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Arsenic immobilization through regulated ferrolysis in paddy field amendment with bismuth impregnated biochar

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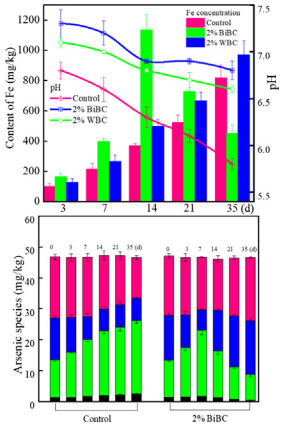
HIGHLIGHTS

- Bismuth-impregnated biochar (BiBC) decreased the bioavailability of arsenic in paddy soils through regulation of ferrolysis.
- Addition of BiBC to arsenic-contaminated soil promoted the reduction of iron oxides.
- The reduced iron ions facilitated arsenic adsorption onto the BiBC surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Iron minerals are important for arsenic immobilization in paddy fields; however, intensive ferrolysis causes arsenic (As) release. Bismuth-impregnated biochar derived from wheat straw (BiBC) was synthesized to immobilize arsenic by regulating the ferrolysis process in a paddy field. Further X-ray based analysis (XRD and XPS) results demonstrated that crystal particles of bismuth oxide and bismuth oxychloride were loaded on the biochar surface, helped create additional micropores and improved its specific surface area. The bioavailability of As, as determined via (non)specifically adsorbed As, decreased as the amended dosage of BiBC increased, while wheat straw biochar (WBC) resulted in arsenic release. The presence of biochar caused a faster reduction rate of iron oxides; however, BiBC promoted the sequential co-precipitation of iron and arsenic ions. Adsorption kinetic experiments indicated that ferrous ions facilitated precipitation of As on the surface of BiBC. The XRD analysis of soil samples showed BiBC facilitated the formation/stability of FeOOH. Thus, amendment with BiBC regulated ferrolysis to buffer iron leaching, which contributed to arsenic immobilization under flooding conditions. This study demonstrated the feasibility of As immobilization by metal-impregnated biochar in paddy soils.

1. Introduction

Arsenic (As) is a highly toxic and carcinogenic metalloid element that existed ubiquitously in natural environments (Zhang et al., 2017).

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Both natural geogenic release (derived from activity of plants and microorganisms) and anthropogenic activities (including sewage irrigation, atmospheric deposition and mine exploitation) worsen arsenic pollution. This inevitably leads to higher risk of human health hazards such as skin and liver cancers (Ahamed et al., 2006; Bhowmick et al., 2018; Sharma et al., 2014). Arsenic contamination in soil fields has resulted in disastrous environmental and human health effects all over the world, especially in Bangladesh, India, Korea and China (Kwon et al., 2017; Liao et al., 2016; Shrivastava et al., 2017). Therefore, the development of eco-friendly and cost-effective methods to immobilize As(III) in soil is a top research priority (García-Carmona et al., 2017).

Using the soil solid phase such as biochar, oyster shells waster, metal oxides and their precursors have been tested as effective and stable amendments for As mitigation in soils (Chen et al., 2018; García-Carmona et al., 2017). When applied to soil, biochar has shown promise as a material with a number of environmental benefits. It reduces heavy metal bioavailability (Cd, Pd) (Mohan et al., 2014), increases soil fertility as well as affixes carbon and lowers greenhouse gas emissions (Zhang et al., 2012). However, application of biochar often results in arsenic release in paddy soils under anaerobic conditions (Choppala et al., 2016). The release of arsenic could be attributed to the interfacial behavior between soil minerals and biochar. The contained organic matter and various functional groups on the surface of biochar could serve as electron donors to mediate both the reduction of ferric iron and As(V) (Choppala et al., 2016; Yang et al., 2016). Moreover, anaerobic conditions also result in arsenic reduction from pentavalent arsenic (As(V)) to trivalent arsenic (As(III)) and brings a high risk of As(III) release (Brammer, 2009). It was reported that biochar is unable to adsorb uncharged or the electronegative form of As(III) because of its negatively charged surface, poorly developed porosity, and lower surface area (Zhu et al., 2016). Unfortunately, it is more difficult and problematic to remove As (III) than As(V) because of high mobility and toxicity of the former forms (Zhu et al., 2018), which results in a bio-accessibility increase of arsenic in soil and phytotoxicity to crops (Vithanage et al., 2013). A large number of efforts have been made to prepare metal modified (e.g., iron and manganese species) carbon through impregnation methods for treatment of arsenic (Asadullah et al., 2014; Yu et al., 2017). MnO_2-modified biochar has been proved the ability to remediate As-contaminated soil effectively and mitigate As accumulation in rice (Yu et al., 2017). Biochar impregnation with metals or metal oxides brought about a positive charge and activated adsorption sites, promoted the development of specific surface area, and increased the number of functional groups, thereby increasing the adsorption of and negatively charged anionic contaminants because of the electrostatically attractive forces through positively charged metallic ions (Loganathan et al., 2013).

In As-contaminated soil, arsenic is primarily immobilized with iron oxides, organic matter and clay minerals (Vithanage et al., 2013). The potential risks depend on the mobility and availability of arsenic, which are mainly controlled by redox conditions (Shrivastava et al., 2017). Iron oxides are the predominant arsenic adsorbents in hydromorphic soils (paddy soils, which are widespread throughout southern China). Iron redox cycling and leaching processes, known as ferrolysis, significantly affects the geochemistry of hydromorphic soils (Brinkman, 1970). Ferrolysis increases arsenic adsorption in these soils through the formation of amorphous iron oxides which expose arsenic to more active adsorption sites (Jiang et al., 2017). However, little information is available concerning the regulation of ferrolysis to immobilize arsenic in paddy fields. Amorphous iron oxides have poor stability and considerable solubility in acidic conditions, which may destroy the adsorption sites in paddy fields (which are often flooded). Herein, we report the synthesis of bismuth-impregnated biochar (BiBC) for efficient immobilization of arsenic through regulation of ferrolysis in paddy fields. This study intends to (i) characterize the synthesized BiBC, (ii) investigate variation of arsenic fractionation in paddy fields amended with BiBC, and (iii) explore possible mechanisms for variation of arsenic fractionation in paddy soils amended with BiBC.

2. Materials and methods

2.1. Preparation of biochar material and soil samples

Bismuth-impregnated biochar (BiBC) was prepared according to the method outlined in our previous study with a slight modification (Zhu et al., 2016). Briefly, 10 g milled and sized wheat straw (particle size: 0.6–0.8 mm) was added in a flask (250 mL) with100 mL of $Bi(NO_3)_3 \cdot 5H_2O$ (0.05 M) solution, stirred vigorously for 3 h at 80 °C. The mixture was dried and then heated to 200 °C for 60 min to make hemicellulose undergo limited devolatilization and carbonization (Cao and Harris, 2010), then pyrolyzed in a furnace at a setting temperature (300, 450 and 600 °C) for 60 min at a heating rate (10 °C min^{-1}). Wheat straw biochar (WBC) was prepared in exactly the same way as BiBC but excluding the bismuth solution addition. Finally, both the BiBC and WBC were sieved to <2 mm in diameter and washed with a $NaHCO_3$ solution (0.01 M) and distilled water for three times successively. The arsenic-contaminated paddy soil (top soil 0–20 cm) was sampled from the Yixing City, Jiangsu Province. All soil samples were air-dried and sieved to <2 mm in diameter. The physical and chemical properties and related determining methods are showed in Table S1 (Appendices).

2.2. Application for arsenic immobilization in paddy soil

Batch incubation experiments were conducted to evaluate the influence of WBC and BiBC on arsenic fractionation in paddy soil. For each subsample, 100 g arsenic contaminated soil was added to a 250-mL flask with a 25% (*w*/*w*) of soil moisture (adjusted by distilled water). All flasks were sealed with sterile sealing film and incubated at 25 ± 1 °C in the dark for 7 days. Then, BiBC (1%, 2%, and 5% (*w*/*w*)) and WBC (1%, 2% and 5% (*w*/*w*)) were included. No biochar materials were added to the control sample. All flasks were prepared in triplicate and then waterlogged by addition of 100 mL distilled water and incubated at 25 ± 1 °C in the dark for 35 days after being resealed with sterile sealing film. 0.5 g of soil sampling was carried out at the 3rd, 7th, 14th, 21st and 35th day to analyze the fractionation of arsenic after incubation.

The HCl extractable total Fe(II) (E-Fe(II)) derived from amorphous and poor crystallinity iron oxides could be reduced by microorganisms or soil reducing substances (O'Day et al., 2004), which played an important role in iron transportation and leaching in paddy field or sediment. To investigate the influence of biochar inclusion on variation of arsenic fractionation and HCl extractable Fe during the incubation period, 2% BiBC or 2% WBC were added in to a 250-mL flask containing 100 g of arsenic-contaminated soil. No biochar materials were added to the control sample. All flasks were maintained under identical conditions as described above. On days 0, 3, 7, 14, 21 and 35, three replicate flasks of each treatment were sampled (0.5 g) to determine the concentration of As fractionation and concentration of HCl extractable Fe. The pH was also determined. All flasks were maintained at 25 ± 1 °C in the dark for 35 d.

2.3. Adsorption kinetic experiments

To investigate the influence of the presence Fe(II) ions on the adsorption process of arsenic by bismuth-impregnated biochar, adsorption experiments were conducted as follows: 0.1 g BiBC was added to a 100-mL centrifugal tube. Then, 10 mg/L of arsenic solutions with different concentrations of ferrous sulfate (0, 5, 10 and 20 mg/L) were added to each tube. All tubes had a final solution volume of 50 mL and were shaken at 200 rpm for 24 h at 25 ± 1 °C to reach equilibrium. The water sampled from each tube was filtered through a 0.45-μm PTFE filter (Millipore, MA, USA) after standing for 24 h.