that it could facilitate sustainable disposal of excessive green wastes such as leaves, branches, and residual flowers (Chen et al., 2019; Zhao et al., 2018). Producing biochar via pyrolysis is a green and eco-friendly strategy to potentially achieve the maximum value-added benefits of green wastes (Zhao et al., 2018). In this study, biochar derived from *Platanus orientalis* branches (RawBC), and its Fe-modified biochar (FeBC) were used as soil amendments to investigate their effects on the bioavailability and transportation of As, Cd, and Pb in a soil-rice system, under continuously flooded (CF), and alternately wet and dry (AWD) water management conditions. Previous studies (e.g., Yin et al., 2017; Qiao et al., 2019) showed that Fe-loaded biochar could increase the immobilization of PTEs through surface (co)precipitation. Due to the water regime-induced changes of redox potential, factors such as pH and chemical speciation of S and Fe also change, which might affect the behavior of PTEs being stabilized by biochar (Rinklebe et al., 2020). We hypothesize that RawBC and FeBC would change the mobility of PTEs, thus affect their bioavailability and bioaccumulation in rice plants. The specific objectives of this study are to: (1) determine the effect of RawBC and FeBC application on the rice plant growth, soil enzyme activities, and bioavailability and uptake of As, Cd, and Pb in the soil-rice system; and (2) investigate the impact of different water management regimes on the biochar-induced changes of rice plant growth, soil enzyme activities, and (im)mobilization of As, Cd, and Pb in the paddy soil.

2. Materials and methods

2.1 Biochar preparation and characterization

RawBC was prepared by pyrolyzing *Platanus orientalis* Linn (Oriental plane) branches at a temperature of 650°C under an oxygen-limited condition for 2 h. The obtained biochar was passed through a 2-mm stainless steel sieve prior to the experiment. To prepare the FeBC, the RawBC was added into a $FeCl_3 \cdot 6H_2O$ solution at a ratio of 20:1 (biochar:Fe, w/w), and stirred vigorously, followed by 1 h of sonication at 25°C for homogeneous mixing. The FeBC was oven-dried at 60°C until attaining a constant weight, and subsequently pyrolyzed again at 650°C for 1 h for better loading of Fe to obtain the FeBC (Dong et al., 2016).

The physicochemical characterization of the biochar samples including the measurement of Brunauer–Emmett–Teller (BET) specific surface area (SSA), collecting scanning electron microscope (SEM) images, energy dispersive X-ray (EDX) spectrometry, and Fourier transform infrared (FTIR) spectroscopy were conducted using methods described previously (Yang et al., 2016).

2.2 Soil sampling and characterization

A soil contaminated with As, Cd, and Pb was collected from the 20-cm surface layer of a paddy field in Shangyu County, China, which was polluted by surface runoff from nearby mine tailings. The studied soil is classified as a silty clay loam soil according to the Chinese soil classification system (Gong, 1999). A 3-mm stainless steel sieve was used to pass the air-dried soil. The soil physicochemical properties were analyzed according to standard methods (Lu, 2000). The total concentration of As, Cd, and Pb in the soil was analyzed by digesting the soil (0.15 g) in $HF–HClO_4–HNO_3$ (7-5-1 mL) (Carignan and Tessier, 1988). The soil was weakly acidic (pH = 5.8), and contained 20.6, 45.8, and 33.5% clay, silt, and sand. The total concentration of As, Cd, and Pb was 141.3, 0.5, and 736.2 mg kg^{-1}, respectively.

2.3 Pot experiment

The pot experiment was conducted at Zhejiang A&F University in Hangzhou City, Zhejiang Province, China. Briefly, 3% (w/w) of RawBC and FeBC were added into the sieved paddy soil, and homogenously mixed before being placed into plastic pots (24 cm × 22 cm). Every treatment had four replicates, with 8 kg of co-contaminated soil in each pot. Pots (including the control with no amendment) were complemented with a compound fertilizer which contained a N:P:K ratio of 15:12:18. The fertilizer was supplemented at a rate of 0.085 g kg^{-1} (dry weight), which was according to the local rice production practice. The rice cultivar selected in this experiment was Xiushui-519. Five healthy rice seedlings pre-cultivated for 38 days in the selected soil were transplanted into each pot. Ten days after transplanting, 0.085 g kg^{-1} of the compound fertilizer and 0.0425 g kg^{-1} of urea were applied to each pot. The experiment was carried out in a randomized block design. For the continuously flooded (CF) treatment, the pots were irrigated daily until the soil moisture reached nearly saturation, and then were continuously flooded until 10 days before the harvest. For the alternately wet and dry (AWD) treatment, the pots were re-flooded when small cracks were present on the surface soil. After 132 days of cultivation, the above-ground parts of rice plant were harvested (4 July to 12 November 2018). The plant samples were separated into rice straw and grain. All plant samples were oven-dried at 65°C until attaining a constant weight, and then ground to pass a 0.25-mm sieve.

2.4 Analyses of soil and plant samples

Soil pH and total organic carbon (TOC) content of the untreated and biochar-treated soil samples were analyzed according to Chen et al. (2020). The potentially available concentrations of Cd, Pb, and Fe were extracted from a portion of 5 g air-dried soil with 25 mL diethylenetriaminepentaacetic acid (DTPA) solution (Lindsay and Norvell, 1978). The potentially available concentration of As was extracted with 75 mL NaH_2PO_4 solution from 5 g air-dried soil (Wenzel et al., 2001). Soil urease and catalase enzyme activities were determined by the methods described by Dick et al. (1996). A portion of 0.3 g plant samples (straw and brown rice) were digested with nitric acid using a microwave digester (DigiBlock ED54, LabTech CO, China) for As, Cd, and Pb measurements in the straw and brown rice (Lu, 2000). All the extracted elements were measured using inductively coupled plasma optical emission spectrometry (ICP-OES Optima 2000, PerkinElmer Co., USA).

2.5 Data analysis

Statistical analysis of the data was performed by SPSS 17.0 software program. Analysis of variance (ANOVA) and Duncan's multiple range test were used to determine the significant differences between treatments, with the significance level set at P=0.05.

The quality control for total As, Cd, and Pb determination in the soil and plant were checked by analyzing reagent blanks, and certified reference materials GBW-07405 (soil) and GBW-07603 (plant) obtained from the China Standard Materials Research Center. The recoveries of As, Cd, and Pb in soil and plant samples ranged from 87.5% to 99.5%.

3. Results

3.1 Characteristics of the raw and modified biochars

The physicochemical properties of the two biochar samples are shown in Table 1. The pH of FeBC (pH=4.41) was lower than that of RawBC (pH=9.25). The carbon content, Olsen-P concentration, and SSA of RawBC were higher than FeBC, whereas the ash content and electrical conductivity of FeBC were higher than those of RawBC (Table 1).

From the SEM images (Fig. 1A,B), it was observed that both biochars had evenly arranged tube bundle structures, which could be attributed to the original shape of the biomass. However, after Fe loading, the pore structure on the biochar surface seemed to be blocked, and thus the cross section of FeBC was honeycomb-shaped. The FTIR spectra showed that RawBC had more abundant functional groups on its surface than FeBC (Fig. 1C), including olefin (650-1000 cm^{-1}) and aromatic C=C (1448-1576 cm^{-1}) functional groups. According to the EDX spectra, 6.9% chlorine (Cl), and 3.9% Fe were detected in

FeBC, while they were not detected in RawBC (Fig. 1D).

Table 1 Selected physicochemical properties of the raw biochar (RawBC) and Fe-modified biochar (FeBC)

Biochar	RawBC	FeBC
pH	9.25±0.14	4.41±0.03
C (%)	69.34±1.05	59.91±1.21
H (%)	2.74±0.23	2.24±0.35
N (%)	1.11±0.01	0.94±0.01
Ash content (%)	9.66±0.33	15.34±0.20
CEC[a] (cmol kg^{-1})	21.59±0.56	16.7±0.37
EC[b] (dS m^{-1})	0.37±0.02	4.49±0.04
SA[c] (cmol kg^{-1})	215.9±0.37	183.6±0.38
SSA[d] (m^2 g^{-1})	110.7±2.35	74.5±1.43
Olsen P (mg kg^{-1})	24.47±0.59	1.35±0.16
Total P (g kg^{-1})	1.93±0.06	3.03±0.11
Total Fe (g kg^{-1})	7.59±0.60	54.61±3.16
Total Pb[e] (mg kg^{-1})	6.97±0.56	11.92±0.54

[a] CEC: cation exchange capacity

[b] EC: electrical conductivity.

[c] SA: surface alkalinity.

[d] SSA: specific surface area.

[e] Concentration of As and Cd was below the detection limit.

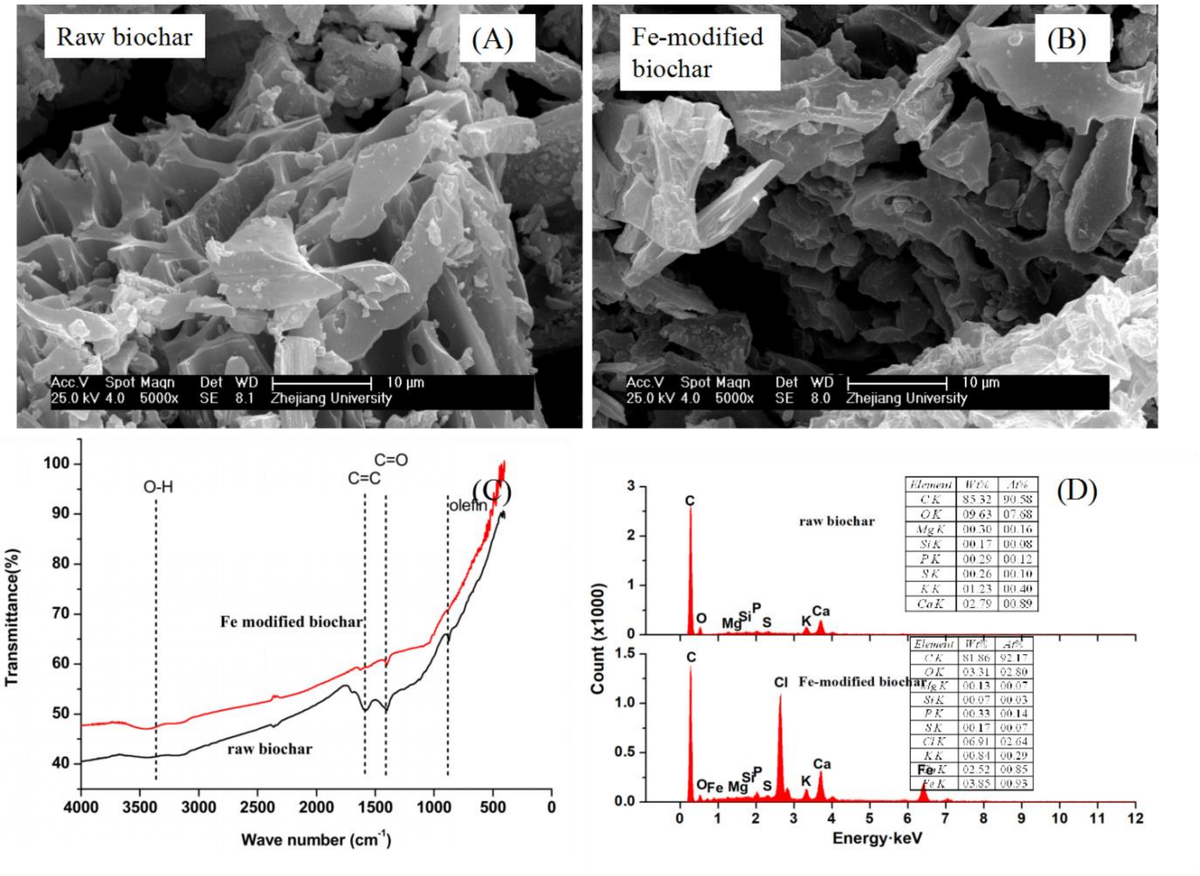


Fig. 1. Scanning electron microscope (SEM) images of RawBC (A), and FeBC (B); Fourier transform infrared (FTIR) spectra (C), and energy dispersive X-ray spectra (EDS) and elemental contents (D) of RawBC and FeBC.

3.2 Biochar and water regime-induced changes in the soil pH, TOC, and Fe availability

Compared to the untreated control, application of RawBC significantly (P<0.05) increased the soil pH respectively by 0.74 and 1.33 units under AWD and CF treatments, while the addition of FeBC decreased the soil pH by 0.17 and 0.13 units under AWD and CF treatments (Fig. 2A). The CF treatment had higher pH than AWD irrespective of the type of biochar applied. Application of both biochars significantly (P<0.05) increased the soil TOC content, and the effect under AWD treatment was more effective than

CF treatment (Fig. 2B). RawBC was more effective than FeBC in increasing the soil TOC content. For instance, in the CF treatment, the TOC content increased from 20.7 mg kg^{-1} in the control to 34.7 mg kg^{-1} in the RawBC-treated soil, while it increased from 20.7 mg kg^{-1} in the control to 32.4 mg kg^{-1} in the FeBC-treated soil. Both RawBC and FeBC significantly decreased (P<0.05) the DTPA-extractable Fe concentrations as compared to the control. Interestingly, application of FeBC caused a more pronounced decrease in DTPA-extractable Fe (43-63%) than RawBC (32-56%) (Fig. 2C). Compared to the AWD treatment, the average concentration of DTPA-extractable Fe was higher in the CF treatment.

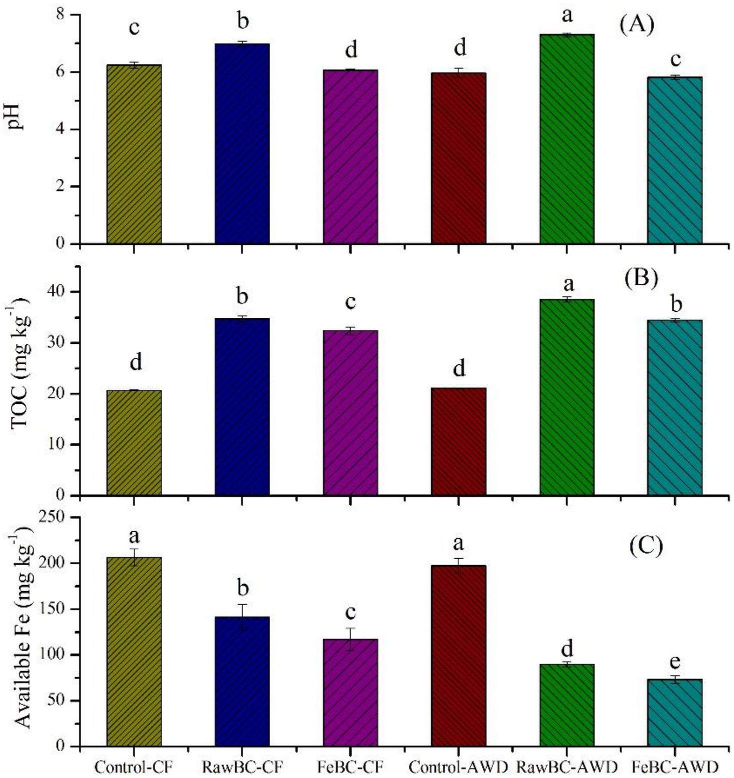


Fig. 2. Effect of biochar applications on soil pH (A), total organic carbon (TOC) (B), and available Fe (C). Treatments: RawBC: raw biochar; FeBC: Fe-modified biochar. CF: continuously flooded; AWD: alternately wet and dry. Error bars indicate standard error of the means (n=4). Different letters indicate significant differences between treatments (P<0.05).

3.3 Biochar and water regime-induced changes on the potential availability of As, Cd, and Pb

Application of FeBC significantly (*P*<0.05) decreased the potentially available concentration of As in the soil under both CF and AWD water regimes by 41.7 and 38.8%, respectively, as compared to the control (Fig. 3A). The average concentration of available As was lower in the CF than AWD treatment. Both biochars significantly (*P*<0.05) decreased the potentially available Cd concentration in the soil as compared to the control. However, RawBC was more effective than FeBC and decreased the available Cd concentration up to 37.3% under the CF water regime treatment. Concentrations of DTPA-extractable Cd in the FeBC- and RawBC-treated soils were 5% and 23.4% lower in AWD treatment than in CF treatment (Fig. 3B).

Addition of FeBC caused a significant decrease in the concentrations of DTPA-extractable Pb in both the CF (13.6%) and AWD (34.9%) water regime treatment. Under AWD treatment, RawBC significantly (*P*<0.05) decreased the DTPA-extractable Pb concentration by 16.2%. The DTPA-extractable Pb concentration in the soil under AWD condition was lower than that of CF treatment.

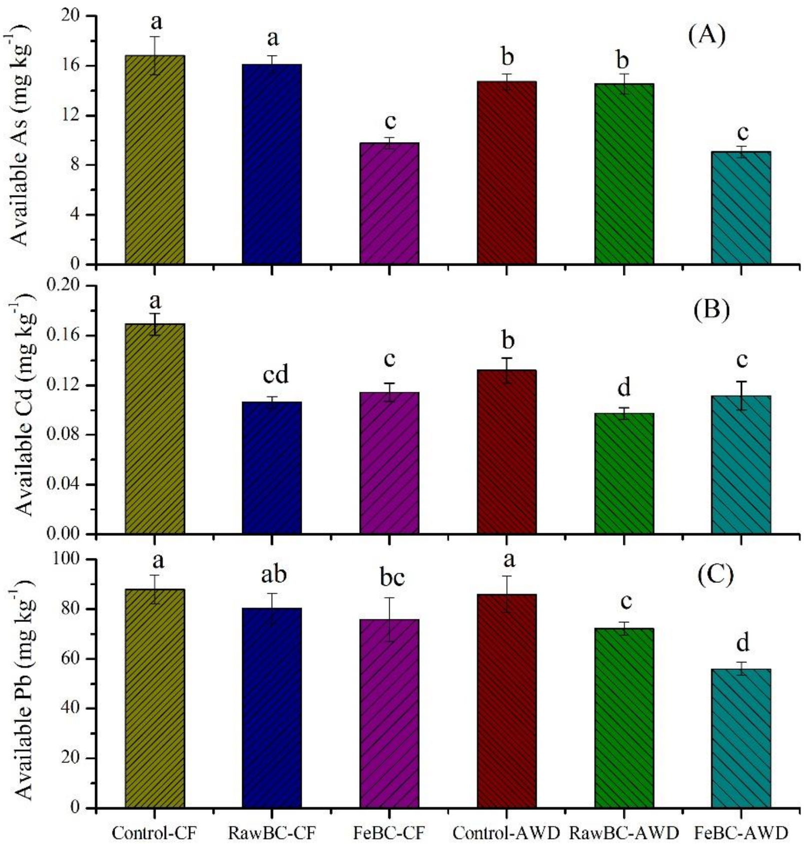


Fig. 3. Effect of biochar applications on soil available As (A), available Cd (B), and available Pb (C). Treatments: RawBC: raw biochar; FeBC: Fe-modified biochar. CF: continuously flooded; AWD: alternately wet and dry. Error bars indicate standard error of the means (n=4). Different letters indicate significant differences between treatments (*P*<0.05).

3.4 Biochar and water regime-induced changes on the concentration of As, Cd, and Pb in rice straw and brown rice

Application of RawBC and FeBC, particularly the later, significantly (*P*<0.05) decreased the As concentration in rice straw (Fig. 4A). The maximum reduction of As concentration in rice straw (61.5%) by FeBC was in the AWD water regime treatment, as compared with the control. Application of FeBC decreased the As concentration in brown rice by 73.2% in CF treatment, and by 80.1% in AWD treatment, while the application of RawBC had no significant effect on As concentration in brown rice (Fig. 4D). The concentration of As in the AWD treatment was 5-15% lower than that in CF treatment with both biochar treatments.

Addition of FeBC caused a significant (*P*<0.05) increase in the concentration of Cd and Pb in rice straw as compared to the control and RawBC treatments under both CF and AWD water regimes (Fig. 4B,C). For example, as compared to the control, FeBC increased the Cd concentration of rice straw by 390.1% and 169.0% in CF and AWD treatments (Fig. 4B), and Pb concentration by 281.1% and 57.4% in CF and AWD treatments, respectively (Fig. 4C). The concentration of Cd and Pb in rice straw was lower under CF treatment than AWD treatment in the biochar-treated and untreated soils (Fig. 4B,C).

The RawBC and FeBC showed different impacts on Cd and Pb concentrations in brown rice (Fig. 4E,F). The application of FeBC significantly (*P*<0.05) increased the Cd concentration in brown rice by 268.8%

(CF treatment) and 263.6% (AWD treatment) as compared to the control (Fig. 4E). The application of both the biochars increased the concentration of Pb in brown rice as compared to the control (Fig. 4F). For example, the brown rice concentration of Pb in the RawBC treatment was about 138.7% (CF treatment) and 90.1% (AWD treatment) higher than that of the control. As compared to the control, FeBC addition increased the brown rice concentration of Pb by 96.7% (CF treatment) and 68.4% (AWD treatment). The concentration of Pb in brown rice grown under CF treatment was higher (98.6% with RawBC-85.2% with FeBC) than that grown under AWD treatment.

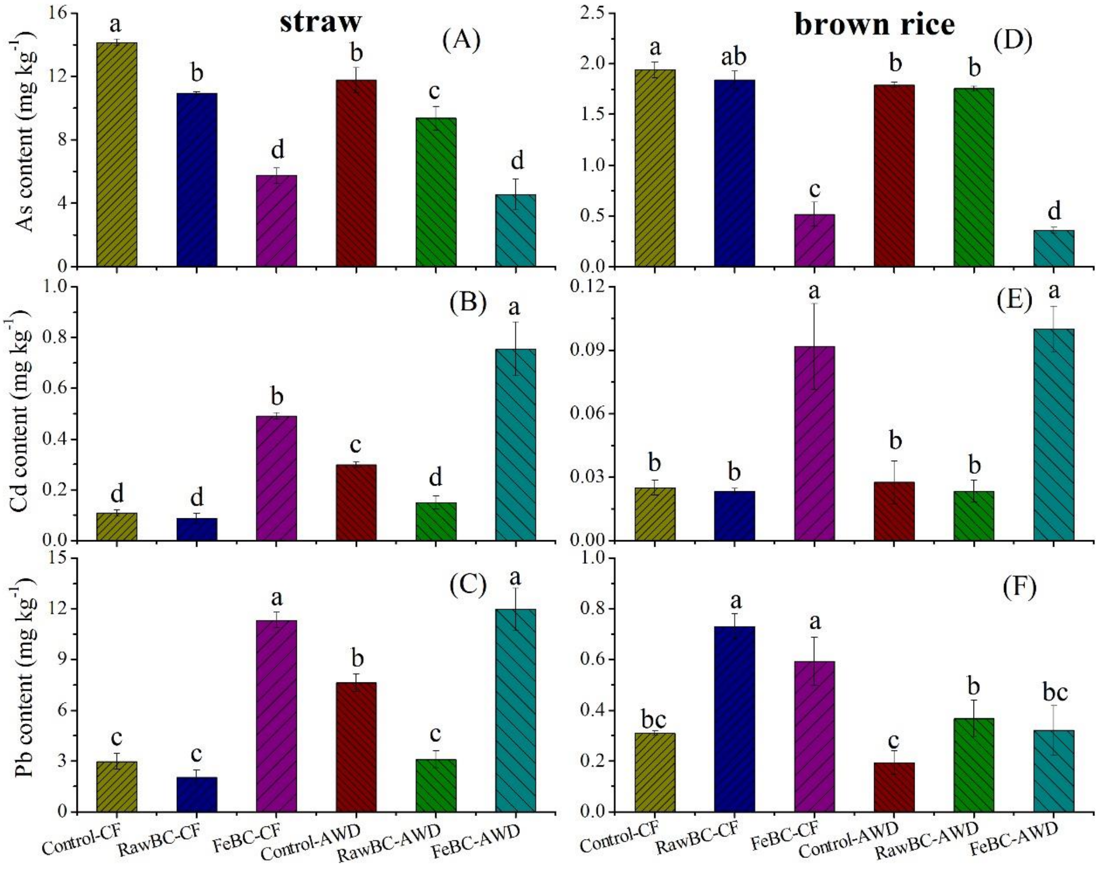


Fig. 4. Effect of biochar applications on As, Cd and Pb accumulation in straw (A, B, C), and brown rice (D, E, F). Treatments: RawBC: raw biochar; FeBC: Fe-modified biochar. CF: continuously flooded; AWD: alternately wet and dry. Error bars indicate standard error of the means (n=4). Different letters indicate significant differences between treatments (*P*<0.05).

3.5 Biochar and water regime-induced changes on soil enzyme activities

Application of RawBC enhanced the urease and catalase activities in the soil, while these enzymes activities decreased in FeBC-treated soil as compared to the control (Fig. 5A,B). Urease activity in the RawBC-treated soil increased by 18.6% and 20.4%, respectively, under CF and AWD treatments. The RawBC-induced increase of catalase activity was 6.4% (CF treatment) and 6.7% (AWD treatment). The FeBC addition caused a significant decrease of urease activity by 10% and 15% in CF and AWD treatments, respectively, as compared to the control (Fig. 5A). Application of FeBC resulted in a significant decrease in the catalase activity by 12.0% and 12.8% under CF and AWD treatments, respectively, as compared to the control (Fig. 5B).

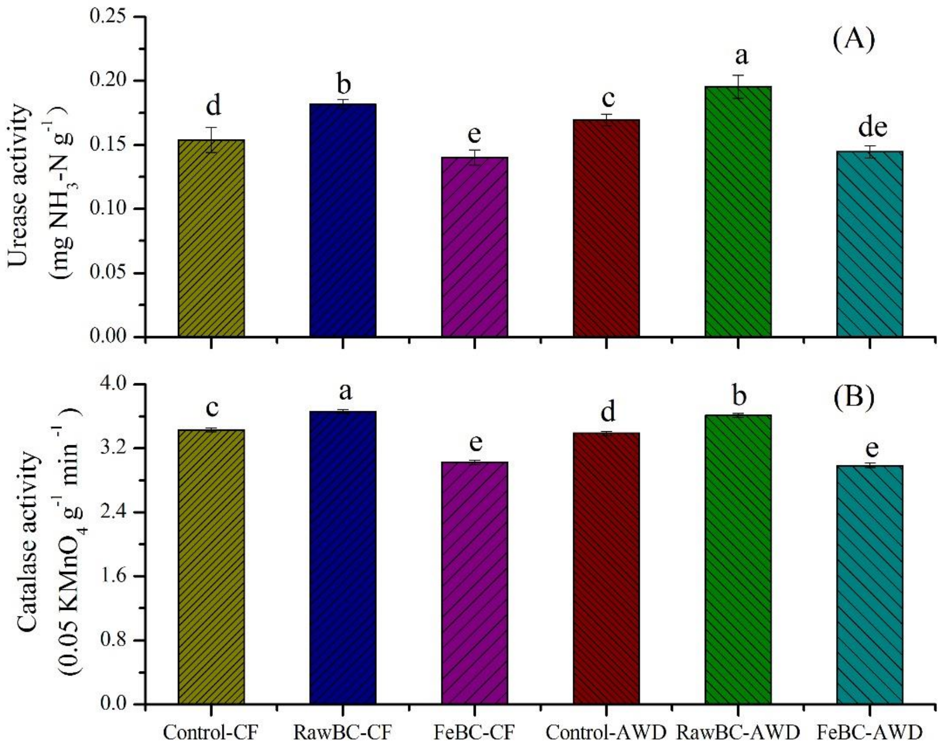


Fig. 5. Effect of biochar applications on soil urease activity (A) and catalase activity (B). Treatments: RawBC: raw biochar; FeBC: Fe-modified biochar. CF: continuously flooded; AWD: alternately wet and dry. Error bars indicate standard error of the means (n=4). Different letters indicate significant

differences between treatments (P<0.05).

3.6 Biochar and water regime-induced changes on rice growth and yield

The addition of RawBC and FeBC increased the rice straw yield by 74.3% and 89.2%, respectively, in the CF treatment, and by 37.5% and 63.7%, respectively, in the AWD treatment, as compared to the control (Fig. 6A). Both biochars increased the grain yield by 60.3% in the CF treatment, and by 32.4% in the AWD treatment, as compared to the control (Fig. 6B).

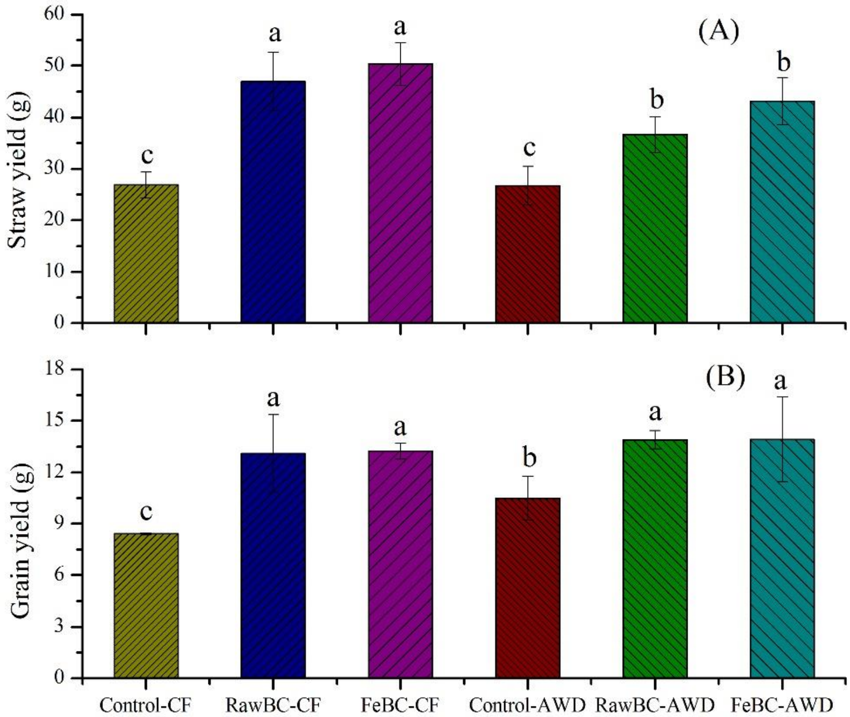


Fig. 6. Effects of biochar applications on the (A) straw yield and (B) grain yield of rice. Treatments: RawBC: raw biochar; FeBC: Fe-modified biochar. CF: continuously flooded; AWD: alternately wet and dry. Error bars indicate standard error of the means (n=4). Different letters indicate significant differences between treatments (P<0.05).

4. Discussion

4.1 Modification-induced changes on biochar properties

The ash content of FeBC was higher than RawBC, which might be due to the abundant surface mineral elements on FeBC (Fig. 1D). The pH of FeBC was lower than RawBC, which can be explained by the release of a high amount of H^+ due to the hydrolysis of Fe (Yin et al. 2017). Additionally, reduction of basic functional groups (Fig. 1C) also contributed to the decrease of pH. Due to the modification, Fe-compounds were loaded on FeBC, thus increasing the total-Fe content, and the existence of Cl^- led to the increase of EC.

4.2 Soil pH, TOC and available Fe

The RawBC-induced increase of soil pH might be owing to the high pH of the biochar (pH=9.25; Table 1). The hydrolysis of soluble alkaline minerals (K, Ca, Na) might also have contributed to the increase of soil pH (Lu et al., 2014). By contrast, the decrease of pH in the FeBC-treated soil could be due to the biochar's acidic pH (pH=4.4; Table 1), and a higher amount of H^+ released during the hydrolysis of exogenous Fe from FeBC (Yin et al. 2017).

Different water regimes also contributed to the variation of soil pH, and the lowest pH value was reported under the CF treatment. Under CF treatment, we assume that flooding the soil might decrease the soil redox potential (Eh). The production of CO_2 and organic acids originated from microbial activities and decomposing organic matter might explain the lower pH in the continually flooded soils than the AWD water regime (Shaheen et al., 2014). Furthermore, these results can be explained by the increased TOC and dissolved organic carbon in the biochar-treated soil under the CF treatment (Rinklebe et al., 2020).

Application of RawBC and FeBC significantly increased TOC content, likely because of their own high carbon contents (Table 1). Application of RawBC had more apparent effect than FeBC in increasing TOC content, which was attributed to the higher carbon content of RawBC than FeBC (Table 1). It was found that the soil under AWD treatment had a higher content of TOC than under CF treatment, due to the fact that AWD treatment provided a more suitable condition for soil aggregate formation, which inhibited or slowed down the degradation of soil TOC (Liang et al., 2009).

The DTPA-extractable Fe concentrations were higher under the CF treatment than AWD treatment (Fig. 3C), which might be explained by the potential decrease of soil Eh, and associated decrease of soil pH under CF conditions as compared to AWD. The higher solubility of Fe under reducing acidic conditions agrees with Shaheen et al. (2014). Application of biochars, particularly FeBC decreased the DTPA-extractable Fe concentration as compared to the control (Fig. 3C). The lower Fe availability in the RawBC-treated soil as compared to the control might be due to the increase of soil pH. According to Hu et al. (2018), application of FeBC might inhibit the activity of Fe-reducing bacteria, which might explain the lower concentration of available Fe in FeBC than RawBC treatment.

4.3 Bioavailability and uptake of As, Cd, and Pb

4.3.1 Arsenic

FeBC was more effective than RawBC in reducing the phytoavailability (Fig. 3) and uptake of As by rice straw (Fig. 4A) and grains (Fig. 4D). This might be explained by the potential immobilization of As by Fe compounds, likely through forming amorphous Fe (III)-arsenate compounds (Mensah et al., 2020). The decrease of As uptake in the FeBC treatment could largely be attributed to the sequestration of As in Fe-plaque on rice root surfaces, which agrees with Yin et al. (2017). The biochar-induced decrease of bioavailability and uptake of As under flooding conditions might be explained by redox mediated interactions between the surface functional groups of biochar and As species (Amen et al., 2020). The functional groups (e.g., semiquinone-type free radicals, phenolic-OH, C=O) could act as electron acceptors, and play an important role in oxidizing As(III) to less mobile and less toxic As(V) (Yuan et al., 2017; Niazi et al., 2018; Amen et al., 2020). The redox reactivity in the case of Fe-modified biochar could also affect the depletion of As availability. Arsenic species, including As(III) and As(V), could undergo redox reactions in the presence of strong oxidizing and reducing agents on the biochar surface resulting in strong innersphere complexation of As on the biochar surface (Yuan et al., 2017; Shaheen et al., 2019; Amen et al., 2020).

The lower soil pH in the FeBC treatments than the control and RawBC treatments could have played a key role in the extent and rate of redox reactions of As on FeBC surfaces (Shaheen et al., 2019; Zhong et al., 2019; Amen et al., 2020). Functional groups on the surface of biochar, such as -NH, -OH and –COOH, could be protonated under low pH. The bioavailability and mobility of As therefore could decrease through the formation of ion-pair interaction mechanism between the negatively charged As species and positively charged biochar functional groups (Shaheen et al., 2019). In addition, the oxidation of As(III) to As(V) in the presence of redox-active species was pH-controlled, which could be ascribed to the unique activities of the redox moieties on biochar (Yuan et al., 2017; Bandara et al., 2020). Under acidic and neutral conditions, the transformation from As(III) to As(V) occurred by hydroxyl free radicals (•OH) and H_2O_2 produced from the activation of O_2 by phenolic −OH and semiquinone-type persistent free radicals (Zhong et al., 2019).

Higher bioavailability (Fig. 3A) and uptake of As in the RawBC treatment than FeBC treatment (Fig. 4A,D) might be due to the higher pH and P concentrations of RawBC than FeBC (Table 1), which increased the soil pH and P concentration in RawBC treatment as compared to the control and FeBC treatments (Fig. 2A), and this might have increased the release of As in the RawBC-treated soil (Beiyuan et al., 2017).

The concentration of As in rice straw and brown rice was lower in AWD treatment than CF treatment (Fig. 4A,D). This might be due to the decrease of redox potential of soils under the flooded treatment which could inhibit As translocation from roots to shoots (Arao et al., 2009). Hu et al. (2013) suggested that under aerobic condition, the concentration of As in rice grain decreased, while the Cd concentration increased. Hua et al. (2011) found that aerobic conditions reduced the uptake of As by rice straw and brown rice because Fe^{3+} in aerobic condition had better effect to stabilize As in solid phases than Fe^{2+} in anaerobic condition, thus reducing As availability for rice uptake.

It is worth mentioning that according to the National Food Safety Standards of China: Contaminant Limits in Food Products (Ministry of Health, 2012), the limit of As in brown rice is 0.2 mg kg^{-1}. The concentration of As in rice grains in the case of FeBC application under AWD and CF treatment was close to this limit and was 0.3 and 0.5 mg kg^{-1}, respectively (Fig. 4A,D). The FeBC treatment was able to decrease the As concentration from 1.8 mg kg^{-1} in the control to 0.3 mg kg^{-1}, and thus reduced the risk of transferring As into human bodies via consumption of rice.

4.3.2 Cadmium

RawBC and FeBC showed contradictory effects on the availability (Fig. 3B) and uptake of Cd (Fig. 4B,E). Although FeBC decreased the DTPA-extractable Cd, it increased the Cd concentration in straw and brown rice as compared to the control (Fig. 3B; Fig. 4B,E). The higher efficiency of RawBC in immobilizing Cd and decreasing its uptake could be explained by the biochar's higher pH, CEC, and more abundant surface functional groups than FeBC (Table 1, Fig. 1). The decrease of Cd bioavailability and uptake in the biochar-treated soil as a result of associated increase of soil pH agreed with other studies (e.g., Lu et al., 2014; Chen et al., 2019). Biochar could also fix and inactivate Cd by complexing on surface functional groups, and forming precipitates, and/or via cation exchange (Yin et al., 2017; Bandara et al., 2020).

The impact of FeBC on increasing the uptake of Cd could be due to the low pH of FeBC (Table 1), and the associated decrease of soil pH as compared to the control and RawBC treatments (Fig. 2A). The decline in soil pH with FeBC application might have decreased Cd sorption on biochar surfaces, and thus increased Cd desorption and solubility (Yin et al., 2017; Bandara et al., 2020), substantiating that Fe amendments including Fe-modified biochar might increase Cd mobility through soil acidification.

The decrease of Cd solubility and uptake under flooding conditions could be due to the precipitation of Cd with sulfides under reducing conditions, while the increase of Cd solubility under relatively aerobic conditions in the AWD treatment might be due to the oxidation of sulfide to sulfate, and hence release of associated Cd to the pore water, which is in agreement with other studies (e.g., Shaheen et al., 2016; Yin et al., 2017).

4.3.3 Lead

The decrease of Pb availability in the RawBC-treated soil can be likely due to the associated increase of soil pH, which is in agreement with other studies (e.g., Lu et al., 2014; Li et al., 2020; Palansooriya et al., 2020). The decrease of Pb availability in the RawBC treatment could be due to the biochar's high P concentration; the available P in RawBC might be released into the soil, which might bind with Pb to form a poorly soluble phosphate precipitate, thereby decreasing the mobility of Pb in soil. The immobilization of Pb using phosphates is well documented and reported (e.g., Seshadri et al., 2017; Li et al., 2019). For example, Li et al. (2019) found that phosphates on biochar provided sorption sites to immobilize Pb via the formation of $Pb_3(PO_4)_2$.

The decrease of Pb availability in the FeBC-treated soil could be explained by the increase of Fe in the treated soil, and the possible binding/occlusion of Pb on Fe oxides (Rinklebe et al., 2016). The hydrolysis of Fe^{3+} on the surface of FeBC could form a colloid to adsorb Pb^{2+} in the soil, which might be the reason that the concentration of Pb in the FeBC-treated soil was lower than the RawBC-treated soil (Li et al., 2015). Besides, Fe^{3+} in the soil would be reduced to Fe^{2+} under anaerobic environment. The release of Fe^{2+} into the soil solution consequently would compete with Pb^{2+} for the adsorption sites on soil surface, which might lead to higher concentration of available soil Pb in CF treatment than AWD treatment (Fulda, et al., 2013). The functional groups and phosphates on both biochars, particularly RawBC could provide efficient sorption sites to chelate Pb and form stable compounds with C−O−Pb−O−C structures. In this respect, Wu et al. (2017) and Li et al. (2019) found that the carboxylic functional groups and phosphate on biochar had a high affinity to immobilize Pb through surface complexation and precipitation, respectively.

Interestingly, although RawBC decreased DTPA-Pb and Pb concentration in straw, the treatment increased Pb translocation to the grains, and thus increased the Pb concentration in brown rice as compared to the control. The impact of RawBC on the translocation of Pb to grains was higher than FeBC (Fig. 4C,F). This could be attributed to the different impacts of both RawBC and FeBC on the formation of Fe/Mn plaques on rice roots. The FeBC might increase the Fe/Mn plaques on rice roots, while RawBC might decrease it as compared to the control. Therefore, Pb was likely less immobilized by Fe/Mn plaques on rice roots in the RawBC-treated soil than FeBC-treated soil, and consequently higher Pb translocation rate was observed in rice plants grown in RawBC-amended soil than the untreated and

FeBC-treated soils. In this respect, Li et al. (2016) reported that the amount of Fe plaques on rice roots, and the concentration of Pb in the Fe plaques were reduced in raw rice-straw biochar amended soils. Furthermore, Li et al. (2020) found that the amount of Pb-ferrihydrite complexes on rice roots, as examined using Pb L_3-edge XANES, was also decreased with 5% coconut fiber biochar, indicating that Pb retention by Fe/Mn plaques was inhibited by the presence of coconut fiber biochar in the soil.

4.4 Soil enzyme activities

In this study, the application of RawBC increased the soil pH, which might be a possible cause for promoting soil urease and catalase activities. Activities of these enzymes decreased in the FeBC-amended soil, which might be attributed to the reduction of soil pH (Fig. 2A), and the high concentrations of Cl^- (Fig. 1D) from FeBC increased the ionic concentration, which inhibited soil urease and catalase activities. The porous structure of biochar might provide a better environment for the growth of soil microorganisms, and therefore might increase soil enzyme activities (Yang et al., 2016; Nie et al., 2018). The above theory also supported the increase of urease and catalase activities in the RawBC-amended soil. The enhancement of urease and catalase activities in the RawBC-treated soil could also be due to the associated decrease of PTE bioavailability and toxicity (Yang et al., 2016; Bandara et al., 2020). Urease activity was higher in AWD treatment than CF treatment, which could be due to the sensitivity of urease activity to soil moisture. Catalase activity was higher in CF treatment than AWD treatment, which might be caused by the death of some microorganisms under drought conditions (Sardans et al., 2005).

4.5 Rice growth and yield

Application of biochars increased rice straw and grain yields (Fig. 6A,B). This might be due to the biochar-induced improvement of soil physicochemical properties, and nutrient supply (Dong et al., 2015). In the current study, all treatments were applied with exogenous fertilizers, and the application of biochar contributed to the utilization of fertilizer in the soil, and thus improving the rice yield. The phytotoxicity of PTEs was another important factor in influencing the rice growth. High concentration of As and Pb in the soil would make these elements to accumulate in rice plant parts, thereby inhibit the absorption of essential nutrients and restrain plant growth (Sardar et al., 2013). Since biochar application reduced the available concentration of As, Cd, and Pb in the soil, grain yield production was increased. Nutrients absorbed by rice plants were used for improving the yield of rice grain after biochars were applied.

Straw and grain yields under AWD treatment were higher than CF treatment, which might be attributed to the transpiration rate of rice plants. An aerobic condition caused by the AWD treatment would reduce the transpiration rate of rice plants, improve the oxidation activity of rice roots, and thus promote rice growth (Yang et al., 2009). Hu et al. (2012) indicated that intermittent irrigation conditions would promote plant growth, which had the same result with our study. Talukder et al. (2014) also pointed out that aerobic condition was considered an effective way for controlling water scarcity and improving rice yield.

5. Conclusions

Based on our findings, we can conclude that the modification using Fe decreased the ability of oriental plane (*Platanus orientalis* Linn) branches biochar to improve rice plant growth and reduce the uptake of As by rice plants and mitigate the potential risk more than the RawBC. However, the Fe-modified biochar caused a decrease in the activity of soil urease and catalase, and an increase in the uptake and concentration of Cd and Pb in rice straw and brown rice as compared to the control and RawBC treatments.

Furthermore, water management regime affected the bioavailability of As, Cd, and Pb in the biochar-treated soils, and the bioavailability of As and Pb was lower under the AWD treatment than the CF one, whereas the opposite happened with Cd.

These results demonstrate that the Fe-modified biochar can be used for remediation of As contaminated paddy soils under alternately wet and dry irrigation system, while the raw biochar might be more suitable for remediation of Pb under alternately wet and dry irrigation system, and Cd under continuously flooded system. However, these results should to be further verified under field conditions. Besides, future research is warranted to provide new insights into the modification of biochar using different iron materials, e.g., zero valent irons, and to explore the redox-mediated interactions between these PTEs and both raw and Fe-modified biochars under systematic changes of soil redox potential.

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