Does Biochar Alter the Speciation of Cd and Pb in Aqueous Solution?

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Cadmium and lead contamination in bodies of water has been a serious concern because of risk to the environment. A laboratory experiment was initiated to investigate the efficacy of biochar (BC) in removing cadmium and lead (Cd and Pb, respectively) from solution. After absorption by BC, the fractions of Cd and Pb at different solution temperatures were measured. The adsorption data were described by Langmuir isotherm with maximum adsorption capacities of 6.36, 6.47, and 6.74 mg Cd g^{-1} and 50.05, 55.86, and 63.09 mg Pb g^{-1} at 25, 35, and 45 °C, respectively. The adsorption capacities were affected by Cd/Pb initial concentration, pH, BC particle size, BC dosage, and reaction time. Biochar adsorbed the Cd and Pb mainly as species bound with carbonate (> 50%) and organic compounds (~40%). Exchangeable and residual fractions of Cd and Pb were less than 10%. Results from this study indicate that BC is highly effective in the adsorption of the heavy metals Cd and Pb through binding with carbonates.

Keywords: Biochar (BC); Cadmium; Lead; Contaminated water; Fourier transform infrared spectroscopy

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INTRODUCTION

The accumulation of heavy metals (e.g. cadmium (Cd), lead (Pb), copper (Cu)) in bodies of water poses a potential ecological risk of contamination due to their persistent nature and non-biodegradability (Hou *et al.* 2013; Gupta *et al.* 2014). This is a serious concern because of the ability of the heavy metals to cause toxic effects and health disorders (Rignell-Hydbom *et al.* 2009). With the worldwide over-expanding of population, there has been increased contamination in water bodies (rivers and lakes). Population pressures (especially the heavy metals contamination) have caused an acceleration of the progressive deterioration of water quality and environmental problems. This can be attributed to increased domestic, municipal, agricultural, and industrial activities; effluent being discharged into water bodies; and an overall increase in environmental degradation resulting from urbanization (Bundschuh e*t al.* 2012; Szalinska *et al.* 2013; Tang *et al.* 2013b; Haydar *et al.* 2014). There is urgency to protect and conserve and freshwater bodies so that they can be used for sustainable development, and it is necessary that feasible measures be taken to dispose of effluents contaminated by heavy metals in a way that prevents or controls the pollution. Among the amendment techniques, adsorption is one of the most effective techniques to remove pollutants from water (Kampalanonwat and Supaphol 2014).

Biochar (BC) can be defined as the carbonaceous residue of incomplete burning of carbon-rich biomass (feedstock) that is pyrolyzed at a low temperature (300 °C to 500 °C) under limited oxygen concentrations and not fully carbonized (Chen *et al.* 2008; Cao *et al.* 2009). Biochar is considered to be an effective adsorbent for heavy metals and organic pollutants from waste water (Chen *et al.* 2011a; Tang *et al.* 2013a; Xu *et al.* 2013). Biochar also is regarded as a predominantly stable and recalcitrant organic carbon compound that tends to improve soil (Norfolk soil) quality (Novak *et al.* 2009). Kim *et al.* (2013) studied the properties of BC made from *Miscanthus* and showed that a higher pyrolytic temperature resulted in BC with a higher proportion of aromatic structures and fewer polar functional groups. A high efficiency has been found when using BC to remove heavy metals from aqueous solution; this has been attributed to the special structured carbon matrix with a high degree of porosity and an extensive surface area (Chen *et al.* 2011b; Kim *et al.* 2013). Biochar has been increasingly recognized as a multifunctional material that often shows good performance in various agricultural and environmental applications, especially in addressing pollution problems (Lehmann *et al.* 2011; Venegas *et al.* 2015). In previous studies, BC has been found to efficiently immobilize Cd in soil (Cui *et al.* 2013b). It also effectively adsorbed Pymetrozine (Cui *et al.* 2013a). Also, BC has been shown to immobilize heavy metals, resulting in a significant reduction in the bioavailability and leaching potential of the heavy metals in water and soil (Devi and Saroha 2014).

Among the various methods of wastewater contaminant removal, adsorption has been shown to be an efficient technology. So various adsorbents have been developed, such as BC, fly ash, and activated carbon (González *et al.* 2011; Lalhmunsiama *et al.* 2013; Wang *et al.* 2013). Biochar may be considered as a potential adsorbent. Many studies have been carried out to evaluate different potential adsorbents to remove pollutants, with consideration of costs, efficiency, and the presence of special characteristics, such as various functional groups and BET surface area (Uchimiya *et al.* 2013; Jin *et al.* 2014). The use of BC in the removal of heavy metals from contaminated water has been widely studied due to its adsorption ability such as removal of cadmium and lead from water (Liu *et al.* 2010; Kim *et al.* 2013; Khare *et al.* 2014). A study by Mohan *et al.* (2007) showed that the BC's (oak bark) ability to remove Pb and Cd is remarkably higher than that of commercial activated carbon when considered in terms of the amount of metal adsorbed per unit surface area (0.5157 mg m^{-2} for Pb and 0.213 mg m^{-2} for Cd). Biochar produced at a high pyrolytic temperature (500 °C) had a high pH and surface area, which was responsible for a Cd sorption capacity up to 13.24 mg g^{-1} in solution (Kim *et al.* 2013). There are many studies on BC adsorption of heavy metals and immobilized in different fractions (Pan *et al.* 2009; Jiang *et al.* 2012) and most on the soil heavy metals fractions, but there has been very little research on the effects of BC on Cd and Pb fractions after adsorption, which can directly influence heavy metal stabilization with BC amendment (Devi *et al.* 2014). Therefore, it was hypothesized in the current study that BC can efficiently adsorb Cd and Pb from solution. It also was proposed that the adsorption process would be affected by the speciation of Cd/Pb ions.

The objective of this study was to investigate the efficiency of peanut-derived BC to remove Cd and Pb from aqueous solution. The effects of solution pH value, temperature, contact time, particle size, and initial concentration were investigated. Kinetics, isotherms, and thermodynamics of the adsorption process were also evaluated. The Langmuir and Freundlich Models were used to describe equilibrium isotherms. The Cd and Pb fractions were detected with different extracting agents, and the functional groups of BC were identified with Fourier transform infrared (FTIR) spectroscopy. The authors tried to find the mechanism from BC adsorption Cd and Pb process and the fractions change after BC adsorption.

EXPERIMENTAL

Materials

BC preparation and characterization

Pyrolysis of peanut hull at 450 °C was carried out at the Sanli New Energy Company, Henan Province (China), producing a black powder that was used as BC in experiments. Biochar was then ground by machine to pass through a 2-mm sieve. Important BC properties are listed in Table 1 and were determined using standard procedures. Fourier transform infrared (FTIR) spectroscopy (Thermo Nicolet NEXUS 670, USA) was employed to observe the functional groups of BC.

Table 1. Basic Properties of BC

pH (H_2O)	Organic carbon (g kg^{-1})	Surface area (m^2 g^{-1})	Total N (g kg^{-1})	Total P (g kg^{-1})	Total K (g kg^{-1})	CEC (cmol kg^{-1})	Total Cd (mg kg^{-1})	Total Pb (mg kg^{-1})
10.05	588.2	10.64	9.40	13.21	21.52	24.39	0.05	2.31

CEC: Cation Exchange Capacity

Methods

Experimental design

The metal adsorption/desorption experiments were performed using a batch equilibrium technique. Stock solutions (1000 mg L^{-1}) of Cd and Pb were prepared by dissolving analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ in deionized water. For each experiment, 0.1000 g of the adsorbent was mixed with 50 mL of Cd and Pb aqueous solution in a 100-mL polyethylene bottle with 0.01 M $NaNO_3$ ionic strength. To determine BC dosage and most efficient particle size of the BC, preliminary experiments were done at room temperature (25 °C) with BC dosage from 0.1 to 1 g per 50 mL, with particle sizes of 0.15 to 2 mm, at the specified pH with shaking at 180 rpm. At the end of each experiment, the mixtures were immediately filtered without BC loss (Nylon Membrane Filters pore size=0.22 µm, *d*=2 cm. The residual BC was washed with deionized water) and cadmium and lead concentrations in the filtrate were determined. The BC with highest Cd and Pb adsorption were selected from the BC at different temperatures for investigating the adsorption kinetics. The details of the adsorption conditions and initial concentrations of Cd and Pb were totally identical. During the adsorption, 50 mL samples were shaken for 5, 15, 30, 60, 120, and 480 min. The samples afterwards were filtered in order to determine the Cd and Pb concentrations. Two widely used models (pseudo-first-order and pseudo-second-order model) were employed to investigate the adsorption kinetics. The equations of the pseudo-first-order and pseudo-second-order models were expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{1}$$

$$\frac{t}{Q_t} = \frac{1}{k_1 \times Q_e^2} + \frac{t}{Qe} \tag{2}$$

In these equations, Q_e is the amount of the metal adsorbed per unit weight of BC (mg g^{-1}); Q_t is the amount of the metal adsorbed per unit weight of BC at t min (mg g^{-1}); t is the contact time (min); and k_1 and k_2 are the apparent adsorption rate constant of the first-order and second-order model (min^{-1} and mg $(mg\ min)^{-1}$), respectively.

The impact of solution pH on the metal sorption was investigated in the same way, except that the initial pH was adjusted to values ranging from 4.0 to 8.0 by adding 0.1 M NaOH or 0.1 M HNO_3. At the end of 2 h, the bottle contents were filtered, and from the filtrate the residual amount of Cd and Pb in solution was detected. At the same time, the pH values were also recorded after the adsorbents-metal suspensions had reached equilibrium.

Adsorption isotherms were obtained using 0.1000 g BC in 50 mL solution at a constant pH of 6.0 and 0.01 M $NaNO_3$ ionic strength. During these experiments, the initial concentrations varied from 5 to 40 mg L^{-1} for Cd and 25 to 200 for Pb mg L^{-1} at a temperature of 298 K, 308 K, and 318 K. At predetermined time intervals the samples were taken out, and the residual Cd and Pb concentrations were detected with Flame Atomic Absorption (AAS; TAS-986, Persee, China). Three reagent blank samples were also designed in each batch of adsorption experiments. Two typical isotherm models of Langmuir and Freundlich were used to simulate the experimental data. The equations of the Langmuir (3) and Freundlich (4) adsorption models were expressed as,

$$Q_e = \frac{C_e \times K \times X_{max}}{1 + C_e \times K} \tag{3}$$

$$Q_e = K_F \times C_e^{\frac{1}{n}} \tag{4}$$

where Q_e is the amount of the metal adsorbed per unit weight of BC (mg g^{-1}), C_e is the equilibrium concentration of solution (mg L^{-1}), X_{max} is the maximum adsorption capacity (mg g^{-1}), and K is the constant related to interaction energies (L mg^{-1}). K_F is an affinity coefficient ($mg^{(1-n)}$ L^n g^{-1}), and n is an empirical constant (Liu *et al*. 2010).

The speciation of Cd and Pb were performed using the modified four-stage procedure recommended by European Community Bureau of Reference (BCR) (Janoš *et al.* 2007). The procedure is briefly summarized below:

Step 1. (Exchangeable fraction): 50 mL of $NaNO_3$ (0.01 mol L^{-1}) was added to filtered BC for 16 h (overnight) at room temperature in a mechanical shaker. The extract was separated from the solid residue by centrifugation for 20 min.

Step 2. (Carbonate fraction): 50 mL of a freshly prepared 0.01 mol L^{-1} CH_3COONa was added to the residue from Step 1 and the pH was adjusted to 2 using HNO_3. The vessel was shaken for 16 h at room temperature in a similar way as described for the first step.

Step 3. (Organic fraction): 50 mL of 30% hydrogen peroxide (8.8 mol L^{-1}) and HNO_3 (0.02 mol L^{-1}) mixture was added carefully in small aliquots to the residue from Step 2. The vessel was loosely covered with a watch glass and digested at room temperature for 1 h with occasional manual shaking at 85°C water bath for 1 h. The sample was then shaken, centrifuged, and the extract was separated as described in Step 1.

Step 4. (Residual fraction): The solid residue was digested using an electric heating plate digester with a mixture of HNO_3 and $HClO_4$ (4:1) for 2 h.

The concentrations of Cd or Pb in the adsorption/desorption experiments were determined using a flame atomic absorption spectrophotometer (FAAS; TAS-986, Persee; China). All experiments were conducted in triplicate. Control experiments without BC were carried out in order to determine the degree of removal of Cd or Pb from solution by the plastic flask.

Statistical analysis

All data were expressed as means plus or minus one standard deviation. Differences between the treatments were examined using a two-way analysis of variance (ANOVA, confidence level p<5%). All statistical analyses were carried out using SPSS, version 20.0 (SPSS Institute, USA).

RESULTS AND DISCUSSION

Characterization of BC

Fourier transform infrared spectroscopy was used to identify functional groups (like carboxyl and hydroxyl) that are potentially capable of adsorbing metal ions. This analysis revealed the presence of several functional groups that might potentially affect the binding of metal ions onto the biomatrix (Fig. 1a, b). Biochars before absorption and after absorption exhibited similar spectra. Wave numbers of 3447 cm^{-1}, 1629 cm^{-1}, and 1565 cm^{-1} indicate the presence of –OH, C=C groups, and C=O stretching of aromatic rings on the biomatrix surface, respectively. The band numbers 1416 cm^{-1}, 1117 cm^{-1}, 876 cm^{-1}, and 469 cm^{-1} can be attributed to CO_3^{-2}, PO_4^{-3}, aromatic C-H, and Si-O-Fe groups, respectively.

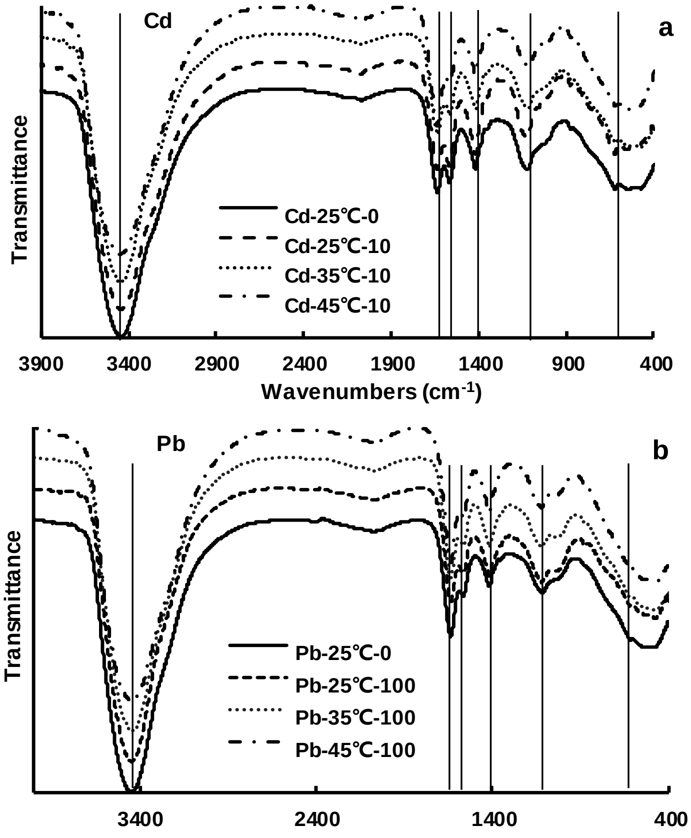

Fig. 1. FTIR spectra of peanut hull BC (a) before and (b) after Cd/Pb adsorption

Effect of Solution pH

The pH affected the adsorption of Cd and Pb onto the BC in the solution system (Fig. 2a, b). Figure 2a shows that the adsorption capacity of BC for Cd rose strongly with increasing pH in the range 4 to 5, and then more gradually with further increases in pH. In the case of Pb, adsorption also rose with increasing pH, but the rise was more gradual. The small letters appearing with the plotted symbols indicate homogeneity groups. At pH < 6, most of the Cd and Pb were present in their free ionic forms (Cd^{2+} and Pb^{2+}). Therefore, all the other experiments in this study were carried out at the optimum initial pH of 6.0 to achieve maximum heavy metal adsorption capacity.

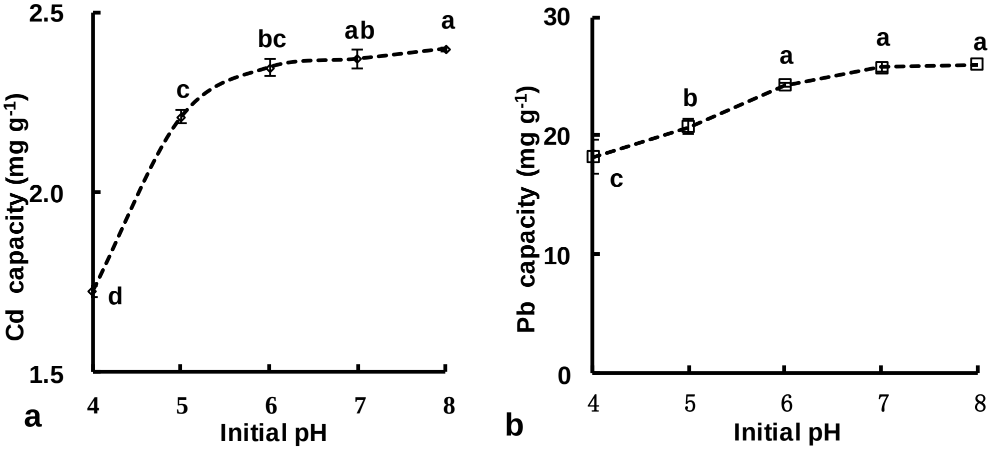

Fig. 2. Effect of pH on (a) Cd and (b) Pb adsorption capacities by BC in solution (The different low case letters indicate a significant difference between the treatments in a single year, $p < 0.05$, n =3, mean ± S.D., the same as follows)

The solution pH was increased when the BC added in the solution and the increased rate were low when the pH was high than 5.5 after BC adsorption equilibrium (data not shown).

Effect of BC Particle Size and Dosage

The particle size and dosage of BC affected the adsorption of Cd and Pb in solution (Figs. 3a, b and 4 a, b). The adsorption capacities greatly increased with a BC particle size of ≤ 2 mm compared with a particle size of > 2 mm, from 27.2% to 143.4% for Cd (Fig. 3a) and 18.5% to 34.2% for Pb (Fig. 3b), respectively. The heavy metal removal efficiency of BC increased (> 90%) with increasing dosage of BC (0.1 g BC 50 mL^{-1}) (Fig. 4 a, b).

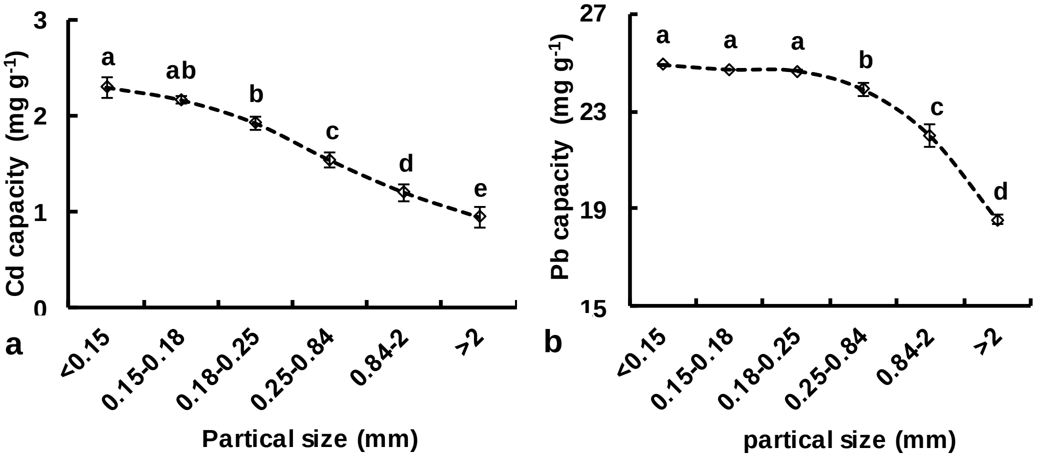

Fig. 3. BC particle size effect on adsorption capacity of (a) Cd and (b) Pb

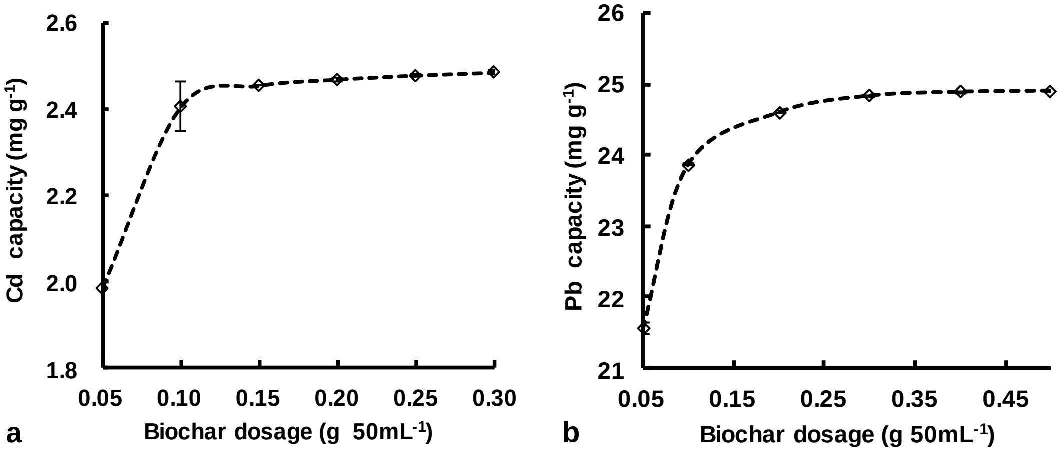

Fig. 4. Adsorption capacity of (a) Cd and (b) Pb as affected by BC dosage

Adsorption Kinetics

The contact time was invested in Table 2(a, b). The Cd and Pb adsorption increased with increasing time nearly linearly for the first 60 min and then it reached a plateau in each case. Furthermore, in 60 to 480 min, the adsorption rate became slower until equilibration (Figs. 5a and 5b).

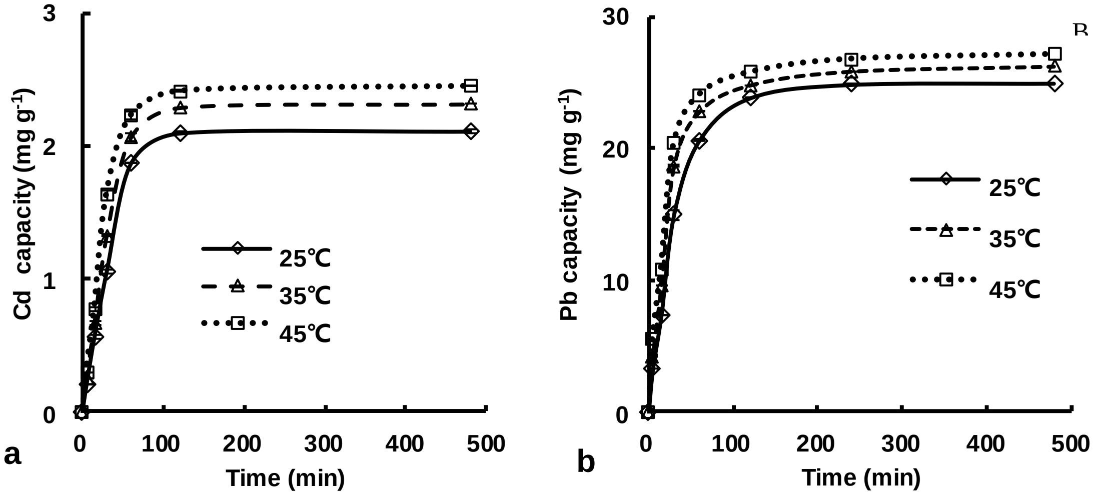

Fig. 5. Effect of contact time on (a) Cd and (b) Pb adsorption capacities by BC

When the typical first-order and second-order adsorption kinetic models were fitted by the adsorption data, the pseudo-first-order model described the Cd adsorption behaviors with coefficients of determination (R^2) falling in the range 0.984 to 0.987 compared with R^2 values of 0.880 to 0.886 for the second-order model (Table 2). In the Pb adsorption behaviors, the pseudo-second-order model closely described the data, with coefficients of determination (R^2) ranging from 0.933 to 0.938 compared with R^2 values of 0.819 to 0.988 for the first-order model (Table 2).

Table 2. Parameters of Cd and Pb Adsorption Kinetics

Treatments	Temperature	Pseudo-first-order model		Pseudo-second-order model	
		k_1	R^2	k_2	R^2
Cd-BC	25 °C	0.031	0.986	0.019	0.880
	35 °C	0.035	0.987	0.020	0.886
	45 °C	0.033	0.984	0.022	0.888
Pb-BC	25 °C	0.024	0.988	0.002	0.933
	35 °C	0.020	0.854	0.002	0.938
	45 °C	0.021	0.819	0.003	0.938

Adsorption Isotherms

To estimate the adsorption capacity and to evaluate the adsorption intensity of Cd and Pb onto BC at different temperature, Langmuir and Freundlich models were used to fit the experimental data for the investigated heavy metal ions on BC (Table 3). The *K* value (energy of adsorption) increased with an increase in temperature from 25 °C to 45 °C by 74.1% and 207.4% for Cd and by 15.4% and 38.5% for Pb. The maximum BC adsorption capacity also increased by 1.7% and 6.0% for Cd and by 11.6% and 26.1% for Pb compared 35 °C, 45 °C to 25 °C. The experimental data for Cd and Pb systems were correlated by Langmuir and Freundlich models, but the Langmuir model (R^2=0.97 to 0.99) was better fitting than the Freundlich model (R^2=0.96 to 0.98) in the Cd adsorption experiment, and the Freundlich model (R^2=0.97 to 0.98) was better fitting than the Langmuir model (R^2=0.94 to 0.95) in the Pb adsorption experiment.

Table 3. Constants and Correlation Coefficients of Langmuir and Freundlich Models for Cd and Pb Adsorption by BC

Treatments	Temperature	Langmuir model			Freundlich model		
		K	X_{max}	R^2	K_F	n	R^2
Cd-BC	25 °C	0.27	6.36	0.99	1.79	2.63	0.96
	35 °C	0.47	6.47	0.99	2.34	3.18	0.96
	45 °C	0.83	6.74	0.97	3.37	4.14	0.98
Pb-BC	25 °C	0.13	50.05	0.95	13.68	3.61	0.98
	35 °C	0.15	55.86	0.94	15.08	3.54	0.97
	45 °C	0.18	63.09	0.95	16.81	3.41	0.97

The Cd and Pb adsorption isotherms were studied at different initial concentrations ranging from 0 to 40 mg L^{-1} for Cd and 0 to 200 mg L^{-1} for Pb (Fig. 6a, b). The adsorption constants and correlation coefficients for Cd and Pb onto BC obtained from the Langmuir model are given in Table 3. The *K* value is related to the affinity of BC towards the metal ions and BC has a higher affinity for Cd than for Pb.

The data clearly show that adsorption of both Cd and Pb on BC was greatly affected by temperature. Higher temperatures resulted in higher adsorption capacities of heavy metals.

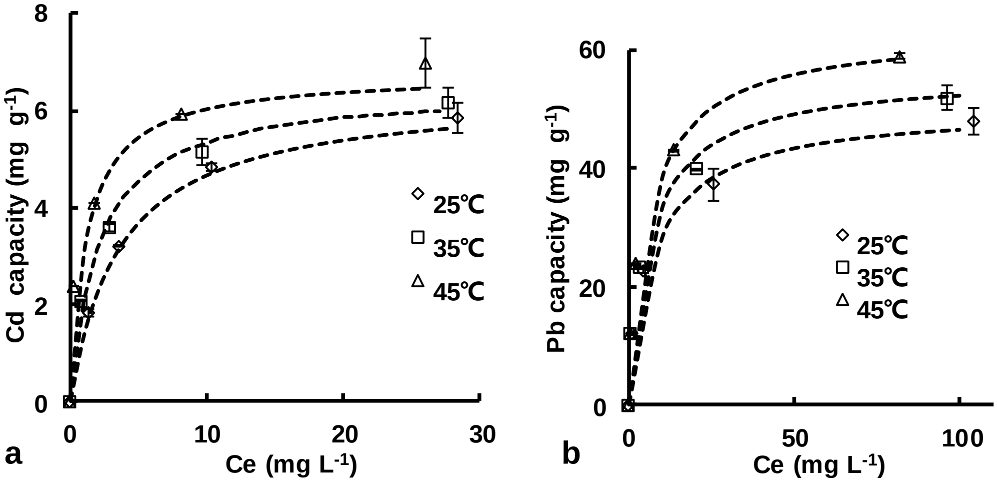

Fig. 6. Sorption isotherms of (a) Cd and (b) Pb by BC at different temperatures

Fractions of Cd and Pb in Desorption

To differentiate varieties of BC groups, Cd and Pb in soils were divided into exchangeable, carbonate, organic, and residual fractions with different extracting agents. More than 90% of Cd and Pb adsorption was primarily associated with carbonate and organic binding. The BC that adsorbed Cd from the solution had primarily acclimated into the carbonate fraction rather than the organic forms when the temperature increased, and a similar tendency was observed with Pb adsorption. Less than 15% Cd and 6% Pb were exchangeable and residual forms bounded with calcium and magnesium or bonded with the soil matrices.

The different treatments resulted in a distinctively different Cd distribution fractions. Relative to temperature change, Cd fractions shifted from organic and carbonate fractions to the residual fraction (Figs. 7a, b, and c). The Pb fractions weakly shifted from the carbonate fraction to the organic fraction (Figs. 7d, e, and f).

Discussion

Biochar was found to be effective in removing Cd and Pb from solution. The Cd and Pb adsorption was affected by solution pH, temperature, contact time, BC particle size, and heavy metal binding sites. Liu *et al.* (2009) also reported that BC samples (produced from pinewood or rice husk at 300°C) were quite effective for lead removal in solution with capacities of 4.25 and 2.40 mg g^{-1}, which contained a large amount of oxygen-containing groups on the surface. This could be explained by the fact that the characteristics of BC were important factors, as well as electrostatic interactions, precipitation, and other reactions (Acemoğlu and Alma 2004; Özcan *et al.* 2006; Tang *et al.* 2013a).

When the solution pH was increased, the BC adsorption capacity increased. So the solution pH was a key factor in the adsorption efficiency of BC. Therefore, even if attractive and coordinating interactions are not strong, they will be more effective at adsorbing cations than if they were only on the surfaces of BC. The greatest adsorption of Pb^{2+} and Cd^{2+} occurred at the highest pH values (Mohan *et al.* 2014). Increased pH enhanced the adsorption capacity, which may be attributed to the formation of insoluble hydroxyl complexes, especially for the Pb ion (Kula *et al.* 2008).

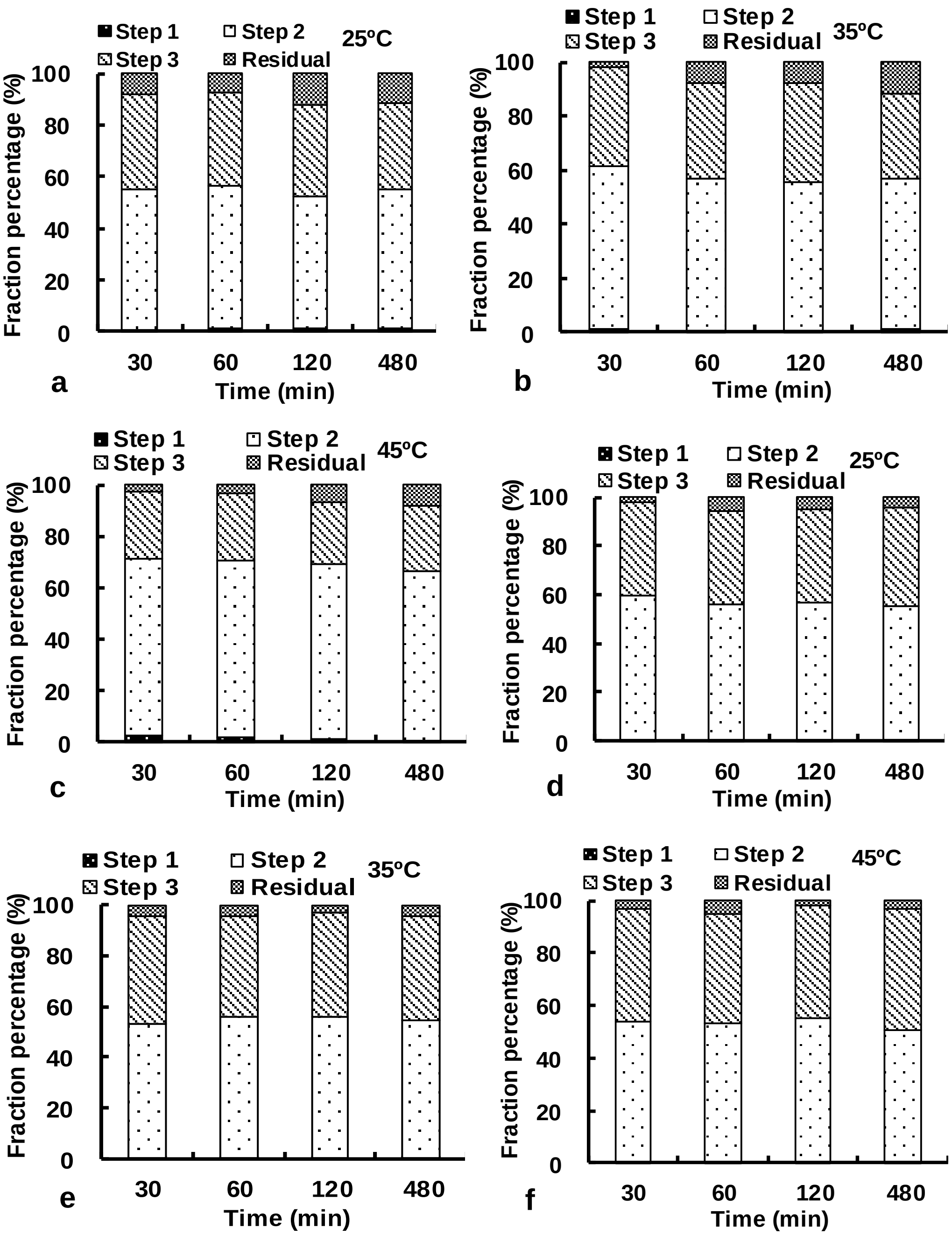

Fig. 7. Distribution of different fractions of Cd and Pb desorption reagent. (a) Cd, 25 °C; (b) Cd, 35 °C; (c) Cd, 45 °C; (d) Pb, 25 °C; (e) Pb, 35 °C; (f) Pb, 45 °C

The heavy metals chemical speciation was changed with higher pH. Qiu *et al.* (2008) also found that Pb^{2+} comprised greater than 89% of total Pb at pH ≤ 6.01, indicating its predominance in acidic solution. At pH 7.05, the percentage of Pb^{2+} decreased to 76%, while $PbOH^{+}$ rose to 16%. When pH was raised to 8.85, a significant reduction of 35.6% in positive charge was observed. Based on these considerations, a solution pH at 6, but not 7 or even higher, was chosen for the present work. Some of the adsorption of heavy metals by BC occurs through the electrostatic interactions between positive metal species and negative functional groups. For example, the metal ions K^{+}, Na^{+}, Ca^{2+}, and Mg^{2+} can exchange with anionic groups of BC. Such interactions can involve the electrostatic outer-sphere complexation and co-precipitation and inner-sphere complexation with complexed humic matter and mineral oxides of BC (Lu *et al.* 2012). Therefore, all of the other experiments in this study were carried out at an optimum initial pH of 6.0, so as to achieve the greatest concentration of metals in the form of ions.

The results showed that the adsorption rate increased as the dosage of BC was increased. The adsorption rate also increased with decreasing particle size. The adsorption rate increased substantially when the dosage was increased from 0.05 to 0.10 g 50mL^{-1}, but introducing an incremental amount over 0.10 g 50 mL^{-1} of adsorbent gave a less significant increase. Therefore, adsorbent dose was held at 0.10 g 50 mL^{-1} in all the subsequent experiments. The adsorption rate changed with the amount of BC in most cases, confirming that adsorption rate is dependent on the amount of adsorbent (Mohan *et al.* 2007). The BC adsorption Cd and Pb capacity increased with decreasing particle size, which can linked to the relationship between the surface area of the BC and rate of diffusion of the Cd and Pb. Surface area increases with smaller BC particle sizes, resulting in shortened diffusion paths and presenting a better opportunity for Cd and Pb ions to penetrate all internal pore structures (Lu *et al*. 2012). This explains high absorption at low particle size.

The effect of contact time was investigated in Table 2. The Cd adsorption data well fitted the pseudo-first order kinetic model, but the Pb adsorption data was well fitted the second order kinetic model. So it was apparent that different models fitted different heavy metals by using BC. The difference in behavior of the two metals, in this respect, is reflective of the fact that the sum of the adsorption in each case depends on several aspects the adsorption processes, such as external film diffusion, surface adsorption, and intra-particle diffusion (Kizito *et al.* 2015). A relatively rapid initial rapid uptake may be attributed to a physical process occurring mainly through mass transfer based on ion concentration gradient between the solid and liquid phases (Kizito *et al.* 2015). The second slower phase may be indicative of the end of physical sorption and probably corresponds to the ionic balance between the solid and liquid phase with slight desorption occurring for the physically bound Cd and Pb ions (Kucic *et al.* 2013).

With the increase in temperature, the BC adsorption capacity of the metals increased, suggesting that the adsorption was an endothermic process. This was attributed to the sufficient energy provided by the higher temperature for metals ions to reach and adsorb onto the interior structure of the absorbents (Cui *et al.* 2013a). The adsorption data had been fitted by Langmuir and Freundlich models. The Langmuir model fitted the data well, suggesting that the adsorption involved energetically equivalent independent sites without significant multilayer interactions. The fact that the Freundlich model was also fitted well (R^2>0.96, 1/n<1) allows for, but does not require, a heterogeneous nature of biochar surfaces (Kizito *et al*. 2015).

The removal of metals by BC was evidenced by FTIR analysis, based on evaluation of absorbances for the functional groups formed during the pyrolysis process. After the Cd and Pb were adsorbed by BC, the wave numbers of the peaks became larger, *i.e.*, the band at 3443 cm^{-1} and 3446 cm^{-1} were shifted to 3447 cm^{-1} (Cd) and 3448 cm^{-1} (Pb) after Cd/Pb adsorption. The same effects were found by Lu *et al.* (2012). This effect maybe can be attributed to an important role of BC's organic functional groups in the binding or complexing of heavy metal ions or the equivalent replacement of the cations (such as Ca^{2+}, Mg^{2+}). Also, the BC structure may also be changed with the physico-chemical reaction with Cd/Pb on the surface or inner part such as the metals speciation translating from organic and carbonate fractions to the residual fraction (Chen *et al.* 2013). Mohan *et al.*

(2012) also reported that the functional groups were formed by pyrolysis during BC production, which attributed to the changed the BC surface and inner structure and allowed more than just surface oxygenated groups or co-precipitation or surface precipitation to contact and interact with Pb^{2+} and Cd^{2+} ions were responsible for the enhanced hydrophobicity and affinity for Cd and Pb ions. The high removal ability of BC varies with the content of various mineral components, organic groups, and inorganic groups, such as CO_2^{-3} and PO_3^{-4}, originating from the raw material pyrolysis process. These components played an important role in the sorption nature of BC (Xu *et al.* 2013).

The acid extractable Cd and Pb significantly decreased with the increase of BC dosage. Heavy metal ions were normally located on the outer surface of the BC independently for the function groups. When those retention sites were effectively saturated, further ions adsorbed to the network of pores and fissures that form BC's complex inner micro-structure, resulting in higher removal capacity (Han *et al.* 2013; Beesley and Marmiroli 2011). The degree of carbonization (namely the partitioning mechanism: on noncarbonized organic fraction and by the surface adsorption on carbonized fraction) was also related the adsorption capacity of Cd and Pb on BC, which depended on changes in the material during the pyrolysis process (Veksha *et al.* 2014; Trakal *et al.* 2014). The sorption process of Cd and Pb on BC arose from site-specific interactions occurring mostly on the different BC function groups (Farrell *et al.* 2013).

The Cd and Pb speciations in the BC were separated in four fractions, namely as an exchangeable fraction, a carbonate fraction, an organic fraction, and a residual fraction. The exchangeable fractions Cd and Pb maybe had chemical reaction with positive ions (Ca^{2+}, Mg^{2+}, and so on). During the adsorption process, the Pb or Cd also competed with each other for BC binding sites such as organic groups, and inorganic groups, which were initially occupied with Ca^{2+} or Mg^{2+}. For these reasons, the exchangeable fraction of Cd/Pb could be easily activated and also be released by eluents such as $NaNO_3$ solution (Chen *et al*. 2011). The carbonate fraction exhibited stronger binding of Cd and Pb with BC compared with the exchangeable fraction and were more difficult to be released. While the removal of metals by BC resulted not only from the complex formation with ionized hydroxyl-O-groups but also from the precipitation of metals with CO_2^{-3} and/or PO_3^{-4} that were rich in BC (Xue *et al.* 2012). The present results confirmed that greater than 90% of the adsorption of Cd and Pb was due to carbonate and organic bonding on BC, while less than 5% Cd and 1% Pb remained in exchangeable and residual forms. Adsorption on the organic fraction of the Cd and Pb can be attributed to complexation with humic matter of BC such as free carboxyl functional groups, free hydroxyl functional groups and others. Carbonate and organic bound Cd and Pb may have high bioavailability in acidic solution, which represents a potential heavy metal pool (Liang *et al.* 2013). In the residual fraction, the metals have the strongest association with the crystalline structures of the BCs and are therefore are the most difficult to separate (Lu *et al.* 2012). In the present work the adsorption process was completed in a short time, so only a small part of Cd and Pb was present in the residual fraction (Anju and Banerjee 2010).

With the solution temperature change, the Cd fraction shifted from an easily solubilizing fraction to a stabilized fraction. This indicated that the mobility of Cd was higher than that of Pb. Therefore, Cd might have more of a leaching risk. It can further be elaborated that the adsorption process was complex and involved more than one mechanism.

CONCLUSIONS

1. This study focused on the removal of Cd and Pb ions by BC from aqueous solution. The results indicate that BC has a huge potential to adsorb heavy metals.
2. Biochar's adsorption capacity for Cd and Pb was affected by BC dosage, contact time, particle size, Cd and Pb concentration, solution temperature, and BC functional groups. The results indicated that plant-residue or agricultural waste derived BC can act as an effective surface sorbent, but that care needs to be taken when using these sorbents for the treatment of mixed waste streams.
3. Carbonate and organic fractions of BC were mostly (> 90%) responsible for the adsorption of Cd and Pb from solution.
4. It can be concluded that BC is suitable for the removal of Cd and Pb ions from wastewater because of its high adsorption capacity, natural and abundant availability, and low cost.

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