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Reduced arsenic accumulation in indica rice (*Oryza sativa* L.) cultivar with ferromanganese oxide impregnated biochar composites amendments☆

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ABSTRACT

The effects of biochar (BC) and ferromanganese oxide biochar composites ($FMBC_1$ and $FMBC_2$) on As (Arsenic) accumulation in rice were determined using a pot experiment. Treatments with BC or FMBC improved the dry weights of rice roots, stems, leaves, and grains in soils containing different As contamination levels. Compared to BC treatment, FMBC treatments significantly reduced As accumulation in different parts of the rice plants ($P < 0.05$), and $FMBC_2$ performed better than $FMBC_1$ did. Furthermore, exposure to 2% $FMBC_2$ decreased the total As concentration in the grain by 68.9–78.3%. The addition of FMBC increased the ratio of essential amino acids in the grain, decreased As availability in the soil, and significantly increased the Fe and Mn plaque contents. The reduced As accumulation in rice can be attributed to As(III) to As(V) oxidation by ferro - manganese binary oxide, which increased the As adsorbed by FMBC. Furthermore, Fe and Mn plaques on the rice root surface decreased the transport of As in rice. Taken together, our results demonstrated the applicability of FMBC as a potential measure for reducing As accumulation in rice, improving the amino acid content of rice grains, and effectively remediating As-polluted soil.

1. Introduction

Arsenic (As) is a metalloid element that is toxic and carcinogenic to living organisms. Some anthropogenic activities such as mining, the use of phosphorous fertilizers and arsenical pesticides, or irrigation with contaminated water can lead to excessive As contamination of agricultural soils (Naidu et al., 2006). As mainly occurs in the water-soluble, exchanged, and stationary fractions of contamination soil (Herreweghe et al., 2003). Among these fractions, the water-soluble (mainly containing As in the AsO_3^{3-} and AsO_4^{3-} form) and exchanged states are active in soil. Active As species can be easily taken up by plants, subsequently accumulate in the edible parts of crops, alter the amino acid (AA) concentration of the rice cultivars (Dwivedi et al., 2010), and finally harm human health by consumption through the food chain (Lubin and Fraumeni, 2000; Camm et al., 2004). Therefore, adopting appropriate measures to reduce the activity of As in the soil and decrease its concentrations in crops (especially rice) grown in As-contaminated regions is urgently needed.

Rice is the dominant staple food in many parts of the world. In China, 187 million tons of rice are produced annually, which accounts for approximately 35% of the global production (Mohanty et al., 2010). Amino acids are present at higher levels than synthesized proteins in rice and play important roles in human health because they are essential for life-sustenance. Therefore, the quality and safety of rice are particularly important, especially in China. Compared to other cereal crops, rice has a high propensity to take up As from As-contaminated soils, resulting in As-accumulation in rice grains (Marin et al., 1993; Williams et al., 2007). Zhao et al. (2009) reported that rice had the highest As mobility in xylem transport among the non-hyper accumulator plant or other plants investigated. Heavy metals toxicity, including As, altered the AA concentrations present in rice cultivars (Dwivedi et al., 2010). Thus, one of the most effective measures for reducing As transport from

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the soil to rice grains, which has attracted considerable research interest, is changing the conditions used to grow rice. Implementation of this strategy will require the oxidation of the highly mobile As(III) to the less mobile As(V). Thereby, enhancing the adsorption and immobilization capacity of As(V) by Mn and Fe oxides can be one of the practicable options.

To date, many measures for reducing the available As content in soil, such as replacement, immobilization, electro-kinetics, soil flushing and phytoremediation, have been investigated to control the transfer of As from the soil to rice grains (Kumpiene et al., 2008; Balasubramanian et al., 2009; Marques et al., 2009; Wuana and Okieimen, 2011; Komárek et al., 2013). Among these methods, soil flushing, soil replacement, electrokinetics, and phytoremediation are not very efficient for large polluted areas and slightly contaminated farmland due to their high-cost, long time needed for remediation, and propensity to cause secondary pollution. Previous data obtained from greenhouse and field experiments have shown that phytoremediation requires extensive periods (up to hundreds of years in some situations), depending on the pollution levels (Vangronsveld et al., 2009). Electro-kinetics requires a considerable amount of energy and can damage the physical and chemical properties of soil (Cang et al., 2012). Recently, substantial research has focused on immobilization because it is simple, low-cost, and highly efficient process (Wuana and Okieimen, 2011). Many chemical absorbents have been proposed as treatments for As-contaminated soils, such as carbonaceous materials, clay minerals, biochar (BC), iron compounds, iron modifications of carbon, and Mn oxides (Warren and Alloway, 2003; Kumpiene et al., 2008; Marques et al., 2009; Beesley et al., 2011). These chemical absorbents can decrease the bioavailability of As by adsorption and precipitation. For example, iron compounds and Mn oxides can change the physical and chemical properties of paddy soil, increase the functional groups, and decrease the chemo-availability of As in the soil (Warren and Alloway, 2003; Kumpiene et al., 2008). BC has been clearly shown to be capable of As adsorption, but its ability to change As speciation in the environment is limited (Beesley et al., 2011).

To develop novel absorbents with adsorption and oxidation properties that could increase their remediation efficiency in paddy soil, some researchers have attempted to synthesize artificial composites. Hassan et al. (2014) used carbon-based stabilizing materials for remediating As-contaminated soils. Yu et al. (2017b) reported that the As content of rice grain was decreased following the addition of Mn oxide-impregnated BC composites to As-contaminated soils. Zhang et al. (2007) developed a novel adsorbent composed of Fe-Mn binary oxides for removing of As from water and showed that Fe-Mn binary oxides were more effective in As immobilization than pure Fe or Mn oxides.

Fe-Mn binary oxides and BC have shown excellent As immobilization and, therefore, harnessing their obvious advantages to develop new adsorption materials is necessary and promising. Few studies have evaluated the effects of ferro-manganese oxide biochar composites (FMBCs) in reducing As bioavailability in paddy soil. Our previous results showed that FMBC increased the As adsorption capacity of soil by 1.5-fold, and the removal rate of As from water reached 95% (unpublished data). Therefore, the aims of the present study were to: (i) investigate the effects of FMBCs and BC on As speciation and concentrations in rice, (ii) determine whether FMBCs could reduce As availability in paddy soil, and (iii) explore the possible mechanisms mediating the reduced As uptake by rice.

2. Material and methods

2.1. Chemicals and reagents

A standard As(III) stock solution was prepared by dissolving $NaAs_2O_3$ in NaOH, and arsenate As(V) standards, dimethylarsenate(DMAA), and monomethyl arsenate(MMAA) were purchased from Sigma-Aldrich(St. Louis, MO, USA). The ultrapure water used in all experiments was further purified (18 MΩ cm^{-1}) from deionized (DI) water, using a Millipore-Q water -purification system (Merck Group, Germany).

2.2. Preparation of Fe-Mn oxide-modified BC composites

BC was produced from corn straw via slow pyrolysis at 600 °C for 2 h in a muffle furnace under a nitrogen gas (N_2) atmosphere (flow rate:600 mL min^{-1}). To generate $FMBC_1$, 12.432 g BC was soaked in 40 mL $KMnO_4$ (0.24 M) solution and 40 mL $Fe(NO_3)_3$(0.06 M) solution, after which it was subjected to ultrasonic dispersion for 2 h, dried for 22 h in a water bath (95 °C), and then pyrolyzed at 600 °C for 0.5 h under an N_2 atmosphere. The weight ratio of BC to $KMnO_4$ and $Fe(NO_3)_3$ in $FMBC_1$ was 25:4:1. To generate $FMBC_2$, BC was soaked in 40 mL each of $KMnO_4$ (0.18 M) and $FeSO_4$ (0.06 M) solutions by the same procedure, and the resulting weight ratio of BC to $KMnO_4$ and $FeSO_4$ was 18:3:1. Untreated BC was used in these experiments for comparison purposes. The properties of BC and both FMBC composite materials are presented in Table 1. The carbon, hydrogen, and nitrogen contents of BC and FMBC were determined using an elemental analyzer (Elementar Analysen systeme GmbH, Hanau, Germany). The ash contents of BC and the FMBC composites were defined as the mass remaining after heating the mixtures in an open crucible at 750 °C until a constant weight was obtained. The pH was measured in a 1:10 (w/w) BC: water suspension after shaking the mixture for 1 min and then allowing it to stand for 30 min at 25 °C. The volatile matter was determined as the weight lost after heating the char to 950 °C in a covered crucible and maintaining that temperature for 7 min (Uchimiya et al., 2011). The total surface of the FMBC composites and BC was measured by analyzing nitrogen adsorption at 77 K in an Autosorb-1 gas analyzer (Quantachrome Instruments, Boynton Beach, USA). The Mn and Fe contents of the FMBCs were determined using atomic adsorption spectrometry (AAS; Zeenit 700, Analytik Jena AG, Jena, Germany) after dissolution in oxalic and sulfuric acids. The available K content of BC and the FMBCs was measured after extraction with 1.0 M NH_4OAC.

2.3. Pot experiment

Contaminated paddy soils with high-, moderate-, and low levels of As contamination were investigated in this study. Contaminated soil samples from plow layers (0–20 cm) of the three As-contaminated paddy soils were collected in Shimen County (Hunan Province, China). The soil samples were air-dried and sieved through a 5-mm nylon screen before the conducting pot experiments. The properties of each soil sample are shown in Table 2. Next, 2.5 kg samples of the three paddy soil samples with different contamination levels were each placed in a pot. FMBC and BC were added to the soil samples at 0.5% (12.5 g pot^{-1}), 1% (25 g pot^{-1}), and 2% (50 g pot^{-1}) of soil weight. The pot experiment was conducted

Table 1
Physicochemical characteristics of biochar and ferromanganese oxide-biochar composite.

Amendments	C	N	H	Ash	K	S_{BET}	pH_{pzc}
	(%)				mg kg^{-1}	(m^2 g^{-1})	
BC	75.55	1.91	2.95	16.77	112.3	60.97	8.93
$FMBC_1$	67.27	1.83	2.38	27.53	261.4	208.0	9.60
$FMBC_2$	53.82	1.41	2.22	36.61	259.2	7.53	3.17