Comparison of cadmium and lead sorption by *Phyllostachys pubescens* biochar produced under a low-oxygen pyrolysis atmosphere

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HIGHLIGHTS

- Low oxygen atmosphere could improve sorption capacity of metals.
- The biochar had more favorable adsorption for Pb^{2+} than Cd^{2+} .
- Precipitation with ash mechanisms dominated Pb^{2+} sorption on the biochars.
- Coordination with π electron mechanisms dominated Cd^{2+} sorption.

GRAPHICAL ABSTRACT

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ABSTRACT

Phyllostachys pubescens (PP) biochars produced under a low oxygen pyrolysis atmosphere (oxygen content 1–4%) were prepared as sorbents for investigating the mechanisms of cadmium and lead sorption. A low-oxygen pyrolysis atmosphere increased biochar ash and specific surface area, promoting heavy metal precipitation and complexation. The maximum sorption capacity (Q_m) of Pb^{2+} obtained from the Langmuir model was $67.4 \text{ mg} \cdot \text{g}^{-1}$, while Q_m of Cd^{2+} was $14.7 \text{ mg} \cdot \text{g}^{-1}$. The contribution of each mechanism varied with increasing oxygen content at a low pyrolysis temperature. Mineral precipitation with Pb^{2+} was the predominant mechanism for Pb^{2+} removal and the contribution proportion significantly increased from 17.2% to 71.7% as pyrolysis oxygen atmosphere increased from 0% to 4%. The results showed that cadmium sorption primarily involved coordination with π electrons, at 54.1–82.6% of the total adsorption capacity. The PP biochar shows potential for application in removing heavy metal contaminants, especially Pb^{2+} .

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1. Introduction

Biochar has been successfully applied for soil remediation, carbon sequestration, climate change mitigation, and carbon farming

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(Ahmad et al., 2014; Bell and Worrall, 2011; Mohan et al., 2014). In recent years, biochar has been widely applied to water and wastewater for the removal of organic and inorganic contaminants, especially for the effective removal of heavy metals, including lead (Pb^{2+}) and cadmium (Cd^{2+}) (Ding et al., 2016; Dong et al., 2014; Wang et al., 2015). Depending on the biochar type, heavy metals can be removed by different mechanisms: precipitation with minerals (e.g., phosphate and carbonate); surface complexation with oxygen-containing functional groups (e.g., phenolic, carboxyl, and

hydroxyl groups); and coordination of heavy metals with π electrons (e.g., Pb^{2+} - π and Cd^{2+} - π) (Cui et al., 2016; Lu et al., 2012; Wang et al., 2015). Experiments have confirmed that the proposed mechanisms could be attributed to properties of the biochar, such as ash content, zeta potential, surface area, and other surface characteristics (Fang et al., 2014; Liu et al., 2015; Mohan et al., 2014). Different biochar properties also influence the adsorption capacities for different heavy metals (Ding et al., 2016; Inyang et al., 2012; Xue et al., 2012). Examination of exact mechanisms for Pb^{2+} and Cd^{2+} sorption on biochars produced under different conditions is crucial. However, there are relatively few studies devoted to simultaneously providing qualitative and quantitative information regarding the relative contribution of the involved mechanisms and comparing sorption mechanisms for different heavy metals on biochars produced under different pyrolysis conditions.

Properties of biochars are not only strongly dependent on biomass feedstocks but also on production conditions (Enders et al., 2012; Luo et al., 2015). Many studies have attempted to explore the relationships between biochar properties and pyrolysis conditions, which include temperature (Dong et al., 2013; Zhang et al., 2013; Zhu et al., 2014), temperature plus heating rate (Angin, 2013), and pyrolysis duration (Cimò et al., 2014; Zhang et al., 2015). However, the effect of different pyrolysis atmospheres for biochar production has been mostly neglected. Compared with a no-oxygen pyrolysis atmosphere, the biochar yield, volatile matter and functional groups are significantly influenced by the presence of oxygen in the pyrolysis atmosphere (Luo et al., 2015). The number of oxygenated groups, carboxyl, phenolic, and ether groups, were rich at low pyrolysis temperature under anoxic conditions (Zhu et al., 2014). Therefore, the changes of oxygenated functional groups should be determined in a low oxygen pyrolysis atmosphere. Biochars formed under gasification usually have an oxygen-containing atmosphere and can exhibit a high mineral content, which could promote the heavy metals adsorption capacity (Inyang and Dickenson, 2015). In addition, Liu et al. (2015) indicated heat treatment at low temperatures under a weak oxidizing atmosphere may create more oxygenated functional groups. However, very little research has focused on establishing the relationship between Pb^{2+} or Cd^{2+} sorption and biochar properties based on different pyrolysis atmospheres (Luo et al., 2015). Therefore, further effort is required to examine the exact mechanisms of heavy metal sorption on biochars produced under different pyrolysis conditions.

In this research, biochars were obtained under a 0–4% oxygen content atmosphere through slow pyrolysis of *Phyllostachys pubescens* (PP) at 450 °C and 700 °C, and the physicochemical properties of samples were characterized. The objectives were to: (1) determine the sorption capacity of Pb^{2+} and Cd^{2+} on biochars produced under different pyrolysis atmospheres; (2) investigate the surface properties of biochar produced under pyrolysis atmospheres with different oxygen contents; and (3) compare the different mechanisms of Pb^{2+} and Cd^{2+} removal from water by the biochars on a qualitative and quantitative basis. This study could help to support the use of macroporous, low cost PP biochar for Pb^{2+} and Cd^{2+} removal from mainstream wastewater treatment.

2. Methods

2.1. Preparation of biochar samples

The biomass materials of pubescens (*Phyllostachys*, Indosasa McClure) were used as feedstocks for biochar production. *Phyllostachys pubescens* are mainly distributed in the south of the Yangtze River of China, and 85% of the PP in the world are located in this region. The PP were collected in Binzhou, Hunan Province,

China, and subsequently washed with ultrapure water three times to remove attached dust, and then dried at 80 °C for more than 24 h.

The biochar samples used in this study were produced by slowly pyrolyzing the dried PP in a lab-scale quartz tube furnace (OTF-1200X-80, Hefei Kejing, China) with a trace gases mixed gas supply system (CGM-2F, Hefei Kejing, China) under the varying conditions shown in Table 1. The samples were placed in a tubular furnace and air was evacuated. A gas mixture, with a set oxygen and nitrogen flow ratio (Table 1), was passed through the tubular furnace. The process of evacuating the furnace and passing through the mixed gas was repeated, and the process took about 60 min in total. The gas mixture was continuously supplied during the pyrolysis process, with gas flow maintained at 0.4 L min⁻¹. The reactor was heated with a heating rate of 20 °C min⁻¹. These biochars were cooled to room temperature under the predetermined atmospheric conditions. The resultant PP biochars were ground through 120–180- μm (80–120 mesh) sieves. Finally, the PP biochars were stored in scintillation vials with polypropylene caps and polyethylene liners in the dark until required for the sorption experiment.

2.2. Batch sorption experiment

The $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ solution was prepared using $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Guaranteed reagent, Sigma-Aldrich, USA). All the tested $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ solutions contained 5 mM NaNO_3 as the background electrolyte to maintain ionic strength, and the pH was pre-adjusted to 5.0 ± 0.05 by adding either 0.1 M HNO_3 or NaOH solutions before testing. Next, 2 g L⁻¹ of PP biochars were added to 50-mL vials at an initial concentration of 100 mg L⁻¹ for both $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$. The vials were shaken at 140 rpm and obtain the sample from 0 to 50 h to determine $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ in the liquid phase to analyze the adsorption kinetics. Adsorption isotherms were produced with the initial $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ concentration in the range of 100–800 mg L⁻¹. All vials were shaken at 140 rpm at 25 °C for 24 h. After shaking, all mixtures were filtered through a 0.22- μm Millipore filter. The influence of coexisting ions on adsorption was studied at appropriate pH with the addition of different concentrations of Ca^{2+} (0–30 mg L⁻¹) and Fe^{3+} (0–30 mg L⁻¹), K^+ (0–30 mg L⁻¹), NH_4^+ (0–50 mg L⁻¹), humic acid (HA; 0–100 mg L⁻¹), Cd^{2+} (0–1.5 mmol L⁻¹), or Pb^{2+} (0–1.5 mmol L⁻¹). The impact of pH on biochar adsorption was examined by adjusting the pH of the initial Cd^{2+} or Pb^{2+} solutions (100 mg L⁻¹) to ensure equilibrium solution ranging from 2.0 to 7.0, because precipitates are formed under high solution pH. The $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ concentrations in the filtrate were analyzed with a flame atomic absorption spectrophotometer (Z-5000, Hitachi, Japan) at 229.0 and 283.3 nm, respectively. The experiments were performed in triplicate, with appropriate blanks without biochar samples or without heavy metals. As the mass loss was negligible, sorption of solutes by biochars was determined by mass balance.

2.3. Sorption mechanisms

2.3.1. Biochar characterization

The specific surface area was determined by using Brunauer–Emmett–Teller isotherm method and the pore volume was estimated using the Barrett–Joyner–Halenda method at 77 K (Quantachrome Nova 3200e, USA) with a N_2 adsorption–desorption. The surface structure and elemental content distribution of the biochars were analyzed using scanning electron microscopy (SEM; S-4800, Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDX; 7593-H, Horiba, Japan). The pH of samples was measured in a suspension of 1:10 sample/deionized water using a combination electrode. The suspension was shaken for 1 h before measurement. The existence and crystalline form of chemical pre-

Table 1

Biochar preparation conditions (A is the pyrolysis temperature, B is the pyrolysis time, C is the oxygen content in the pyrolysis atmosphere, expressed as the oxygen to nitrogen gas content ratio, D is the raw material particle size).

Sample	A (°C)	B (h)	C (%)	D (μm)
P1	450	3	0	106–150
P2	450	3	1	106–150
P3	450	3	2	106–150
P4	450	3	4	106–150
P5	700	3	0	106–150
P6	700	3	1	106–150
P7	700	3	4	106–150

cipitates after Pb^{2+} and Cd^{2+} sorption were checked using a D/Max-IIIa powder X-ray diffractometer (Rigaku Corp., Japan). The patterns were collected in the angular range from 5° to 60° with 0.02° step size. The solid phases were identified using the Jade 5.0 software (Materials Data Inc., Livermore, CA, USA). The surface charge properties of biochars were evaluated by zeta potential measurements, which were conducted at different equilibrium pH using an electroacoustic spectrometer (ZEN3600 Zetasizer, UK). The isoelectric point (pH_{IEP}) of the biochars, defined as the pH value at which the electrokinetic potential equals zero, was determined by plotting zeta potentials against pH (Fang et al., 2014). The elemental (C, H, N) analyses were performed with an Elemental Analyzer (Elementar Vario EL III instrument, Germany).

Qualitative analysis of oxygen functional groups used Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The FTIR data were recorded in the $4000\text{--}400\text{ cm}^{-1}$ region with a Thermo Nicolet FTIR spectrophotometer (model 6700) using KBr pellets. The XPS experiments were carried out on a Thermo Scientific Escalab 250Xi instrument equipped with Al K α radiation ($h\nu = 1486.6\text{ eV}$). Binding energies for the high-resolution spectra were calibrated by setting C 1s at 284.8 eV . The XPS core level spectra were analyzed using XPS Peak 4.1. Quantitative analysis of oxygenated acidic groups and basic components for samples were determined using Boehm titration method (Goertzen et al., 2010; Oickle et al., 2010). A more detailed account of Boehm titration is available in the Supporting Information.

2.3.2. Quantitative analysis of different mechanisms to Pb^{2+} or Cd^{2+} sorption

The calculation of the contribution of different mechanisms to Pb^{2+} and Cd^{2+} sorption on biochars has been reported (Cui et al., 2016; Wang et al., 2015). The calculation method of the sorption attributed to precipitation with minerals (Qp), oxygen functional groups complications (Qf) and coordination of heavy metals with π electrons ($Cd^{2+}\text{--}\pi$ or $Pb^{2+}\text{--}\pi$) interaction ($Q\pi$) was as follows: (a) most ash from the PP biochars were removed by the acid dipping procedure in the supporting information, and the oxygen-containing functional groups were not changed. The reduced amount of heavy metals sorption on the biochars before and after demineralization could be considered as the contribution of the removed minerals, which was calculated as shown in Eq. (1); (b) when the biochars were washed with acid, a decrease in pH before and after Pb^{2+} or Cd^{2+} sorption on acid-washed PP biochars occurred as a result of the complication with the oxygen-containing organic groups. The pH change as an indicator for the calculation of oxygen containing group effect has been reported in a previous paper and the operation method was based on (Wang et al., 2015). Moreover, the carboxyl and hydroxyl groups of biochar release H^+ ions by exchange interactions, which could result in pH changes in the solution (Cao et al., 2009; Mohan et al., 2007). The pH decrease was used as an indicator of the

amount of H^+ release, thereby calculating the adsorbed Pb^{2+} by the oxygen-containing functional groups complexation (Qf). (c) The amount of sorbed Pb^{2+} or Cd^{2+} on biochar after the acid dipping procedure (Qa) was taken as the result of the π interaction and functional groups complexation together. Therefore, the amount of $Q\pi$ could be calculated as shown in Eq. (2). The contribution percentage of different mechanisms to the overall Pb^{2+} and Cd^{2+} sorption was then calculated using the Qf/Q_t , $Q\pi/Q_t$ and Qp/Q_t ratio.

$$Qp = Qt - Qa, \quad (1)$$

$$Q\pi = Qa - Qf, \quad (2)$$

where Qp is the amount of Pb^{2+} or Cd^{2+} sorption attributed to the precipitation with minerals, Qt is the total sorption of Pb^{2+} or Cd^{2+} on biochar, Qa is the amount of sorbed Pb^{2+} or Cd^{2+} on biochar after the acid dipping procedure, $Q\pi$ is the amount of Pb^{2+} sorption resulting from $Pb^{2+}\text{--}\pi$ interaction, and Qf is the oxygen functional groups complications.

2.4. Statistical analysis of the experimental data

The kinetics of Pb^{2+} or Cd^{2+} sorption on biochars were simulated using pseudo first order kinetic equation (Eq. (3)), pseudo second order kinetic model (Eq. (4)), intraparticle diffusion model (inner model, Eq. (5)) and Elovich model (Eq. (6)), which can be presented as follows (Inyang et al., 2012; Wang et al., 2015):

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

$$Q_t = k_3 t^{0.5} + b \quad (5)$$

$$Q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad (6)$$

where Qt (mg g $^{-1}$) and Qe (mg g $^{-1}$) are the amounts of metals sorbed at time t and at equilibrium, respectively. k_1 is the pseudo first order rate constant (h $^{-1}$), k_2 is the rate constant of the pseudo second order adsorption (g mg $^{-1}$ h $^{-1}$), k_3 is the intraparticle diffusion rate constant (mg g $^{-1}$ h $^{-0.5}$), b is the intercept (mg g $^{-1}$), α (mg g $^{-1}$ h $^{-1}$) is the initial adsorption rate, and β (g mg $^{-1}$) is the desorption constant at time t.

Langmuir (Eq. (7)) and Freundlich (Eq. (8)) models were used to fit the Pb^{2+} or Cd^{2+} adsorption isotherm data (Kołodziejńska et al., 2012):

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

$$Q_e = K_F C_e^n \quad (8)$$

where C_e is the equilibrium aqueous concentration of metals (mg L $^{-1}$). The parameters K_L and K_F are the adsorption coefficients of Langmuir and Freundlich (L mg $^{-1}$ and (mg g $^{-1}$)(mg L $^{-1}$) $^{-n}$), respectively. Q_m is the maximum adsorption capacity of the solute (mg g $^{-1}$). The n is the Freundlich constant related to the surface site heterogeneity.

In this study, the experiments of kinetics and adsorption isotherms were conducted in triplicate. Significant differences were tested using Duncan's multiple range test ($P = 0.05$) by SPSS 17.0. The kinetics and adsorption isotherms were fitted using Origin Pro 8.0 (Origin Lab, USA).

3. Results and discussion

3.1. Adsorption kinetics and adsorption isotherms

As shown in Fig. 1, the adsorption for Cd^{2+} or Pb^{2+} was rapid adsorption in the first 8 h, and the adsorption capacity of Pb^{2+} and Cd^{2+} reached 98.9% and 99.8% of adsorption equilibrium capacity at 24 h, respectively. The correlation coefficient (R_2) of the Elovich model was higher than that of other models (Table S1), indicating that the experimental data fitted better to the Elovich model, which is similar to adsorption of Zn(II) to a meat and bone meal biochar (Betts et al., 2013). For biochar P5, the initial adsorption rate (α) of the Elovich model for Pb^{2+} was 9.43 times greater than that for Cd^{2+} . The Elovich equation has been used to infer a number of transport-limited reaction mechanisms, including bulk and surface diffusion (Cheung et al., 2000). The Elovich model describes reactions that are biphasic, with an initial, rapid reaction followed by a slower progress. This has been observed in other sorption reactions and may imply reactions limited by diffusion (Betts et al., 2013). Cheung et al. (2000) described heavy metal sorption on biochar with the Elovich model and inferred from the results that the mechanism of metals sorption was limited by diffusion through pores in the biochar.

The sorption isotherms of Pb(II) and Cd(II) onto PP biochar are presented in Fig. 1 and the fitting parameters of are listed in Table S2. The adsorption amounts of Cd(II) and Pb(II) of the material both increased rapidly in the low concentration range, and then increased gradually as the initial concentrations increased. The correlation coefficient values ($R_{\text{adj}}^2 > 0.94$) demonstrate that the Freundlich model is more suitable than the Langmuir model for describing the adsorption process.

The Freundlich adsorptive capacity (K_f) for Cd(II) and Pb(II) increased substantially with oxygen content increase at low pyrolysis temperature, but the adsorption capacity of the PP biochar showed little change with oxygen content increase at 700 °C. In particular, Q_{max} increased dramatically from the P1 to P4 samples, possibly due to the considerable increase in surface area with the trace oxygen atmosphere, which may have enhanced the number of adsorption sites. For each sample, the adsorption capacity for Pb(II) was larger than that for Cd(II) . The maximum adsorption capacity of Pb(II) reached 67.45 $\text{mg}\cdot\text{L}^{-1}$ with P6, whereas it reached 14.68 $\text{mg}\cdot\text{L}^{-1}$ for Cd(II) with P5 (Table S2). Compared with other adsorbent materials, PP biochar demonstrates the potential to act as an effective adsorbent for Pb^{2+} removal in aqueous solution; however, PP biochar shows a poor adsorption capacity for Cd^{2+} (Table S3).

The regeneration property of the as-synthesized biochar was also studied, and the results of the regeneration tests are shown in Fig. S1. For the biochar regeneration, metal-adsorbed biochar was washed in 200 mL of a 0.1 N HNO_3 solution and gently stirred for 1 h. In the regeneration trials, the adsorption capacity decreased for Cd^{2+} or Pb^{2+} adsorption. The adsorption capacity of Pb^{2+} and Cd^{2+} was 68.5–72.3% and 74.3–81.5% of the origin biochar, respectively. These reductions in adsorption capacity were largely due to the structural deterioration and surface mineral loss of the adsorbents.

3.2. Effect of pH and coexisting ions on the adsorption of Cd(II) and Pb(II)

The zeta potential is representative of the surface charge property of a particle interacting with other particles or ions in the surrounding suspension (Yao et al., 2016). Fig. 2a illustrates the zeta potential curves of biochars at different solution pH values. The obtained pH_{IEP} values were 2.1, 1.7, 1.2, 1.5 and 1.5 for P1, P3,

P4, P6 and P7, respectively. The pH_{IEP} value of the biochar is higher at high pyrolysis temperature, which was similarly shown for a biochar derived from hardwood litter (Teixidó et al., 2011). Some studies have shown pH_{IEP} of biochar is within the range of 1–2.5 (Ding et al., 2016; Fang et al., 2014). The pH-dependent curve of the zeta potential displayed a horizontal S-shape with two significant inflection points (pH_a and pH_b), which is similar to the observation by Fang et al. (2014). Their results demonstrated that a platform appeared at pH 5–9 for biochar produced at low pyrolysis temperatures, whereas the platform occurred at pH 6–10 for biochar produced at high pyrolysis temperatures (Fang et al., 2014). There were two different types of pH-dependent functional groups on biochars, carboxyl and hydroxyl groups, which influenced zeta potential at two distinct pH ranges (Fang et al., 2014; Shokri et al., 2012). The zeta potentials of biochars (Fig. 2a) indicate that the surfaces of these biochars were mostly negatively charged. The carboxyl and hydroxyl groups on the biochar act as a buffer substance, retaining a relatively stable zeta potential in the tested pH range from 3.3 to 6.2.

The pH is a major factor affecting adsorption of Cd(II) and Pb(II) in aqueous solutions (Fig. 2b). When the solution $\text{pH} > \text{pH}_{\text{IEP}}$, biochar conducts electric adsorption with metal cations, including Cd(II) and Pb(II) , due to the deprotonation of the adsorbent hydrated surface. The Cd^{2+} adsorption capacity slightly increased from 12.8 to 21.2 $\text{mg}\cdot\text{L}^{-1}$ when pH increased from 5 to 7, which may result from increase in the electrostatic attraction capacity, as zeta potential varied from –25.5 to –32.2 mV. The surface charge properties have an important influence on the adsorption capability and mechanism of heavy metals adsorption onto biochars. When the initial pH is higher (5–7), the pH after equilibrium can be improved by the pH buffer capacity of biochar, and the heavy metals subsequently precipitate (Chen et al., 2014). When the pH is lower, only limited local precipitation occurs because the large number of H^+ ions compete with these divalent metal ions, weakening the adsorption performance at the lower initial pH (Lu et al., 2012).

As shown in Fig. S2, K^+ had little influence on Cd^{2+} and Pb^{2+} removal until the concentration of K^+ exceeded 8 and 20 $\text{mg}\cdot\text{L}^{-1}$, respectively. A slight influence of NH_4^+ on Cd^{2+} and Pb^{2+} adsorption was observed (Fig. S2). However, the HA, which was calculated as total organic carbon, had a sensitive influence on Pb^{2+} removal, and the removal capacity reduced from 38.5 to 28.4 $\text{mg}\cdot\text{g}^{-1}$ while the content of HA was 2 $\text{mg}\cdot\text{L}^{-1}$. Similar results were obtained with cadmium adsorption. This could be attributed to complexation of HA with Cd^{2+} or Pb^{2+} which could hinder the electrostatic energy between the charges on biochar surface and heavy metal ions in aqueous solution. A high concentration of K^+ and NH_4^+ in aqueous solution could preempt surface adsorption sites of adsorbents, such as oxygen functional groups, which could decrease the adsorption capacity of Cd^{2+} and Pb^{2+} . As shown in Fig. S2, Ca^{2+} and Mn^{2+} have little influence on heavy metals removal. Ca^{2+} and Mn^{2+} could precipitate with minerals, such as carbonate, which may compete with heavy metal removal. The stability constants (pKsp) of CdCO_3 (pKsp : 12.00) and PbCO_3 (pKsp : 13.13) were higher than those of CaCO_3 (pKsp : 8.54) and MnCO_3 (pKsp : 10.04). Therefore, it can be speculated that Cd^{2+} or Pb^{2+} was more likely to precipitate than Ca^{2+} and Mn^{2+} . Moreover, the high ionic strength of the solution could influence the activity coefficient of heavy metals, thus decreasing the collisions and contact between the sorbent and solute (Ding et al., 2016).

The effect of coexisting Pb^{2+} on the adsorption of Cd^{2+} , and vice versa, was also evaluated (Fig. S3). In comparison with the single system, the coexistence of Pb^{2+} and Cd^{2+} could strongly influence the adsorption capacity of Cd^{2+} , but had little effect on Pb^{2+} adsorption. Adsorption capacity for Cd^{2+} decreased from 51 $\text{mmol}\cdot\text{kg}^{-1}$ with no Pb^{2+} present to 3 $\text{mmol}\cdot\text{kg}^{-1}$ with 0.5 mM Pb^{2+} . The initial

Fig. 1. Adsorption kinetics (with P5, a and c) and adsorption isotherms (b, d) for Pb^{2+} and Cd^{2+} with PP biochar, respectively. Q_e is the equilibrium adsorbed concentration of Pb^{2+} or Cd^{2+} , $\text{mg}\cdot\text{g}^{-1}$; C_e is the equilibrium concentration of Pb^{2+} or Cd^{2+} , $\text{mg}\cdot\text{L}^{-1}$; and Q_t is the adsorption amount of Pb^{2+} or Cd^{2+} at time t min, $\text{mg}\cdot\text{g}^{-1}$. (Experimental conditions: Temperature $25\text{ }^{\circ}\text{C}$, initial pH 5.0 ± 0.05 , equilibrium time 50 h for adsorption kinetics and 24 h for adsorption isotherms, mass to volume ratio 2 g/L, initial concentration of $100\text{--}800\text{ mg}\cdot\text{L}^{-1}$ (Pb^{2+}) and $50\text{--}600\text{ mg}\cdot\text{L}^{-1}$ (Cd^{2+}), stirring 140 rpm.)

concentration of Cd^{2+} was 1.5 mM. This indicates that the adsorption process in binary systems was more favorable for Pb^{2+} , supporting the findings of earlier research (Ding et al., 2016). Inhibition of adsorption with Cd^{2+} in binary systems may be attributed to the prior interactions between Pb^{2+} and oxygen-containing functional groups, and the stronger complexation capacity of Pb^{2+} with negative charge (Ding et al., 2016; Jin and Bai, 2002; Ma and Dougherty, 1997).

3.3. Characteristics of biochars

The PP biochar was characterized by FTIR spectroscopy (Fig. S4). Pyrolysis temperature and oxygen atmosphere both influence the number of functional groups on the biochar. Compared with biochar produced at $450\text{ }^{\circ}\text{C}$, fatty hydrocarbon (2853 and 2923 cm^{-1}) and other aliphatic functional groups ($1210\text{--}1591\text{ cm}^{-1}$) were gradually weakened and diminished at $700\text{ }^{\circ}\text{C}$. This was accompanied by an increase in volatile organic matter and an increase of the content of aromatic structures after dehydrogenation of carbohydrates (Dong et al., 2013; Fang et al., 2014). As the temperature increased, the number of oxygen-containing functional groups gradually decreased. With increasing oxygen content atmosphere at low pyrolysis temperature ($450\text{ }^{\circ}\text{C}$), the number of lactonic functional groups and micropore volume content of PP biochar increased alongside the surface area (Table 2). A new peak at 1690 cm^{-1} representing lactonic $\text{C}=\text{O}$ groups was consistent with condensation of biochar structure under a 2% and 4% oxygen content pyrolysis atmosphere at $450\text{ }^{\circ}\text{C}$ (Fig. S4). As shown in Fig. S5, XRD spectra of the pre-sorption biochars indi-

cated the existence of calcite (CaCO_3) in PP biochars, which could be a source of carbonate release into the solution. Minerals such as Fairchildite, Whewellite, and Calcitecalcite have also been found in other biochars converted from raw material (Wang et al., 2015; Zhu et al., 2014).

The Raman spectra were also used to analyze the aromatization of PP biochars (Fig. S6). All of the curves exhibited two relatively broad Raman bands with Raman shifts at $1340\text{--}1357\text{ cm}^{-1}$ and $1589\text{--}1598\text{ cm}^{-1}$, which corresponded to the D-band and G-band, respectively. The biochar synthesized at low and high temperature both clearly exhibited two peaks, which indicates the presence of amorphous graphite and graphitic crystallites. The Elemental (C, H, N) analyses of the biochar were also conducted. As shown in Table S4, the results indicated that the carbon content of biochar synthesized at low-temperature varied from 77.24% to 81.32%. The molar ratios of elements were calculated to estimate the aromaticity (H/C) and polarity (O/C, O + N/C) of the biochar. The results indicate higher aromaticity and lower polarity with oxygen content increase.

The FTIR technique is useful for identifying types of chemical bonds in a molecule based on the infrared absorption spectrum, whereas XPS is a surface sensitive technique that measures elemental composition and chemical state in a material. The XPS C1s peaks of P1, P2 and P4 are presented in Fig. S4, which clearly shows that the oxygen groups were prevalent on the surface of biochars. The main peak for the C1s spectra was assigned to graphitic and aromatic carbon at 284.6 eV , phenolic hydroxyl or ether groups at $285.5\text{--}286.2\text{ eV}$, and carboxylic or ester groups at $288.5\text{--}288.8\text{ eV}$. The relative percentages of oxygen-containing

Fig. 2. (a) Zeta potentials of PP biochar at different solution pH values. (b) Effect of equilibrium solution pH values on Cd (II) and Pb (II) adsorption by P4. (Solution volume: 30 mL; adsorbent dose: 2 g L⁻¹; initial concentration: 100 mg L⁻¹; contact time: 24 h).

groups on PP biochars are listed in Table S5. With the increase of pyrolysis oxygen content at 450 °C, C=O declined from 29.4% for P1 to 22.6% for P2 and 12.6% for P4, but the content of C=O or O=C=O increased, which supports the findings of previous research (Harvey et al., 2012). As shown in Table 2, PP biochars produced with oxygen atmosphere at lower temperature contained more lactonic functional groups, which is consistent with XPS data (Table S5). The surface functional groups (e.g., carboxylic, lactonic and phenolic) were adsorption sites for heavy metals (Chen et al., 2015; Lu et al., 2012).

Table 2 presents the oxygen-containing functional groups and total alkalis from the Boehm titration. Lactonic groups sharply increased with promotion oxygen content atmosphere at 450 °C, while other acid functional groups (carboxylic and phenolic) and total basicity were little affected by the oxygen content. However, the total basicity increased with increasing pyrolysis temperature, due to the increasing contents of ash and basic functional groups. Total acidity showed opposite trends to basicity at 700 °C. The organic acids, including carboxylic, lactonic and phenolic acids, decreased and gradually disappeared at high pyrolysis temperature. Table S4 shows the yield and ash content for the PP biochar.

Table 2

Contents of oxygen-containing functional groups and total alkaline contents for PP biochar determined by Boehm titration.

Functional groups	P1	P2	P3	P4	P5	P6	P7
Carboxylic ^a	0.15 ± 0.02	0.18 ± 0.04	0.13 ± 0.06	BDL ^e	BDL	BDL	BDL
Lactonic ^b	0.35 ± 0.12	0.38 ± 0.11	0.70 ± 0.12	0.80 ± 0.16	0.14 ± 0.05	BDL	0.09 ± 0.03
Phenolic ^c	0.12 ± 0.05	BDL	0.11 ± 0.21	0.15 ± 0.04	0.13 ± 0.06	0.07 ± 0.04	BDL
Total basicity ^d	0.25 ± 0.09	0.25 ± 0.10	0.31 ± 0.12	0.33 ± 0.11	1.23 ± 0.12	1.07 ± 0.21	1.13 ± 0.18

^a Contents of carboxylic groups (mmol g⁻¹) calculated as the consumption of NaHCO₃.

^b Contents of lactonic groups (mmol g⁻¹) calculated as the difference in the consumption between Na₂CO₃ and NaHCO₃.

^c Contents of phenolic groups (mmol g⁻¹) calculated as the difference in the consumption between NaOH and Na₂CO₃.

^d Total basicity (mmol g⁻¹) calculated as the consumption of HCl.

^e Below detectable level.

Yields declined gradually with the oxygen content from 0% to 4%, because of the accelerated decomposition of the components of biochar, producing ash. Correspondingly, the ash content considerably increased as the oxygen atmosphere increased and finally stabilized at 22.4% at 450 °C and 25.5% at 700 °C. Ash on the biochar surface is composed of various inorganic compounds, such as carbonate, which could precipitate with Pb²⁺ and Cd²⁺ and improve the heavy metal adsorption capacity.

3.4. Possible mechanisms for Cd(II) and Pb(II) adsorption on biochars

To determine the possible mechanisms for Cd(II) and Pb(II) adsorption on biochars, XPS analysis was employed to identify the type of heavy metal adsorption on the biochar surface (Tang et al., 2015). The XPS was used to analyze the changes in binding energy of C 1s and O 1s in PP biochar before and after adsorption for Pb(II) and Cd(II) (Fig. S7). After adsorption, new peaks were observed that originated from the binding energy spectrum of Pb4f and Cd3d, indicating Cd(II) and Pb(II) were adsorbed on the biochars.

As shown in Fig. S7, the C 1s spectra of P4 before heavy metal adsorption can be curve-fitted into the forms of C—C (284.7 eV), C=O (288.4 eV), and C—O (286.2 eV). After the adsorption of Cd (II) or Pb(II), their C 1s spectra show that the binding energies of the peaks exhibited a certain degree of shift compared with that of P4 before Cd(II) or Pb(II) adsorption. In particular, the binding energy of 285.5 eV, characteristic for C—O, shows a greater degree of shift. Fig. S7(a) also indicates that the peak area ratio of C—O in P4 after adsorption of Cd(II) decreased from 20.18% to 18.04% compared with P4 before adsorption, whereas the peak area of C=O increased from 4.4% to 8.3%. Previous research has indicated that the increase in C=O of carboxylic groups should be beneficial to Cd²⁺ adsorption (Lim et al., 2008). The XPS data suggested the participation of phenolic hydroxyl and carboxylic groups in Pb(II) and Cd(II) sorption by biochars, which has been previously demonstrated (Bian et al., 2014).

Similarly, three characteristic peaks were identified for the O1s spectrum in P4 before and after Cd(II) or Pb(II) adsorption (Fig. S7). Compared with the original P4, the binding energy of O1s on the surface of biochar after adsorption increased slightly, indicating that the O atom was an electron donor during Cd(II) and Pb(II) sorption. It should be noted that Oeh (ethers or hydroxyl) in surface P4 (Fig. S7) slightly shifted from 532.3 to 532.1 eV. This shift was possibly due to the formation of Cd²⁺ or Pb²⁺ complexation in which the oxygen atoms share electrons with Cd, and thus electron densities of oxygen atoms decreases and the binding energy of the oxygen atoms increases.

As shown in Fig. S7, XPS demonstrated that Pb(II) was present as Pb—O (73.6%) or as Pb²⁺ (26.4%) and Cd(II) was present as Cd²⁺ (69.3%) or as Cd—O (30.7%) on the surface of the biochars (Table S6). As shown in Fig. S7(e), two peaks with binding energies of 405.42 and 412.07 eV representing Cd3d5/2 and Cd3d3/2, respectively, were observed in the spectra of P4, indicating Cd²⁺

trapped in polyferric flocs. Another pair of less visible peaks in the same sample appearing at 404.57 and 411.20 eV were also ascribed to Cd3d5/2 and Cd3d3/2, respectively, caused by Cd–O in which Cd²⁺ is bonded to functional groups such as ether, carboxyl and alcoholic hydroxyl groups on the surface of biochars (Li et al., 2016).

The adsorption of Pb²⁺ and Cd²⁺ on P4 was demonstrated by the SEM-EDX spectra (Fig. S8), and the weight percentages of Pb²⁺ and Cd²⁺ in the biochar were 1.92% and 1.17%, respectively. To confirm the contribution of the chemical precipitation for Pb(II) and Cd(II) sorption, the lead loading, and cadmium loading for P1, P3 and P4 were scanned by XRD (Fig. S9). The results were consistent with the trend of ash content increase (Table S5). The biochar samples prepared at higher oxygen atmosphere had a higher mineral ash content, which could enhance precipitation with heavy metals. The XRD spectra of loaded Pb²⁺ on biochars (Fig. S9) showed several new peaks at specific d-values associated with lead minerals, the precipitation mechanism of lead removal by the PP biochars as shown by Inyang et al. (2012). Carbonate released from the biochars can react with lead in aqueous solution to form stable minerals on biochar. Three types of lead minerals, cerussite (PbCO₃), hydrocerussite (Pb₃(CO₃)₂(OH)₂), and lead carbon hydrogen oxide

(2PbCO₃·Pb(OH)₂), were identified in the post-sorption PP biochar, indicating that lead removal by PP biochar could be controlled by the three precipitation mechanisms. However, lead minerals (for example hydrocerussite or lead carbon hydrogen oxide) on the biochar surface could be dissolved when pH was relatively low, resulting in a significantly decreased lead adsorption content (Fig. 2). As indicated in Fig. S9(b), only a new peak of CdCO₃ (otavite, syn), with the typical 20.84, 27.75, 33.43, 41.32, 48.43, 57.43 degree in the 2θ, were observed on post-sorption biochar for Cd²⁺. The formation may be due to the reactions with Cd²⁺ and the dissolution components, carbonate, and carbonate minerals such as calcite, have also been found in other biochars (Trakal et al., 2016; Xu et al., 2013). As shown in Fig. S5, Since Whewellite and Calcite cannot be dissolved, the precipitation reactions between heavy metals and insoluble carbonate may have occurred on the surface of the biochar. Biochar samples P3 and P4, which were converted under a 2% and 4% oxygen atmosphere respectively, obtained more absorption peaks. This may be because they could release more carbonate to react with the heavy metals in solution.

According to the sorption of Cd(II) and Pb(II) on original biochar and demineralized biochars, the contribution of different mechanisms to the Cd(II) or Pb(II) on could be calculated by the method

Fig. 3. The estimated contribution of Pb²⁺ (a) and Cd²⁺ (b) sorption on PP biochar, and the contribution percentage of different mechanisms to the overall Pb²⁺ (c) and Cd²⁺ (d) sorption on biochars.

described in the supporting information. The contribution of Qp, Qf, and Q π to Qt on biochars is shown in Fig. 3. The contribution for Pb²⁺ adsorption by PP biochars followed the order Qp > Q π > Qf, whereas the Cd²⁺ adsorption followed the order Q π > Qp > Qf. As shown in Fig. 3a and c, the contribution of Qp significantly increased from 17.2% to 71.7% as the oxygen content of the atmosphere increased from 0% to 4% at 450 °C. At low pyrolysis temperature, the increased oxygen content of the atmosphere may contribute to the formation of surface minerals, such as carbonate, which could remove Pb²⁺ in the form of co-precipitation. Use of a trace oxygen atmosphere in pyrolysis process could cause the increase of biochar specific surface area and number of micropores (Table S7), which could provide more adsorption sites for the Pb- π complexation. When pyrolysis process trace oxygen increased from 0% to 4%, the contribution of Qp increased from 3.25 to 32.1 mg·g⁻¹, which is consistent with the mineral precipitation of lead with increasing oxygen content (Fig. S9).

The contribution of Pb- π complexation in P3 and P6 reached 18 and 23 mg·g⁻¹, respectively, while the corresponding proportions were 34% and 43%, respectively. This indicates a good agreement as surface area and porosity significantly increased (Table S7), which may result from aromatization and increased π chemical bonds with increased pyrolysis temperature. The contribution of both Q π and Q π /Qt increased with increasing pyrolysis temperature from 450 to 700 °C, while that of Qf and Qf/Qt showed the reverse trend. For example, the Qf value of P4 was 7.06 mg Pb²⁺·g⁻¹, while the Qf value of P4 was only 3.58 mg Cd²⁺·g⁻¹ (Fig. 3a). This may be attributed to the amount of oxygen-containing functional groups gradually reducing or disappearing with the temperature increase (Table 2).

The adsorption capacity of Cd²⁺ by PP biochar was relatively low compared with other biochars (Table S3). The Q π and Q π /Qt values of the high-temperature biochars (700 °C) were greater than those of the low-temperature biochars (450 °C). For example, the Q π value of P2 was only 2.15 mg Cd²⁺·g⁻¹, while the Q π value of P6 was 10.2 mg Cd²⁺·g⁻¹, which is approximately 4.7 times greater than that of P2 (Fig. 3b). Similarly, the Q π /Qt value of P2 was 54.4%, but the Q π value of P6 accounted for 83.3% of its Qt value. For the biochars produced at 450 °C, the contribution of both Q π and Q π /Qt increased with increasing pyrolysis oxygen atmosphere from 0% to 4% (Fig. 3d). Conversely, Qp for the trace oxygen atmosphere biochar (P2, P3 and P4) was roughly equal to the pure nitrogen atmosphere (P1). For example, Q π value of P4 was 7.36 mg Cd²⁺·g⁻¹, accounting for 72.6% to the Qt values, while Q π and Q π /Qt value of P1 were only 2.07 mg Cd²⁺·g⁻¹ and 58.5%, respectively.

Overall, the pyrolysis temperature and atmosphere are crucial for both Pb²⁺ and Cd²⁺ sorption capacity of biochars and the contribution of different mechanisms. It could be concluded that Cd²⁺ attracted to the C=C (π -electron) bond would predominant mechanism Cd²⁺ removal, especially for biochar at high pyrolysis temperature. Precipitation between Pb²⁺ and minerals would also play a key role in Pb²⁺ removal from water. For Pb²⁺ adsorption, as the pyrolysis temperature increased, the contribution of Qp increased substantially. The Qp values accounted for 68.2–75.0% of the Qt values at high pyrolysis temperature, indicating that coprecipitation is the dominant mechanisms of Pb²⁺ sorption on biochars. At low pyrolysis temperature, the Qp/Qt values of biochar, except for P1, accounted for 45.3–71.7%, indicating that mineral coprecipitation is the dominant mechanism of Pb²⁺ sorption. For Cd²⁺ adsorption, the Q π values accounted for 63.0–74.1% of the Qt values, indicating that electrostatic adsorption is the dominant mechanisms of Cd²⁺ sorption. Therefore, the cadmium adsorption capacity of PP biochar is far less than the lead adsorption capacity, for which mineral ash plays a critical role.

4. Conclusions

The PP-derived biochars exhibited different sorption capacities for Pb²⁺ and Cd²⁺ under different pyrolysis atmosphere. Importantly, the presence of oxygen in biochar pyrolysis procedure could promote specific surface area and ash content increase at 450 °C. The adsorption capacity of Pb²⁺ was higher than Cd²⁺, which is mainly due to mineral precipitation with Pb²⁺. Precipitation dominated Pb²⁺ sorption on the biochars and its proportion increased as oxygen content increased. With increasing oxygen content, Cd²⁺- π interaction was consistently dominant, whereas the contribution of functional groups complexation reduced. This study provides a method for the preparation of cost-effective biochar for metals adsorption.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.04.051>.

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