Effects of a manganese oxide-modified biochar composite on adsorption of arsenic in red soil

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Abstract

The arsenic adsorption capacity of a manganese oxide-modified biochar composite (MBC), prepared by pyrolysis of a mixture of potassium permanganate and biochar, was investigated in red soil. Adsorption experiments using batch procedures were used to estimate the arsenic adsorption capacities of the absorbent materials. Adsorption and desorption isotherms, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to characterise the prepared adsorbent materials, and a plausible mechanism for arsenic removal by MBC was proposed. Arsenic in red soil–MBC mixtures exhibited lower mobility than that in soils amended with pristine biochar. The improved removal performance of soil–MBC mixtures was attributed to a lower H/C ratio, higher O/C ratio, higher surface hydrophilicity, and higher surface sorption capacity, even though the impregnation of manganese oxide decreased the specific surface area of the biochar. Arsenic retention increased as the biochar content increased, mainly owing to an increase in soil pH. Several oxygenated functional groups, especially O–H, C=O, Mn–O, and Si–O, participated in the adsorption process, and manganese oxides played a significant role in the oxidation of arsenic. This study highlights the potential of MBC as an absorbent to immobilize arsenic for use in contaminated land remediation in the red soils region.

Keywords: Arsenic, adsorption, manganese oxide-modified biochar, red soil, oxidation

1. Introduction

Arsenic is a ubiquitous trace element that is potentially toxic to living organisms.

Arsenic originally derived from lithogenic sources occurs in surface soils, and can

be mobilized through weathering reactions, biological activity, and geochemical reactions, which results in environmental implications. Anthropogenic activities, including uncontrolled industrial discharge from mining and metallurgical industries, combustion of fossil fuels, and the use of arsenic pesticides, herbicides, and crop desiccants, can create additional As contamination in soils, and surface and groundwater (Jiang and Singh, 1994; Mandal and Suzuki, 2002; Marin et al., 1993; Mohan and Pittman, 2007). Contaminated soils with arsenic levels over 1 g/kg have been found in many countries around the world (Smith et al., 1998). The mobility, toxicity, and bioavailability of As in soil–water–plant systems depend on the species, and its sorption and desorption processes (Smedley and Kinniburgh, 2002; Violante and Pigna, 2002). The As(III) and As(V) oxidation states of As (arsenite and arsenate, respectively) are the primary forms of As in soils and aquifers (Ferguson and Gavis, 1972), and have different sorption behaviours (Arai et al., 2001; Goldberg and Johnston, 2001). Given this difference in behaviour, several methods have been commonly applied to remove As from contaminated soils or surface water, including precipitation, adsorption, membrane separation, ion exchange, and permeable reactive barriers. None of these methods are ideal, as each method has one or more disadvantages with a limited scope of application. For instance, some methods have proven too costly or are ineffective and require further remediation (Balasubramanian et al., 2009; Kumar et al., 2004; Leupin and Hug, 2005; Shih, 2005). Comparing all the advantages and disadvantages of the above-mentioned methods, adsorption processes are still considered highly efficient

and low cost methods for removing As from soils or wastewater because of their cost-effectiveness, minimal by-product generation, and ease of operation (Bissen and Frimmel, 2003; Sullivan et al., 2010; Zhang et al., 2010). Many adsorbents have been developed for the removal of As, including activated carbon (Zhang et al., 2010), iron and iron compounds (Leupin and Hug, 2005; Simeonidis et al., 2011), manganese, zirconium (Luo et al., 2012), and biochars (Beesley et al., 2011; Kołodyńska et al., 2012; Song et al., 2014; Sun et al., 2014).

Manganese-based materials are very effective for the removal and oxidation of arsenic (Lenoble et al., 2004). Because manganese oxides have positively charged mineral surfaces, they can increase the As(III) oxidation rate and allow increased adsorption of As(V) (Lafferty et al., 2010; Villalobos et al., 2014; Ying et al., 2012). Considering that As(V) is readily immobilised and has lower toxicity to humans than As(III), the oxidation of As(III) to As(V) in soils is an appropriate and practical process that has been recommended for remediation of As contamination.

Biochars (BC) produced by the high-temperature, low-oxygen pyrolysis of wood, rice husks, crop residues, and other agricultural wastes (Brewer and Brown, 2012; Glaser and Birk, 2012) can improve soil functions and reduce greenhouse gaseous emissions derived from organic materials. BC possesses a large surface area, and the negatively charged organic functional groups on the BC surface makes this a low-cost adsorption medium for retention of many heavy metals and control of contaminants in soils. Unlike cationic metals, As in the environment mainly exists in the form of oxyanions, which limits the As adsorption capacity of BC. Moreover,

BC may raise the soil pH, which could increase the mobility of As and cause plants to uptake As more readily (Joseph et al., 2010). Given these specific challenges when BC is utilised for reclamation of As, the impregnation of BC with Mn oxides to assist the immobilisation of As in soils can be a better option, as Mn oxides can limit As mobility via anion exchange in soils.

The red soils are major soils in southern China that have specific chemical, physical, and mineralogical characteristics. For the most part, these soils are highly weathered, acidic, poor in organic matter, and inherently infertile. They are highly susceptible to soil erosion, particularly on sloping land, and cannot sustain arable cropping systems without very careful management. In the past decades, large deposits of heavy metals in southern China have been mined to meet the demand of the nation's industrial development, causing enormous pollution challenges. The leakage or discharge of chemicals used for mining processes, such as As, can have adverse effects on the surrounding topsoil and aquifers, further increasing As bioavailability for plant uptake if protective measures are not taken. This can have a chronic toxic impact on the health of humans and animals if As-contaminated food and water are consumed.

The objectives of this work were to: (1) prepare and characterise a Mn oxide-modified biochar composite (MBC), (2) compare the As sorption capacity of MBC with that of pristine BC, and (3) explore the possible mechanisms involved in the sorption of As(III) and As(V) by MBC in red soil.

2. Materials and methods

2.1. Materials

All chemical reagents were purchased from the Guangfu Corporation (China). The red soil samples (0–20 cm) were collected from farmland in Yingtan county of Jiangxi province, China. The soil was mixed to obtain homogeneity using a nursery grade mixer and finally sieved through 0.75 mm nylon sieves for pH and CEC measurements or through 0.15 mm nylon sieves for organic matter content measurements. The pH of the red soil was 5.42, the organic matter content was 14.90 g/kg, and the CEC was 5.90 cmol/kg. Dried ground corn straw was used to prepare BC.

2.2. Sorbent preparation

The synthesis of BC was described in a previous report (Kołodzyńska et al., 2012). Briefly, untreated BC was produced from corn straw through slow pyrolysis at 600 °C for 2 h in a muffle furnace under a N₂ atmosphere with a nitrogen flow rate of 300 cm³/min. Untreated BC was included as an adsorbent for comparison. To prepare MBC, BC (5 g) was soaked in an aqueous KMnO₄ solution (0.079 mol/L, 40 mL) for 24 h and then drained before pyrolysis at 600 °C for 0.5 h under a N₂ atmosphere. The weight ratio of BC to KMnO₄ was 10:1. The obtained samples were rinsed thoroughly, rewashed with deionized water to remove impurities, and dried at 80 °C in oven for 4 h.

2.3. Characterisation of BC and MBC

The carbon, hydrogen, and nitrogen contents of BC and MBC were determined by

elemental analysis (Elementar Analysensysteme GmbH, Germany). The Mn content in BC and MBC was determined by atomic adsorption spectrometry (Zeenit 700), and the pH was measured using an electronic pH meter. The ash content of BC and MBC was defined as the mass remaining after pyrolysis at 750 °C in an open crucible until a constant weight was obtained. The volatile matter was defined as the weight loss after pyrolysis of BC or MBC at 950 °C for 7 min in a covered crucible (Uchimiya et al., 2011). The specific surface areas of BC and MBC were defined as the nitrogen adsorption, which was measured using a gas sorption analyser (Quantachrome, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted for the red soil and red soil amended with BC or MBC to examine adsorbed As (PHI 5000 Versa Probe, Physical Electronics, Inc.).

2.4. Adsorption and desorption isotherms

Adsorption experiments were conducted by batch procedures to estimate the As(III) adsorption capacities of the absorbents. The experiments were conducted in 40 mL brown glass bottles, using 2.0 g red soil and 20 mL aqueous As(III) solution (0, 10, 20, 30, 40, and 50 mg/L) at an ionic strength of 0.01 M (NaNO₃). The initial pH was adjusted to 7 with either 0.01 M HCl or 0.01 M NaOH. BC or MBC (0, 0.5%, 1%, 2%, and 4% of the soil weight) was added to the red soil. The reaction mixtures were agitated at 190 ± 5 rpm and 25 °C for 18 h. Then, the supernatants were passed through filter paper (Whatman No. 42) and the filtrates were analysed for As(III) and As(V). All experiments were performed in triplicate. The treatments were: the red soil (S), red soil with BC (S-BC), and red soil with MBC (S-MBC).

For the desorption experiments, 0.08 g of As-loaded adsorbents from the adsorption test was added to 40 mL of 0.05 mol/L NaNO₃ solution after washing and drying. The vials were shaken at 150 rpm for 48 h to reach an apparent equilibrium, and then the As(III) concentration in the solution was analysed.

2.5. As analysis

As(III) and As(V) were determined by hydride generation–atomic fluorescence spectroscopy (HG-AFS, AFS 9760, Beijing Haiguang Instrument Company, China) coupled with a hollow double-cathode lamp for As analysis. The detection limit for As was 0.05 ng/mL. All samples were analysed within 24 h. To assure accuracy, reliability, and reproducibility of the results, all tests were performed in triplicate. The average and variance in the arsenic concentrations are presented in the figures. A standard sample was run after every 10 samples. The recovery percentages were 90.5–109.5%, and the relative standard deviations of the determination were less than 4.8%.

2.6. FTIR analysis

The functional groups in BC and MBC were characterised using Fourier-transform infrared spectroscopy (FTIR) (Nexus 870, Nicolet, USA). A measured amount of BC or MBC was mixed with KBr (m/m = 1:200), ground into fine particles using a mortar and pestle, and compressed into a translucent sample disk by manual hydraulic pressure. Typically, thirty-two scans were collected.

2.7. Statistical analysis

All statistical analyses were conducted using SPSS 21.0 software (SPSS Inc.,

Chicago, IL). ANOVA was used to measure significant differences between treatments, with a p -value < 0.05 indicating statistical significance.

3. Results and discussion

3.1. Properties of BC and MBC

Table 1 shows the elemental analysis and surface area analysis of BC and MBC.

The ash, volatile matter, and water contents, as well as the pH, were not significantly different between BC and MBC ($p > 0.05$). The Mn content in MBC was 7.41%, whereas BC contained no Mn, suggesting successful Mn impregnation in MBC. The specific surface area dramatically decreased from 60.97 to 3.18 m²/g after impregnation, indicating that manganese oxide was successfully incorporated into the pores or clogged the pore openings on the BC surface in MBC. The O content increased from 5.16% to 10.90% after impregnation, which may reflect an increased number of oxygen-containing functional groups in MBC, indicating its potential for oxidation performance. Owing to the second pyrolysis step, the H/C ratio in MBC (0.0045) was lower than that in BC (0.0205). Both values were lower than that reported (0.05) by Samsuri et al. (2013). BC with low H/C molar ratios has been shown to contain small amounts of organic residues from the original plant, such as cellulose, but have high carbonisation (Chun et al., 2004; Samsuri et al., 2013). The findings of our study indicate that the degree of carbonisation was higher in MBC than in BC. The O/C molar ratios for BC and MBC were 0.0605 and 0.1493, respectively. This ratio is indicative of the content of polar groups content derived from carbohydrates and has been used as an indicator of surface

hydrophilicity (Chun et al., 2004); thus, MBC is considered to have higher surface hydrophilicity than BC. Hu et al (2015) also reported that the O/C ratio is related to the oxygenated functional groups, which play a significant role in As sorption.

3.2. Adsorption isotherms

The Langmuir isotherm model (Equation (1)) was applied to describe the adsorption onto the treatments.

$$q_m = q_e b C_e / (1 + b C_e) \quad (1)$$

Where q_m (mg/g) is the maximum adsorption capacity, b is the Langmuir adsorption constant (L/mg), C_e is the equilibrium concentration in the solution (mg/L), and q_e is the adsorption capacity at equilibrium (mg/g) (Xiong et al., 2010).

The Langmuir constants and correlation coefficients (R^2) are shown in Table 2.

The Langmuir equation assumes monolayer coverage of the sorbates over a homogenous sorbent surface and a finite number of identical absorption sites on the surface. The behaviour of As in the soil was closely associated with the amount of BC or MBC amended to the soil. Batch soil sorption experiments (Fig. 1) showed that very small amounts of As(III) were absorbed in red soil, whereas the S-BC and S-MBC samples showed better sorption ability. For all isotherms (Fig. 1), the adsorption of As increased with increasing equilibrium As concentration. The sorption process for all treatments can be well fitted by linear adsorption. The maximum adsorption capacities calculated using the Langmuir equation were 14.36 and 0.80 mg/g for S-MBC and S-BC, respectively. The results indicated a high surface sorption capacity for arsenic on S-MBC.

To better understand the differences in binding energy for As(III) between BC and MBC, desorption of As(III) was carried out in a NaNO₃ solution. Fig. 2 clearly reveals that desorption of As(III) from all the samples declined dramatically on addition of MBC to the red soil. The maximum desorption rates of As(III) (% = desorbed amount of As(III)/corresponding adsorbed amount of As(III)) were calculated and followed the order of S (40%) > S-BC (20.6%) > S-MBC (7.9%). Thus, the desorption data suggested that the addition of MBC could enhance adsorption of As(III) in red soil. It can be concluded that MBC has good potential to be used as an adsorbent for As(III) in red soil, as it is significantly more effective than pristine BC for As(III) adsorption.

3.3. Effects of amount of BC and MBC on As adsorption

The amount of BC amended to the red soil can influence the As removal efficiency. In this study, both BC and MBC improved the retention of As in the solid phase (Fig. 3). The results revealed that with increasing amounts of amended MBC, the adsorption of As in red soil significantly increased. However, the process was not the same in the presence of BC. MBC adsorbed more As than BC at the same equilibrium concentration. By adding more MBC, greater adsorption capacity can be obtained in red soil. For instance, when the equilibrium concentration was 6 mg/L, the adsorption capacity was 0.5 g/kg for 4% MBC, whereas it was only 0.25, 0.30, and 0.35 g/kg for 0.5%, 1%, and 2% MBC, respectively; however, the adsorption of As did not significantly change with the amount of BC amended to the soil. This result suggested that the enhanced adsorption capacity of As by red

soil amended with MBC could be attributed to the greater degree of carbonisation, higher surface hydrophilicity, and increased number of oxygenated functional groups in MBC.

3.4. Effect of BC and MBC on soil pH

Heavy metal removal is well known to have a considerable dependence on the pH of the soil. The pH of the soil was determined after the sorption experiments, and the results are presented in Fig. 4. The increases in soil pH were correlated with the amount of BC or MBC added. The pH increased by 1.4 units with 4% MBC addition, whereas an increase of only 0.4 units was observed with addition of 4% BC. The pH of the soil increased from 5.42 to 6.35 and from 5.87 to 7.26 for additions of BC and MBC over the range of 0.5% to 4%, respectively. We assume that the lower adsorption of As in the treatments with acidic pH was probably due to the presence of excess H^+ ions that compete with As for adsorption sites. With an increase in the soil pH, the electrostatic repulsion between the positively charged As and H^+ ions is decreased, which may result in an increase in the removal of As in the MBC treatments. As such a pH increase can neutralise acid soil, MBC addition could also potentially prevent red soil acidification.

3.5. FTIR analysis

FTIR has been frequently used to analyse the surface functionalities in BC (Hassan et al., 2014). The FTIR spectra ($400\text{--}4000\text{ cm}^{-1}$) of the soil amended with MBC before and after As adsorption are shown in Fig. 5. The bands around 3435, 2851, and 2929 cm^{-1} correspond to O–H stretching vibrations and were characteristic of

phenolic hydroxyl groups or adsorbed water (Huang et al., 2012; Luo et al., 2012). New peaks appeared after adsorption of arsenic at 2921 cm^{-1} , which could be related to aliphatic C–H vibrations, and at 1634 cm^{-1} , which can be attributed to amide C=O stretching, as observed mainly in proteins (Luo et al., 2012). It is noted that the band at approximately 1007 cm^{-1} in the spectra of the soils after adsorption was much stronger than that before adsorption; this band was attributed to the Si–O stretching vibration. The peaks at 540 and 437.7 cm^{-1} could be related to the formation of Si–O–Mn bonds (Zhang et al., 2007); these bands were not observed in the treatment with 4% MBC after As adsorption. This potentially could be explained by an interaction between Mn–O and As. The FTIR analysis indicated the Mn in the MBC plays an important role in the adsorption process. In contrast, the FTIR spectra (Fig. 6) showed no significant differences between the treatments amended with different amounts of BC after As adsorption.

3.6. XPS analysis

Peaks in the XPS spectra in Fig. 7 are observed at electron binding energies of 532.31 eV for O $1s$, which represented C=O or O–C=O bonds, and Fe $2p_{3/2}$, indicating the presence of Fe(II) and Fe(III) in the oxide (Nesbitt et al., 1998). A peak at 643.34 eV for Mn $2p_{3/2}$ indicated the presence of Mn(II), Mn(III), and a small amount of Mn(IV) in the oxide, in either octahedral or tetrahedral holes, as the binding energies of Mn(IV), Mn(III), and Mn(II) species were very similar and the peak for Mn in low oxidation states was located on the low-energy side (Nesbitt et al., 1998). The spectra results shown in Fig. 8 show that some As was adsorbed

on the surface of soil amended with MBC, whereas no As was observed on the soil surface amended by low amounts of BC and MBC. Though the O 1s quantity decreased, the adsorption capacity of the red soil amended with MBC was higher than that of other treatments, suggesting MBC plays an important role in the process of arsenic adsorption on the soil surface.

The XPS results showed that more As was absorbed into the soil amended with MBC compared with other treatments. From the XPS results (Fig. 7), a plausible mechanism for As(III) removal in the red soils amended with MBC could involve partial oxidation of As(III) to As(V) by Mn oxides and Fe–Mn oxides. Then, As(V) and As(III) are adsorbed on the surface via interactions with functional groups, diffuse into the interior, and finally, achieve equilibrium in the absorbent (Nesbitt et al., 1998; Ourvard et al., 2005).

4. Conclusions

BC and MBC were synthesised in the study to investigate their effects on adsorption of arsenic in red soil. The As adsorption data of BC and MBC were described well by Langmuir adsorption isotherms. The batch soil sorption experiments showed that S-MBC had a much greater sorption capacity for As(III) than the S-BC, although both enhanced the sorption of As(III) in red soil. The retention of As increased with the amount of added BC or MBC, mainly because of an increase in soil pH. FTIR and XPS analyses indicated that the adsorption of As occurred on the surface of the adsorbent, where Mn–O/As bonds, Fe–O/As bonds, and other oxygenated function groups were formed during the adsorption process

on the red soil surface. The XPS results suggested that As(III) removal in the S-MBC was achieved through partial oxidation of As(III) to As(V) by Mn oxides and Fe–Mn oxides. In summary, MBC plays an important role in the adsorption of As and has the potential to prevent red soil acidification and improve soil quality. As biochars are inexpensive, the manganese oxide-modified biochar developed in this study can be used as a promising remediation absorbent to mitigate the risks of As contamination in red soils.

Acknowledgment

The authors are grateful for financial support from the National Science Foundation of China (41273136).

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Figure

Fig.1.Arsenic adsorption isotherms

Fig.2. Arsenic desorption isotherms

Fig.3. Influence of different additions of MBC (A) and BC (B) on the sorption of As in the red soil.

Fig.4. Soil pH after adding different rates of BC and MBC

Fig.5. FTIR spectra of the red soil amended with various amount of MBC (0.01, and 0.04 g per g soil) before and after adsorption of arsenic

Fig.6. FTIR spectra of the red soil amended with various amount of biochars (BC and MBC) (0.005, 0.01, 0.02 and 0.04 g per g soil) after adsorption of arsenic

Fig.7. XPS spectrum of the red soil and mixture of soil with manganese oxides biochar adsorbed arsenic

Fig.8. Mn and As atomic respective percent in XPS spectrum of the red soil and its various mixtures with biochar and modified biochar

Table

Table 1 Physicochemical characteristics of biochar and manganese oxides-biochar composite

Absorbent	Ash	Volatile Matter	Mn	N	C	O	H	pH	S _{BET}
			%						(m ² /g)
BC	10.17	9.32	nd	0.80	85.26	5.16	1.75	10.39	60.97
MBC	12.60	9.76	7.41	0.72	73.00	10.90	0.33	10.75	3.18

Note: S_{BET} means specific surface area by BET analyzed.

Table 2 The constants and correlation coefficients (R^2) of Langmuir model

Treatments	Langmuir		
	q_m /(mg/g)	b/(L/mg)	R^2
S	0.7785	0.0486	1
S-BC	0.8039	0.3206	0.9647
S-MBC	14.3618	0.0007	0.9640