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RESEARCH ARTICLE

Immobilization of Cd(II) in acid soil amended with different biochars with a long term of incubation

Xiaofei Tan[1,2] · Yunguo Liu[1,2] · Yanling Gu[1,2] · Guangming Zeng[1,2] · Xin Wang[3] · Xinjiang Hu[1,2] · Zhichao Sun[1,2] · Zhongzhu Yang[1,2]

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Abstract Biochars derived from bamboo, coconut shell, pine wood shavings, and sugarcane bagasse were applied into Ultisol to investigate their effects on Cd(II) immobilization. After 360 days of incubation, the physical/chemical properties of the Ultisol were improved by the addition of different biochars. As a result, the maximum adsorption capacities of soil for Cd(II) were increased from 8.02 to 9.07–11.51 mmol/kg, and bamboo biochar showed the highest effect on Cd(II) immobilization. The Langmuir model (R^2>0.983) fitted the data better than the Freundlich model (R^2 were 0.902–0.937). Column leaching experiments suggested that biochar can also increase the immobilization of Cd(II) under leaching conditions. Biochar mainly increased the weak/unstable binding force of Cd(II) by soil, such as ion exchange, electrostatic attraction, physical adsorption, and carbonate precipitation. In addition, a significant enhancement of surface complexation was also observed.

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✉ Yunguo Liu
hnuliuyunguo@gmail.com

[1] College of Environmental Science and Engineering, Hunan University, Changsha 410082, People's Republic of China

[2] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, People's Republic of China

[3] College of Resources and Environmental Science, Hunan Normal University, Changsha 410082, People's Republic of China

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Introduction

Alarming amount of heavy metals discharge into soil annually due to various anthropogenic activities (such as mining, excessive fertilizer application, and wastewater irrigation in agriculture, etc.) have led to severe contamination of soils worldwide (Jarup 2003; Houben et al. 2013). Cd(II) is one of the most important metal pollutants which can be taken by crops and accumulate gradually in the human body through food chain, and then it may induce adverse damage to human beings (WHO 1992; Jeong et al. 2012).

Extensive techniques have been developed to tackle heavy metal pollution in soils, while most of them are generally considered to be environmentally disruptive and economically unfeasible in practice (Karami et al. 2011; Jiang et al. 2012b; Jiang and Xu 2013). Recently, soil remediation with biochar is becoming a new hot topic (Beesley et al. 2011; Ahmad et al. 2014b). Biochar research is originated from the soils with high fertility and carbon content called *terra preta* ("dark earth") in the Amazon Basin (Marris 2006). These soils continue to store carbon today and remain nutrient rich. Application of biochar into soil has become a new exciting biotechnology in terms of soil amendment, enhancing of crop yield, mitigating global warming, and carbon sequestration (Lehmann and Joseph 2009; Sohi 2012).

The positive properties of biochar including large specific surface area, porous structure, surface functional groups, and high pH make it possible to be used as an adsorbent to immobilize heavy metals in the soil (Uchimiya et al. 2010; Xu et al. 2013; Zhang et al. 2013; Tan et al. 2015). In addition, the improvement of soil physical/chemical properties by the application of biochar can also play positive roles in improving metal retention (Houben et al. 2013; Hardie et al. 2014; Sun and Lu 2014). Therefore, an integrated understanding of these mechanisms is needed.

Ultisol is an acid soil with low cation exchange capacity (CEC) and pH values as a result of intensive weathering and soil evolution, which shows low adsorption capacity for heavy metals (Jiang et al. 2012a; Jiang and Xu 2013). The alkaline biochar resulted from pyrolysis can mitigate the low pH of acid soil. In the present study, Ultisol is selected to test the effect of different biochars on Cd(II) immobilization. In addition, a longer time of incubation after the addition of biochar was conducted to stabilize the reaction between soil and biochar and make the results closer to the actual application. The objectives of this study were to (1) evaluate the changes in the physical/chemical properties of Ultisol amended with variable biochars after 360 days of incubation; (2) examine the effect of biochars on the immobilization of Cd(II) in Ultisol by batch adsorption experiment, soil column leaching, and BCR sequential extraction procedure; (3) compare the amendment effect of biochars derived from different feedstocks; and (4) gain insight into the effect of biochar on the mechanisms of Cd(II) immobilization in the biochar-amended soils after 360 days of incubation.

Materials and methods

Soil and biochars

The surface sample of Ultisol (0–10 cm) was collected from a site of Changsha, Hunan Province (28° 10.91′ N, 112° 56.82′ E) in China. The soil sample was air-dried and ground to pass through a 2-mm sieve.

Four feedstocks namely bamboo, coconut shell, pine wood shavings, and sugarcane bagasse were collected from a suburb of Changsha, China. These feedstocks were rinsed with water and oven dried (80 °C). A tube furnace (SK-1200 °C, Tianjin Zhonghuan Test Electrical Furnace Co., LTD, China) was used to convert these samples into biochars. For each experiment, about 100 g of the dried samples were fed into a quartz glass tube (5 cm diameter, 20 cm long) designed to fit inside of the furnace. The chamber of tube furnace was sealed and replenished with nitrogen gas (400 mL/min) to keep the inert atmosphere along with the pyrolysis process. The temperature was programmed to rise up to 450 °C at a rate of 7 °C/min and held at the peak temperature for 2 h before cooling to room temperature. The resulted biochars were gently crushed and passed through a 2-mm sieve, then sealed in air-tight containers before use. The resulted biochars from bamboo, coconut shell, pine wood shavings, and sugarcane bagasse were referred as BB, CB, PB, and SB, respectively.

Incubation experiments

Air-dried soil sample of 300 g was placed in 1 L plastic buckets. The soils were wetted with deionized water to 70 % of field water-holding capacity of the soil. Then the soils were preincubated in the dark at 25±2 °C for 10 days. After preincubation, each biochar was added into the buckets at 2 % (oven-dry basis) (Singh et al. 2012). The soil and biochar were mixed thoroughly and then re-wetted with deionized water to 70 % of field water-holding capacity of the soil. All buckets were covered with a plastic lid, and a small hole was made to allow gas exchange but minimize moisture loss, and then incubated at a constant 25±2 °C in dark. The buckets were weighed every 5 days, with water added to maintain constant moisture content throughout the incubation period. After 360 days of incubation, the soil samples were removed from the buckets. Then samples were air-dried for the following experiments. The soils added with different biochars are here referred as BB-soil, CB-soil, PB-soil, and SB-soil.

Characterization of biochar-amended soils

A modified barium chloride method (Lee et al. 2010) was used in this study to determine the CEC for the non-amended soil and biochar-amended soils. The morphological and structural changes of biochar-amended soils after incubation were observed using scanning electron microscope (SEM) (TM3000, Hitachi, Japan). The FTIR spectra (IRAffinity-1, Shimadzu, Japan) of the adsorbent were recorded in the range of 4000–400 cm^{-1}.

Batch adsorption experiments

A stock solution containing 1 g/L $Cd(NO_3)_2$ was prepared using reagent-grade $Cd(NO_3)_2{\cdot}4H_2O$. The different concentrations (50, 100, 200, 250, 300, 400, 500 mg/L) of Cd(II) with 0.001 M $NaNO_3$ as the background electrolyte was diluted from the stock solution and 1 M $NaNO_3$.

One-gram soil samples in duplicate were weighed into a 100-mL centrifuge tube. Then 20 mL of the $Cd(NO_3)_2$ solution of varying concentrations was added into each tube. The suspensions were shaken in a constant-temperature water bath at 25±2 °C for 1 h and then allowed to stand overnight to reach reaction equilibrium. The solution phase of the suspension was then separated from the solid phase by centrifugation at 5000 rpm for 10 min, and the supernatant was taken for future determination. The Cd(II) concentration in the supernatant was analyzed using flame atomic absorption spectrometry (PerkinElmer AA700, USA). The adsorption capacity (q_e, mmol/kg) was calculated according to Eq. (1):

$$q_e = \frac{(C_o - C_e) \times V}{M \times m} \tag{1}$$

Where C_o and C_e are the initial and equilibrium metal ion concentrations (mg/L), respectively; V (mL) is the volume of the suspension; M (g/mol) and m (g) are the molar mass of Cd and the mass of soil, respectively.

To evaluate and compare the effect of biochar on Cd(II) adsorption capacities of soils, Langmuir and Freundlich models were used to fit the experimental data. The equations of the Langmuir and Freundlich adsorption models are expressed by the following equations, respectively:

$$q_e = \frac{Q_{\max} K_l C_e}{1 + K_l C_e} \quad (2)$$

$$q_e = K_f {C_e}^{1/n} \quad (3)$$

Where q_e is the amount of the metal adsorbed (mg/g); C_e is the equilibrium concentration of solution (mg/L); $Q_{\max}$ is the maximum adsorption capacity (mg/g); K_l is the Langmuir constant related to the affinity; and K_f and n are the Freundlich constants, which indicate the adsorption capacity and intensity, respectively.

Sequential extraction

The BCR sequential extraction was conducted by the procedure described in previous studies (Quevauviller et al. 1993; Fuentes et al. 2008). Four sequential extraction steps were conducted to give rise to four different fractions of Cd(II) in soil. 0.11 M acetic acid, 0.1 M hydroxylamine hydrochloride (pH 2), 8.8 M H_2O_2 and 1 M NH_4OAc (pH 2), and HNO_3–HF–$HClO_4$ were applied to extract the acid-soluble fraction, reducible fraction, oxidizable fraction, and residual fraction of the metals, respectively.

Soil column leaching experiment

A glass column (20 cm long and interior diameter of 3 cm) was used for the leaching experiment. One hundred gram of different biochar soils (about 12 cm high) was packed into the column very carefully to a uniform bulk density. Inertia quartz layers were used at the top and bottom of the column to disperse flow throughout the entire area and to reduce the impact of the flow on the colloid movement. The column was leached with 100 mg/L Cd(II) solution from the top of the column using a peristaltic pump (flow rate 6.67×10^{-9} m^3/s) and the leachate was collected continuously at the bottom of the column in 100-mL measuring flasks. The Cd(II) concentration in the leachate was determined as previously mentioned.

Statistical analysis

Statistical analyses were performed using SPSS Ver. 18. A one-way ANOVA followed by a Tukey's test was performed to analyze significant differences in pH, CEC, and Cd(II) adsorption amount between biochar-amended soil and non-amended soil. The results shown in the figures represent the average of three independent replicate treatments. The data obtained in this study are presented as means±standard deviations (SD). The significant level was defined at $p<0.05$.

Results and discussion

Effects of biochar on soil properties

After 360 days of incubation, the measurement of pH showed that adding biochar into Ultisol largely increased the soil pH. The increase of pH in biochar-amended soil is probably due to the release of alkali salts from the organic matrix in the feedstock during pyrolysis (Ahmad et al. 2012; Kim et al. 2013). The pH of the Ultisol increased from 4.78 to 5.80, 5.26, 5.72, and 5.36 when BB, CB, PB, and SB were incorporated, respectively.

The CEC of Ultisol also increased from 5.60 to 9.03, 6.80, 9.75, and 8.88 cmol/kg for BB-, CB-, PB-, and SB-amended soils, respectively (Fig. 1). The higher CECs of biochar-amended soils were mainly ascribed to the carboxylic acid functional groups of incorporated biochar (Lee et al. 2010; Harvey et al. 2011). In addition, the observed CEC of the biochar-amended soil varied with the type of feedstocks. The higher CEC in BB- and PB-amended soils suggested higher carboxylic acid contents were formed in these biochars, which may be attributed to the differences in lignin composition and thermal degradation of corresponding feedstocks (Opsahl and Benner 1995; Harvey et al. 2011).

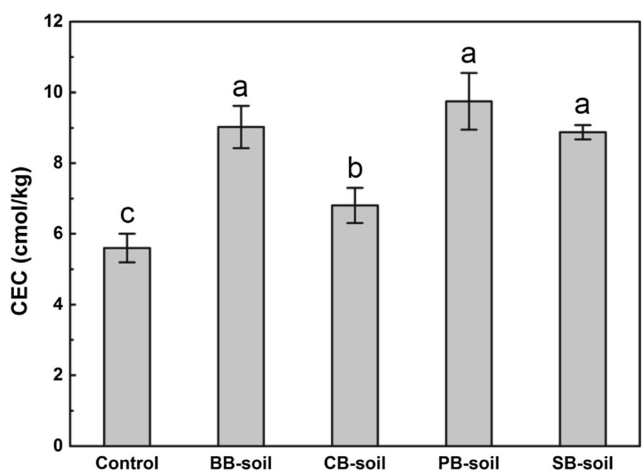

Fig. 1 The cation exchange capacity of different samples. Different letters indicate significant differences between different samples ($p<0.05$)

The SEM images of soil for non-amended soil and four biochar-amended soils are shown in Fig. S1 (Supplementary material). It showed that the surface of soil for non-amended soil was homogeneous (Fig. S1 a, b), while the biochar-amended soils were irregular (Fig. S1 c–f). Previous studies reported that the incorporation of biochar can improve the pore-space structure due to the highly porous nature of biochar (Sun and Lu 2014). Several studies also proposed that application of biochar to soil may create accommodation pores between the biochar particles and the soil aggregates (Jones et al. 2010; Hardie et al. 2014). From the SEM images, we can apparently found that both the two effects may play positive roles in soil pores structure. All the incorporated biochars had porous structure, which can improve the adsorption of metals. In addition, the biochars were embedded in the soil particle or attached on the surface of soil so that the new stable aggregate with new accommodation pores were formed.

Figure 2 shows the FTIR spectra of non-amended soil and four biochar-amended soils. The FTIR spectra showed that the incorporation of four biochars increased the intensity of the bands of functional groups (−OH, −COOH and C=C and C=O), which suggested that the application of biochars into soil significantly increased the proportion of functional groups onto the soil, which contributed to the higher CECs and Cd(II) complexation (Lee et al. 2010; Jiang et al. 2012b).

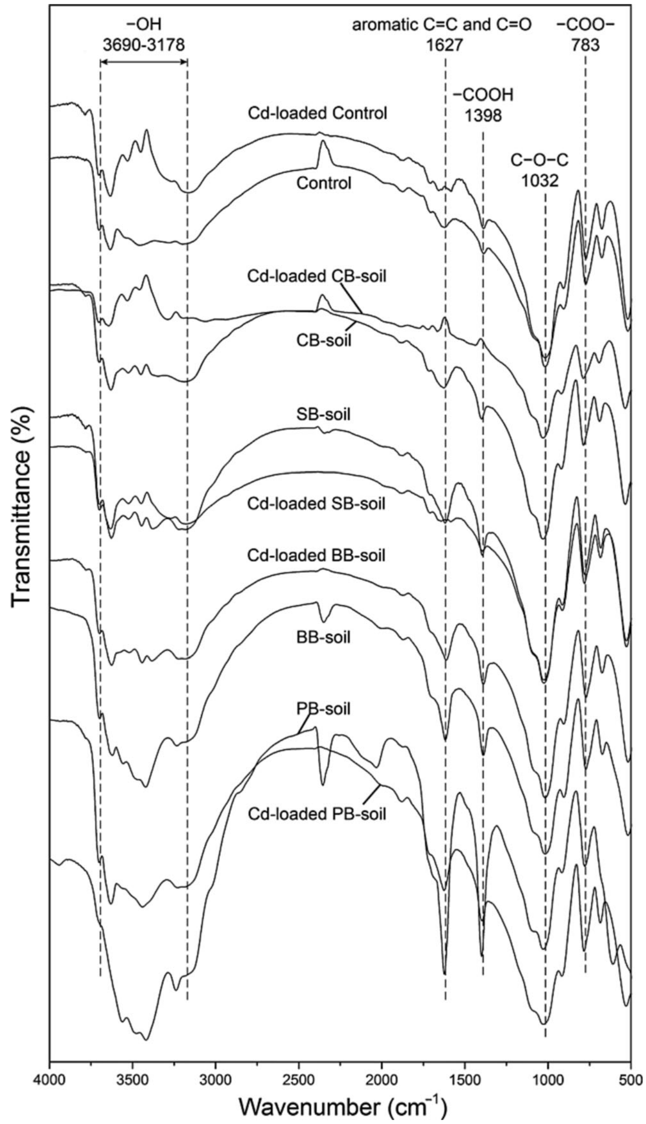

Fig. 2 The FTIR spectra of the soil for control and four biochar-amended soils with and without Cd-loaded

Adsorption isotherms of Cd(II)

The Cd(II) adsorption isotherms of non-amended soil and four biochar-amended soils were studied at different initial heavy metal concentrations ranging from 50 to 500 mg/L, and the results are shown in Fig. 3. The adsorption constants and correlation coefficients for Cd(II) onto soils obtained from Langmuir and Freundlich isotherms are given in Table 1. Correlation coefficients suggested that the Langmuir model (R^2>0.983) fitted the data better than the Freundlich model (R^2 were 0.902–0.937). This suggested that the adsorption behavior observed was predominantly monolayer adsorption (Chen et al. 2011).

As can be seen from the results, the adsorption of Cd(II) on all biochar-amended soils was increased significantly with biochar incorporation. The maximum adsorption capacities of BB-soil, CB-soil, PB-soil, and SB-soil for Cd(II) (11.51, 9.07, 10.37, and 9.91 mmol/kg, respectively) were much higher than that of non-amended soil (8.02 mmol/kg) (p<0.05). Cd(II) adsorption increased by 43.61, 13.16, 29.41, and 23.58 % due to addition of BB, CB, PB, and SB, respectively. BB-soil had the highest adsorption ability followed by PB-, SB-, and CB-soil. This may be attributed to the higher CEC and more functional groups of BB-soil than CB- and SB-soil. In addition, after 360 days of incubation, the pH of the soil increased and BB-soil showed higher pH than CB-, PB-, and SB-soil. With the higher pH of BB-soil, the competition of metal ions and protons for binding sites decreased and more binding sites were released due to the deprotonation of functional groups (Lu et al. 2012). Therefore, more Cd(II) cations can be captured by BB-soil surface due to electrostatic attraction.

BCR fractions of adsorbed Cd(II) by soils

The four fractions of Cd(II) were measured with the BCR sequential extraction procedure after adsorption (the initial Cd(II) concentrations were 50, 200, and 500 mg/L), so as to study the distribution of different forms of Cd(II) in the biochar-amended Ultisol. Figure 4 shows the results obtained after application of the BCR sequential extraction for all soils. As can be seen, the sum of the four fractions is reasonably consistent with the amounts of Cd(II) adsorbed by five soil

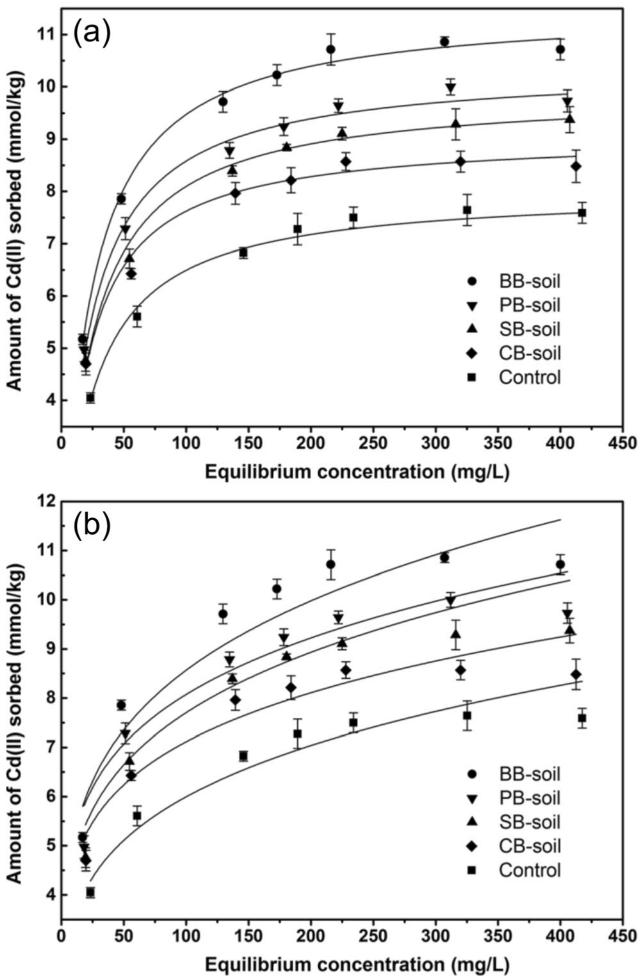

Fig. 3 The Cd(II) adsorption isotherms of control and four biochar-amended soils: **a** Langmuir isotherms, **b** Freundlich isotherms

samples. Cadmium was released during the sequential extraction, and its mobilized forms (acid-soluble and reducible fractions) were more easily extracted (Davidson et al. 1998).

The application of biochars increased the acid-soluble fraction of Cd(II) extracted by acetic acid. The amounts of acid-soluble Cd(II) in the extracts of BB-soil were higher than other samples. The results were in line with the order of adsorption

Table 1 Constants and correlation coefficients of Langmuir and Freundlich models for Cd(II) adsorption onto soils

	Langmuir model			Freundlich model		
	Q_{max}	K_l	R^2	K_f	$1/n$	R^2
Control	8.02	0.043	0.994	2.070	0.231	0.937
BB-soil	11.51	0.047	0.997	3.108	0.220	0.930
CB-soil	9.07	0.053	0.984	2.980	0.189	0.925
PB-soil	10.37	0.048	0.983	3.331	0.192	0.902
SB-soil	9.91	0.045	0.990	2.884	0.213	0.916

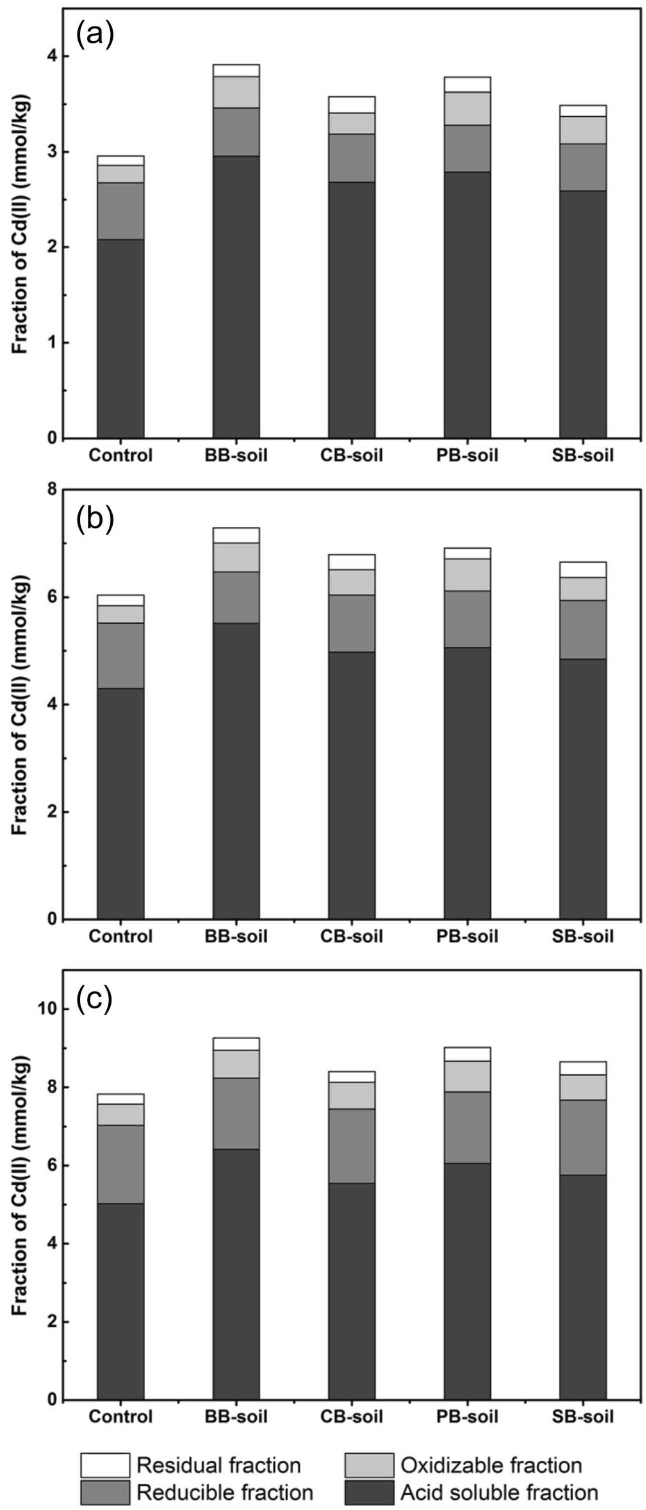

Fig. 4 Fraction of Cd(II) determined by BCR sequential extraction after adsorption at different initial Cd(II) concentrations: **a** 50 mg/L, **b** 200 mg/L, **c** 500 mg/L

ability of these samples. The acid-soluble fraction of Cd(II) are the active and bioavailable parts, which primarily composed of soluble, exchangeable, surface-adsorbed, and carbonate combined heavy metals (Fuentes et al. 2008; Jiang

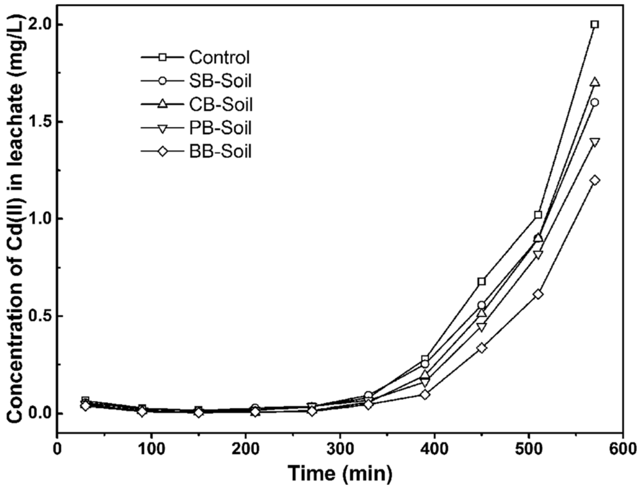

Fig. 5 Dynamics of Cd(II) concentration in leachate after Cd(II) solution went through the soil column during leaching experiment (the initial concentration of Cd(II) was 100 mg/L)

et al. 2012a). The increase in the amount of acid-soluble Cd(II) suggested that biochar mainly increased the weak/unstable binding force of soil for Cd(II) including ion exchange, electrostatic attraction, physical adsorption, and carbonate precipitation. In other words, the adsorption of Cd(II) improved by biochar was partly due to the increase of weak adsorption, which can be further extracted as the acid-soluble fraction of Cd(II). In fact, we can see from Fig. 4 that the increase in the acid-soluble fraction might account for the most proportion of the increase in the total extracted Cd(II). So that, the effect of biochar on the adsorption of Cd(II) by Ultisol mainly reflected in the enhancement of weak/unstable adsorption. The high portion of acid-soluble Cd(II) also proved the high mobility of cadmium which usually presented as easily available fractions in soils (Beesley et al. 2010).

The incorporation of biochars had little influence on the reducible fraction (fraction associated with Fe and Al oxides). To some extent, biochar even slightly decreased the amount of

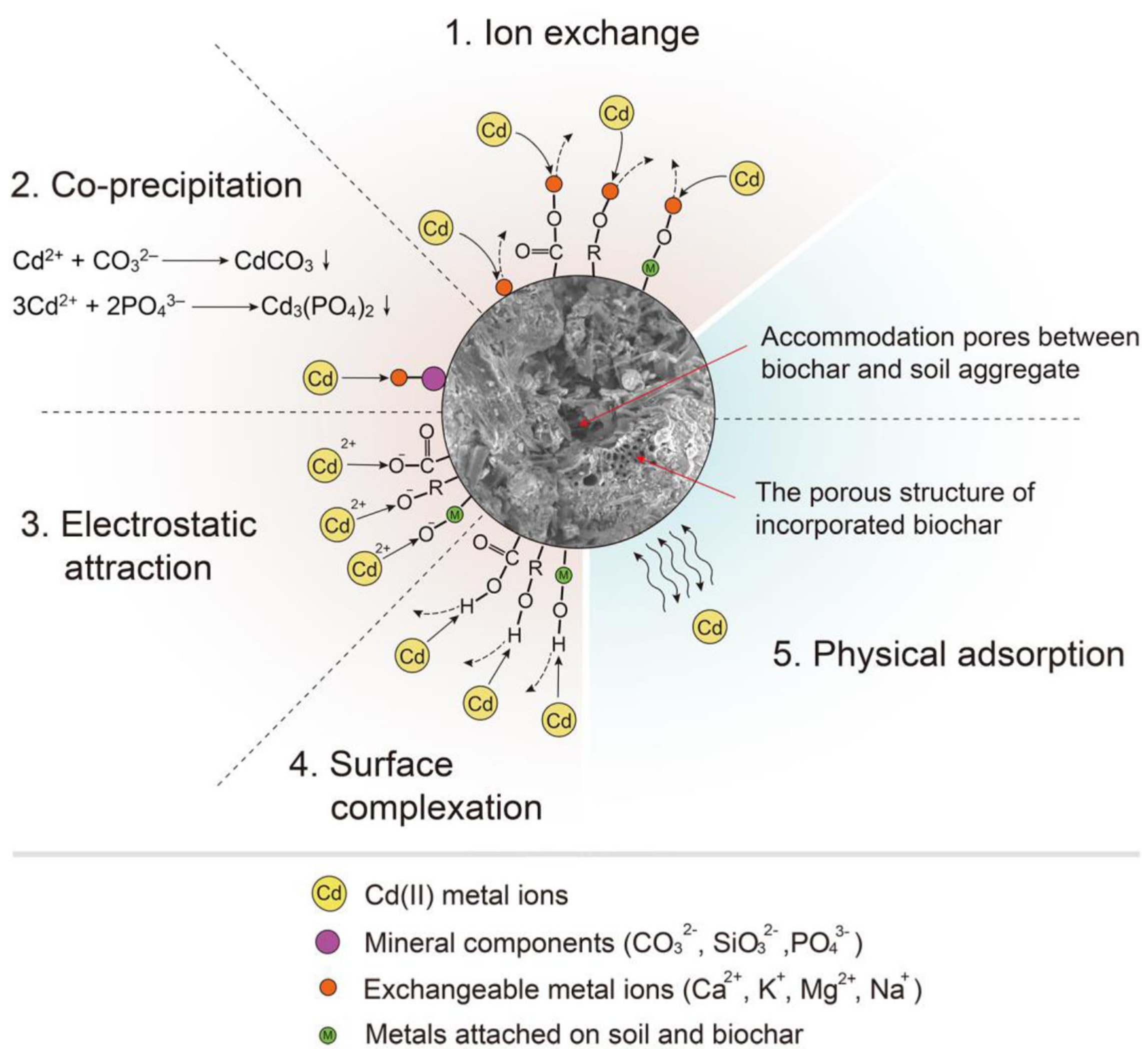

Fig. 6 The involved mechanisms of Cd immobilization on the biochar-amended soil

reducible fraction. Ultisol is rich in iron and aluminum oxides. While, carbonates and phosphates in the biochar may inhibit the formation of Cd complexation with Fe and Al oxides because of their competitive effect (Ahmad et al. 2014a), resulting in decreased Fe and Al oxide-bound Cd(II) fractions in biochar-amended soil.

The amount of oxidizable Cd(II) in the soil increased obviously when biochars were incorporated into the soil, which was mainly resulted from the formation of complexes of Cd(II) with organic functional groups on the biochars (Guo et al. 2006). This effect can also be observed from the FTIR spectra of soils (Fig. 2), that the intensity of functional group bands in the soils decreased after adsorption. However, the proportion of residual Cd(II) remained stable and changed little when biochars were incorporated. This was probably attributed to the short contact time of adsorption and manual addition of the biochars had very little effect on the residual portion of the heavy metals (Jiang et al. 2012a).

Column leaching experiments with biochar-amended soil

To simulate and confirm the positive effect of biochars on the immobilization of Cd(II) under leaching conditions, non-amended soil and four biochar-amended soils were used to adsorb Cd(II) in column leaching experiments (Fig. 5). In the first 330 min, the concentration of Cd(II) in leachate of all the five samples were less than 0.079 mg/L. After 570 min, the concentration of Cd(II) in leachate of non-amended soil was gradually higher than that of four biochar-amended soils, suggesting that the application of biochar can also increase the immobilization of Cd(II) under leaching conditions. The concentration of Cd(II) in leachate of BB-soil was the lowest, which showed that BB-soil had the highest immobilization ability. This is consistent with the results of batch adsorption experiments.

Mechanisms of Cd(II) immobilization on the biochar-amended soil

All possible involved mechanisms of Cd(II) immobilization on the biochar-amended soil are summarized in Fig. 6, which can be divided into the following five parts: (1) ion exchange, (2) co-precipitation, (3) electrostatic attraction, (4) physical adsorption, and (5) surface complexation.

The increased CEC of biochar-amended soils and the high portion of exchangeable Cd(II) fraction indicated that ion exchange played an important role in the Cd(II) immobilization (Fig. 1). Furthermore, the mineral components in the biochars (PO_4^{3-} and CO_3^{2-}) served as additional sorption sites, which can form precipitation with Cd(II). Cd(II) can also exchange with exchangeable metal ions (Ca^{2+}, K^+, Mg^{2+}, and Na^+) to form co-precipitation. The increase in electrostatic adsorption of Cd(II) may be attributed to the existence of large amount of negative surface-charge on biochars. In addition, as biochars increased the pH of soil, part of functional groups in soils were deprotonated and presented in negatively charged form, resulting in the increase of electrostatic attraction. The increase in functional groups and amount of oxidizable Cd(II) both confirmed the complexation mechanism (Figs. 2 and 4). Additionally, the natural porous structure of incorporated biochar together with the accommodation pores between biochar and soil aggregate rebuild the pore structures of amended soil (Fig. S1). The improvement in soil porous properties make physical adsorption perform a significant role in Cd(II) immobilization.

The results of BCR sequential extraction suggested that acid-soluble metals account for the most parts of the increased Cd(II) immobilization, followed by the oxidizable fraction of Cd(II) (Fig. 4). Therefore, biochar mainly increased the weak/unstable binding force of Cd(II) by soil, such as ion exchange, electrostatic attraction, physical adsorption, and carbonate precipitation. In addition, a significant enhancement of surface complexation was also observed.

Conclusions

The incorporation of biochar significantly improved the physical/chemical properties of soil after 360 days of incubation, including pH, CEC, functional groups, and pore structures. These changes in soil properties made a great contribution to the increased Cd(II) immobilization. And, these effects were different due to the different feedstocks of biochar. BB-soil had the highest adsorption ability followed by PB-soil, SB-soil, and CB-soil. The application of biochar can also increase the immobilization of Cd(II) under leaching conditions. Biochar mainly increased the weak/unstable binding force of Cd(II) by soil (such as ion exchange, electrostatic attraction, physical adsorption, and carbonate precipitation) and the strong force of surface complexation. The application of biochar in soil can provide a promising strategy for both soil remediation and carbon sequestration.

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