



Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars



Wenchuan Ding^{a,b}, Xiaoling Dong^b, Inyang Mandu Ime^c, Bin Gao^c, Lena Q. Ma^{d,b,*}

^a Department of Environmental Engineering, Chongqing University, Chongqing 400045, China

^b Department of Soil and Water Science, University of Florida, Gainesville, FL 32611, USA

^c Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA

^d State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210023, China

HIGHLIGHTS

- Sugarcane bagasse biochars were effective in removing Pb from aqueous solution.
- Pyrolytic temperatures significantly impacted biochar properties, thereby their removal capacity and mechanisms.
- The removal mechanisms were investigated based on isotherm and kinetic models, sorption and desorption, and FTIR spectroscopy.
- The removal mechanisms included cation exchange, complexation, intraparticle diffusion and P-induced precipitation.

ARTICLE INFO

Article history:

Received 10 October 2013

Received in revised form 7 December 2013

Accepted 11 December 2013

Available online 3 January 2014

Keywords:

Pyrolysis temperature

Lead

Bagasse biochar

Sorption kinetics

Functional groups

ABSTRACT

The characteristics and mechanisms of Pb sorption by biochars produced from sugarcane bagasse at 250, 400, 500, and 600 °C were examined. The Pb sorption isotherms, kinetics and desorption were investigated. All biochars were effective in Pb sorption and were well described by Langmuir isotherm model and pseudo-second-order kinetic model. The maximum sorption capacity decreased from 21 to 6.1 mg g⁻¹ as temperature increased from 250 to 600 °C. The Pb sorption was rapid initially, probably controlled by cation exchange and complexation and then slowed down, which might be due to intraparticle diffusions. FTIR data and kinetic models suggested that oxygen functional groups were probably responsible for the high Pb sorption onto low temperature biochars (250 and 400 °C) whereas intraparticle diffusion was mainly responsible for low Pb sorption onto high temperature biochars (500 and 600 °C). Decreased phosphorus concentration indicated that P-induced Pb precipitation was also responsible for Pb sorption. Pyrolysis temperature significantly affected biochar properties and played an important role in Pb sorption capacity and mechanisms by biochars.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Lead contamination in the environment is of great concern due to its toxicity to living organism in relatively low concentrations. To adequately protect public health, the European Community Directive 98/83 and the World Health Organization set the allowable level of Pb at 10 µg L⁻¹ in drinking water effective December 2013 (Sublet et al., 2003). The United States Environmental Protection Agency established a zero lead value against the current 15 µg L⁻¹ for public health goal in national primary drinking water regulation (USEPA, 2009). Therefore, it is important to develop economical and effective methods to remove Pb from contaminated water.

* Corresponding author at: State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210023, China. Tel./fax: +86 025 8969 0637.

E-mail address: lqma@ufl.edu (L.Q. Ma).

0045-6535/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved.

<http://dx.doi.org/10.1016/j.chemosphere.2013.12.042>

Biosorption is a cost-effective technology to remove heavy metals including Pb from aqueous solutions (Deng et al., 2007; Lourie and Gjengedal, 2011). Often sorbents are readily available in large quantities and they are environmental friendly. More recently, biochars have received much attention for their strong affinity with organic pollutants and heavy metals (Cao et al., 2009a; Chen et al., 2011; Zhang et al., 2013; Xu et al., 2013). Pb sorption onto biochar involved multiple mechanisms, e.g., ion exchange, precipitation, physical adsorption and complexation (Cao et al., 2009a; Lu et al., 2012). Oxygen-containing functional group is considered as a primary factor responsible for Pb sorption on biochar (Qiu et al., 2008; Liu and Zhang, 2009). In addition, properties of feedstock and pyrolysis conditions also impact the characteristics and mechanisms of Pb sorption on biochar (Zhang et al., 2013).

Sugarcane is a traditional crop widely cultivated in tropical and sub-tropical regions throughout the world, contributing ~75%

world's sugar supply (Baucum, 2009). Sugarcane has become an efficient feedstock for ethanol production in the United States and Brazil long time ago (Dias et al., 2009). Sugarcane bagasse is a by-product generated in large amounts by sugar and alcohol industries. Although the leftover bagasse is currently burned for bioelectricity generation or planned for bioplastic conversion (Neves et al., 2010), innovations for the proper use of sugarcane bagasse are still encouraged. Sugarcane bagasse contains various chemical functional groups (carboxyl, hydroxyl, sulfate, phosphate, and amino), which may help metal sorption onto the biomass (Sud et al., 2008).

Previous work showed that bagasse biochar is characterized by high surface area ($51 \text{ m}^2 \text{ g}^{-1}$, $600 \text{ }^\circ\text{C}$) with micropores and surface chemical functional groups (Darmstadt et al., 2001; Bonelli et al., 2007). It suggested that bagasse biochar could be used as a potential sorbent to remove metals from water. However, limited knowledge is available on Pb sorption by bagasse biochar. Such knowledge may be useful to develop value-added products from sugarcane bagasse for metal removal.

In this study, biochars were produced from sugarcane bagasse via slow pyrolysis using a laboratory-scale reactor at different temperatures ranged from 250 to $600 \text{ }^\circ\text{C}$. Our overall objective was to investigate the effects of pyrolysis temperature on the characteristics and mechanisms of Pb sorption by biochar. The specific objectives of this study were to examine (1) Pb sorption isotherms and kinetics onto biochars; (2) the functional groups responsible for Pb sorption onto biochars; and (3) Pb desorption from biochars.

2. Materials and methods

2.1. Bagasse biochar production

Fresh bagasse collected from a sugar industry in Florida, USA was oven-dried at $105 \text{ }^\circ\text{C}$ and then fed into a lab-scale tubular reactor within a muffle furnace (1500 M , Barnstead International, IA). Nitrogen gas at 69 kPa was used to maintain oxygen-free environment. The furnace temperature was programmed to increase at $10 \text{ }^\circ\text{C min}^{-1}$ until it reached at specified temperatures (250 , 400 , 500 , and $600 \text{ }^\circ\text{C}$). The entire procedure took approximately 2 h . The biochars were allowed to cool at room temperature under a flow of nitrogen gas. They were ground and size fractions between 0.5 and 1.0 mm were used for this experiment. The biochar produced at different temperature are referred to as BC250, BC400, BC500, and BC600.

2.2. Chemicals and chemical analyses

Analytical grade chemicals and reagents were purchased from Fisher Scientific Inc. All solutions were prepared using deionized water. Lead stock solution at 1000 mg L^{-1} was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in deionized water. KOH and HNO_3 solutions were used for pH adjustment. Concentrations of Pb were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Plasma 3200, Perkin-Elmer Inc., MA). The detection limit was $1 \text{ } \mu\text{g L}^{-1}$.

2.3. Characterization of biochars

The biochar pH was measured at solid to water ratio of 1:20 after 0.5 h of shaking using a Fisher Scientific Accumet model AB15 pH meter. Surface area was analyzed using a NOVA 1200 surface area analyzer (Quantachrome Instruments, Boynton Beach, FL) with the BET nitrogen adsorption method at 77 K . Surface charge was characterized by determining its zeta potential following the method of Johnson et al. (1996) using a Brookhaven Zeta Plus

(Brookhaven Instruments, Holtsville, NY). Smoluchowski's formula was used to convert the electric mobility into zeta potential. The elemental composition of bagasse biochars was determined by ICP-AES after digesting with $\text{HNO}_3/\text{H}_2\text{O}_2$ hot-block digestion procedure (EPA, 1986).

Fourier transform infrared spectroscopy (FTIR) was used to characterize the surface functional groups on the biochars before and after Pb sorption. The spectra of samples were determined from 400 to 4000 cm^{-1} wave number by KBr method on a Bruker Vector 22 FTIR spectrometer (Bruker Optics Inc. Billerica, MA), with the average of 64 scans at 4.0 cm^{-1} resolution.

2.4. Sorption and desorption experiments

Kinetic sorption experiments were performed using 60-mL plastic vials at room temperature ($22 \pm 0.5 \text{ }^\circ\text{C}$). Solution of 50 mL containing 20 mg L^{-1} Pb was shaken with 0.1 g of biochar at 200 rpm for up to 32 h on a reciprocating shaker. Aliquots of aqueous samples were withdrawn, filtered through $0.1\text{-}\mu\text{m}$ nylon membranes for metal analysis. The suspension pH was measured before and after the experiment. The amount of metal adhering to the plastic vial was negligible.

Equilibrium sorption isotherms were determined by shaking 0.1 g of biochar with 50 mL of solutions containing $5\text{--}200 \text{ mg L}^{-1}$ of Pb. After shaking for 24 h , solid and liquid were separated by filtration to determine the remaining Pb in solution.

Desorption experiment involved shaking 0.1 g of biochar with 50 mL of 80 mg L^{-1} Pb for 24 h to obtain Pb-loaded biochar. Then, the biochar on the $0.1\text{-}\mu\text{m}$ nylon membranes was rinsed three times. Solution containing 0.1 M HCl was shaken for 0.5 h and 0.1 M KCl was shaken for 24 h with 0.1 g Pb-loaded biochar for Pb desorption. Pb concentrations in the filtrates were determined using ICP-AES.

2.5. Release of P, Ca, K and Na from biochars

The amounts of cations (Ca, K, and Na) released from biochar after Pb sorption were determined. Biochar of 0.1 g (BC250 and BC500) was shaken with solution containing 0 , 20 and 105 mg L^{-1} Pb for 24 h . The concentrations of Ca, K, and Na in the filtrate ($0.1\text{-}\mu\text{m}$ nylon membranes) were determined using ICP-AES. The net cations released were reported by subtracting cations released in the 0 mg L^{-1} Pb solution as background concentration.

Water soluble P concentrations before and after Pb sorption were determined. Biochar of 0.1 g was shaken with 50 mL solution containing either deionized water or 354 mg L^{-1} Pb for 24 h . The soluble P concentrations after filtration ($0.1\text{-}\mu\text{m}$ nylon membranes) were determined using a standard colorimetric method (APHA, 1992).

3. Results and discussion

3.1. Characterization of bagasse biochar

Pyrolytic temperature significantly affected the biochar production, with yield dropping substantially from 77% to 32% as temperature increased from 250 to $400 \text{ }^\circ\text{C}$ and afterwards the decrease becoming more gradual from 32% to 23% as temperature increased from 400 to $600 \text{ }^\circ\text{C}$ (Table 1). This is consistent with the report that major mass loss in biochars occurs between 200 and $400 \text{ }^\circ\text{C}$ (Asadullah et al., 2007). With increasing temperature, the apparent density of biochar reduced slightly from 0.08 to 0.07 g cm^{-3} , however, its surface area increased substantially from 0.6 to $14.1 \text{ m}^2 \text{ g}^{-1}$ (Table 1). The progressive increase in biochar surface area may be attributed to decomposition of organic

Table 1
Element compositions and properties of biochar samples (0.5–1 mm) from sugarcane bagasse under different pyrolysis temperatures (250–600 °C).

	BC250	BC400	BC500	BC600
Na (mg g ⁻¹)	0.29 ± 0.08	0.31 ± 0.08	0.41 ± 0.03	0.45 ± 0.04
K (mg g ⁻¹)	0.39 ± 0.03	3.32 ± 0.05	3.54 ± 0.06	3.54 ± 0.03
Ca (mg g ⁻¹)	1.58 ± 0.11	3.68 ± 0.25	5.03 ± 0.32	5.60 ± 0.33
Fe (mg g ⁻¹)	0.20 ± 0.03	0.37 ± 0.05	8.13 ± 0.73	14.17 ± 0.34
Mg (mg g ⁻¹)	0.28 ± 0.02	0.85 ± 0.03	0.88 ± 0.04	0.94 ± 0.05
pH	5.02	6.98	7.34	7.66
Apparent density (g cm ⁻³)	0.08	0.06	0.07	0.07
BET (m ² g ⁻¹)	0.56	0.78	1.98	14.1
Solution zeta potential (mV)	-23.0	-28.2	-22.9	-28.1
Product yield (%)	77.1	31.6	25.6	22.9
Cation exchange capacity (cmol kg ⁻¹)	6.40	3.82	9.66	4.19

substances and resultant formation of micropores in biochars at high temperature (Katyál et al., 2003). The surface area showed the greatest increase as temperature increased from 500 to 600 °C, while the loss in yield was only from 26% to 23% (Table 1). Hence, increasing pyrolytic temperature induced the development of porous structure in biochars, resulting in higher internal surface area (Bonelli et al., 2007). The zeta potential measurements indicated that the surfaces of biochars were negatively charged (Table 1).

Based on chemical analysis (Table 1), bagasse biochars were abundant in mineral elements such as Na, K, Ca, Fe and Mg, with Fe and Ca contents being the highest. Their concentrations increased substantially with the increase of pyrolysis temperature. For example, Fe and Ca concentrations increased from 0.02 and 0.16% at 250 °C to 1.42 and 0.56% at 600 °C, respectively (Table 1). Similarly, biochar pH also increased with pyrolysis temperature, resulting from alkali salts accumulation during pyrolysis.

Biochar samples BC250 and BC500 were also characterized by FTIR spectroscopy (Fig. 1). Several peaks were observed in low temperature biochar BC250. The symmetric sorption band at 2338 cm⁻¹ was due to C≡C stretching. The peaks at 1722 and 1061 cm⁻¹ were related to C=O stretching of carboxylic acid and C–O stretching of –OCH₃ group, which is attributed to lignin structure in sugarcane bagasse (Garg et al., 2008). The peak at 1595–1572 cm⁻¹ indicated the presence of C=O stretching vibration or may be due to aromatic skeletal stretching bands

(Bilba and Ouensanga, 1996). The peak observed at 1457 cm⁻¹ could be attributed to either asymmetrical (C–H) bending vibration or aromatic C=C ring stretching and the peak at 1390 cm⁻¹ corresponded to symmetrical C–H vibration (GomezSerrano et al., 1996). The presence of negative charges (Table 1) and functional groups (Fig. 1) in biochars suggested that the bagasse biochars are capable of sorbing metal cations.

Compared to BC250, BC500 had fewer peaks, with the peaks at 2338 cm⁻¹ (C≡C), and 1722 and 1595 cm⁻¹ (C=O) being reduced while that at 1061 cm⁻¹ (C–O) disappearing. It indicated that fewer chemical groups were present on the surfaces of high temperature biochar than that of low temperature biochar. Previous studies showed that structure modification of biochar started at 200 °C and intensified between 300 and 400 °C during pyrolysis (Bilba and Ouensanga, 1996). Disappearance of C–O and –OH on biochars may be attributed to dehydration and rearrangement of molecules at high temperature. The alkyl and aromatization were likely developed between 300 and 550 °C (Bilba and Ouensanga, 1996; GomezSerrano et al., 1996). The disappearance of most oxygen-containing surface groups during charring at high temperature would affect on Pb sorption onto sorbent (Karnitz et al., 2007; Kilic et al., 2008).

3.2. Kinetics of Pb sorption

It can be seen in Fig. 2a that Pb sorption by the biochars varied with time and were affected by pyrolytic temperatures. Sorption

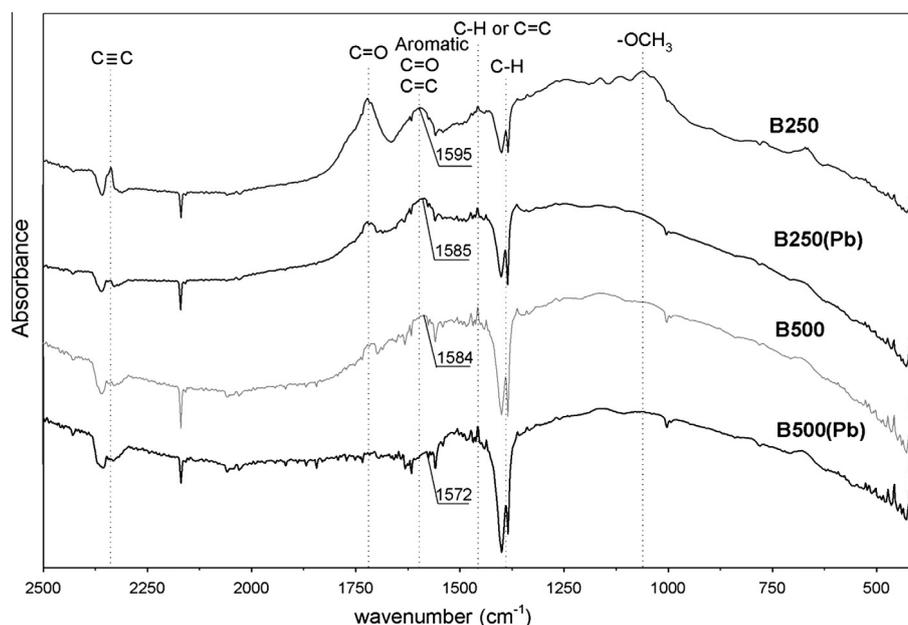


Fig. 1. FTIR spectra of BC250 and BC500 before and after lead sorption. 0.1 g biochar was shaken with 20 mg L⁻¹ Pb for 24 h.

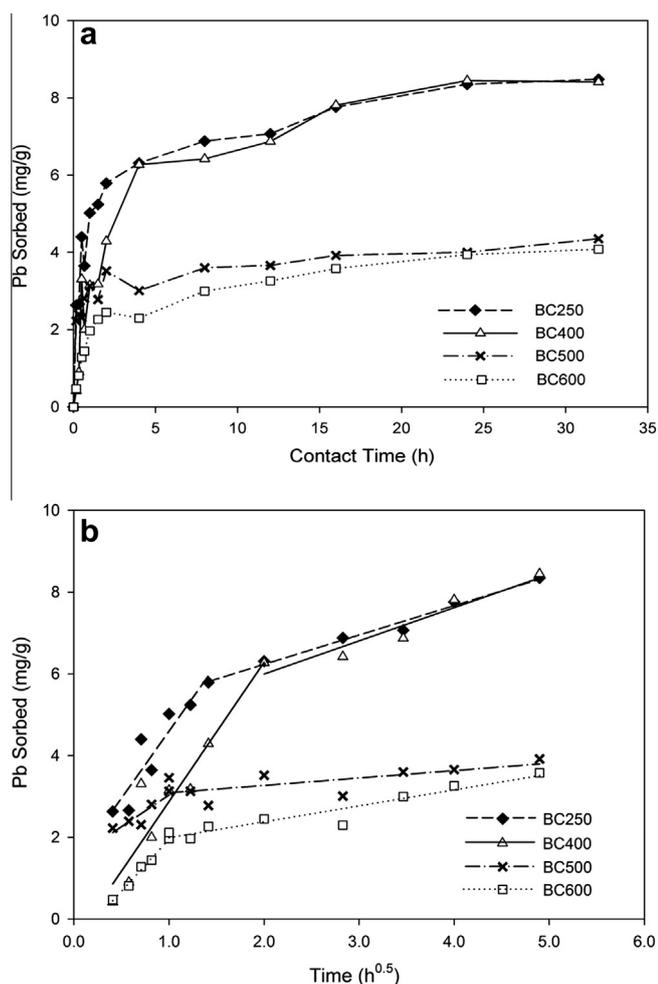


Fig. 2. Sorption kinetics of Pb onto biochars from different temperatures: (a) experimental data, and (b) comparisons between the pre-equilibrium data (symbols) and intraparticle diffusion model simulations (lines). 0.1 g biochar was shaken with 20 mg L⁻¹ Pb for 24 h.

plots were characterized with initial fast reaction during the first 2 h (accounting for 51–81% of sorption capacity) and then slowly reached equilibrium after 24 h, which were similar to pine and oak bark biochars (Mohan et al., 2007). Since equilibrium was reached after 24 h, it was used in following experiments. Low temperature biochars BC250 and BC400 generally had higher sorption capacity than those of BC500 and BC600. To better understand Pb sorption characteristics, the pseudo-first-order model and pseudo-second-order model were used to describe the data. The calculated sorption capacity (q_e) of these two models was obtained from their linear forms. The correlation coefficients (R^2) were calculated by regression analysis.

The results indicated that the pseudo-second-order kinetic model ($R^2 > 0.99$) fit the data better than the pseudo-first-order kinetic model ($R^2 = 0.84–0.96$). Therefore, Pb sorption onto the bagasse biochar was a rate-limited process, which was affected by both biochar sorption capacity and the loaded Pb concentration (Ho and McKay, 2000; Rao et al., 2008). The sorption rate of all biochars were similar except for BC400, which was slightly lower (data not shown). This result suggested that Pb sorption onto the bagasse biochars produced at different pyrolytic temperatures had similar kinetic characteristics.

Due to the porous nature of the bagasse biochars (Das et al., 2004; Bonelli et al., 2007) (Table 1), an intraparticle diffusion model was also applied to describe the sorption kinetics (Weber

and Morris, 1963). The relationship between the amount of Pb sorbed (q_t) and square root of contact time ($t^{0.5}$) of four biochars were plotted in Fig. 2b.

The sorption data of each biochar were fitted with two linear lines of different slope. The first linear section may describe mass transfer of Pb from bulk solution to surface layer while the second section can be attributed to intraparticle diffusion of Pb on biochars (Amin, 2008). The slopes for the first linear section ($k_1 = 1.5–3.4$, $R^2 = 0.83–0.99$) were steeper than the second one ($k_2 = 0.26–0.81$, $R^2 = 0.73–0.98$), which might be explained by the fast Pb transfer from bulk solution to biochar surfaces at the initial time. The slower subsequent interaction was probably attributed to Pb intraparticle diffusion. Fig. 2b also shows that Pb sorption onto the surfaces of BC500 and BC600 possibly completed within 1 h, while for BC250 and BC400, it took more than 2 h. This was consistent with the previous results (Fig. 1) that biochars derived at high temperature had fewer active sites on the external surface than those from low temperature pyrolysis. Therefore, after external binding sites were rapidly occupied by Pb, additional Pb ion migrated slowly to pore spaces inside the biochars.

3.3. Isotherms of Pb sorption

The isotherms of Pb sorption onto different biochars were fit with Langmuir and Freundlich models (data not shown). The results indicated that the Langmuir model ($R^2 = 0.97–0.99$) provided slightly better fit than the Freundlich model ($R^2 = 0.90–0.97$), implying monolayer coverage of Pb on the surface of biochars (Hawari and Mulligan, 2006). The Langmuir maximum sorption capacity Q^0 of biochars decreased from 20.5 to 6.0 mg g⁻¹ as temperatures increased, suggesting low temperature pyrolysis was capable of producing biochar with higher Pb sorption capacity. This was attributed to their relatively high content of binding sites and functional groups (Fig. 1). Though more Pb was sorbed onto low temperature biochars, their bonding strengths were lower ($K_L = 0.051–0.055$ for BC250 and BC400) than high temperature biochars ($K_L = 0.18–0.11$ for BC500 and BC600) (data not shown).

3.4. Pb desorption from biochars

Sorbate recovery is important for metal sorption technology development in industrial practice. Thus lead desorption test was performed using 0.1 M HCl, which has been commonly used in desorption studies as H⁺ is a much stronger competitor for Pb²⁺ (Noeline et al., 2005). In addition, 1.0 M KCl was also used as a mild alternative to better understand Pb sorption mechanism. The amounts of sorbed Pb after reacting with 80 mg L⁻¹ Pb were 15.9, 10.7, 11.4, and 8.3 mg g⁻¹ for BC250, BC400, BC500 and BC600, respectively. The amounts of sorbed Pb by low temperature biochars BC250 and BC400 accounted for 78% and 58% of their sorption capacity; however, those of BC500 and BC600 exceeded the sorption capacity Q^0 . In other words, BC500 and BC600 were saturated with Pb whereas BC250 and BC400 were not.

As expected, HCl was more effective than KCl for Pb desorption from the biochars (Fig. 3). Approximately 73–85% of the Pb on the biochar was desorbed by HCl within 0.5 h, which was 2–5 times greater than those by KCl after 24 h. This was consistent with the fact that H⁺ is much stronger than K⁺ to replace Pb²⁺ due to its high charge density (Hawari and Mulligan, 2006). Furthermore, some of the sorbed Pb could be dissolved by HCl with pH 1. The 15–27% of Pb remained on the biochars after desorption by 0.1 M HCl was probably trapped inside the pore spaces in the biochars. The fact that less Pb was recovered by 0.1 M HCl from BC500 and BC600 (73–77%) than those from BC250 and BC400 (84–85%) was consistent with our hypothesis that intraparticle diffusion played the dominant role for Pb sorption on high temperature biochars.

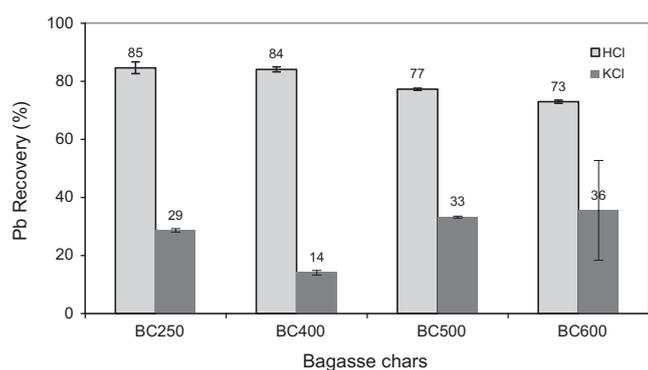


Fig. 3. Desorption of Pb from different biochars. The Pb on 0.1 g biochar, which was reacted with 80 mg L⁻¹ Pb for 24 h, was desorbed by 0.1 M HCl for 0.5 h or 0.1 M KCl for 24 h.

3.5. Mechanisms of Pb sorption by biochars

3.5.1. Chemical functional groups

Two biochar samples (BC250 and BC500) were characterized by FTIR spectroscopy before and after Pb sorption to determine the vibration frequency changes in its functional groups (Fig. 1). Changes in the function groups of BC250 biochar were visible after Pb sorption. After Pb sorption, the sharp peak at 1722 cm⁻¹ (C=O) decreased and meanwhile the peak at 1061 cm⁻¹ attributed to C–O band disappeared, and the peak related to C=O stretching vibration shifted from 1595 to 1585 cm⁻¹ (Fig. 1). These changes implied that oxygen-containing functional groups (hydroxyl, carboxyl and ether) were responsible for Pb sorption by the biochars (Deng et al., 2007; Kilic et al., 2008). These results are in good agreement with Sud et al. (2008), which concluded that complexation and cation exchange between Pb and oxygen-containing functional groups were responsible for Pb sorption.

The impact of Pb sorption on BC500 was limited, consistent with their lower Pb sorption (9.13 mg g⁻¹) compared with BC250 (20.5 mg g⁻¹). Only the shift of the C=O peak was observed (1572–1584 cm⁻¹), typical of their interactions with metal ions. Our data suggested that surface functional groups played an important role for Pb sorption for low temperature biochars (BC250 and BC400). While, for the high temperature biochars (BC500 and BC600), the abundant pore spaces might be playing the dominant role by intraparticle diffusion (Fig. 2b).

3.5.2. Cation exchange

To confirm the contribution of cation exchange, the amounts of cations (Ca, Na and K) released from biochar BC 250 and BC500 after Pb sorption were determined (Table 2). With initial Pb concentrations of 20 and 105 mg L⁻¹, the amounts of Pb sorbed by BC250 accounted for 43% and 62% of its maximum sorption capacity while for BC500 accounting for 64% and 98% (Table 2).

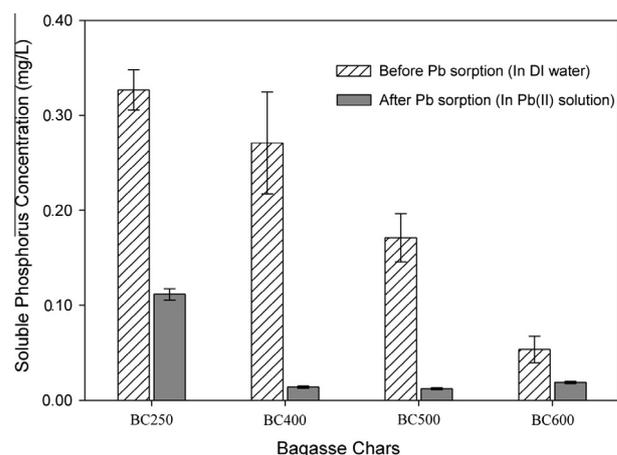


Fig. 4. Phosphate concentrations in solution before and after Pb sorption onto different biochars. 0.1 g biochar was shaken with DI water or 354 mg L⁻¹ Pb for 24 h.

The amounts of cations released to the solution after Pb sorption by two biochars were significant different (Table 2). For low temperature biochar BC250, the amounts of cations released to solution increased by 20.1 mol kg⁻¹, which was almost equal to the increase of sorbed Pb at 21.3 mol kg⁻¹. This result confirmed that cation exchange may play an important role in Pb sorption onto low temperature biochar, with oxygen-containing functional groups (hydroxyl and carboxyl) being likely involved (Mohan et al., 2007). But for high temperature biochar BC500, the total cations released into solution increased by 3.1 mol kg⁻¹, while the amounts of Pb sorbed onto biochar increased by 15.5 mol kg⁻¹. This result indicated that cation exchange was not the dominant mechanism for Pb sorption by BC500, which might be due to the lack of surface functional groups (Fig. 1). It was consistent with the hypothesis that intraparticle diffusion mechanism dominated Pb sorption by high temperature biochar.

3.5.3. P-induced precipitation

Phosphorus has been extensively investigated for Pb immobilization by forming the low soluble Pb–P minerals (Ma and Rao, 1999; Bolan et al., 2003). Hence, besides cations, changes in soluble P concentrations before and after Pb sorption were also determined (Fig. 4). The total soluble P concentrations decreased sharply after Pb sorption, suggesting that precipitations might have occurred between Pb and P during the sorption (Cao et al., 2009a,b). Garcia-Perez et al. (2002) reported that P was one of the major elements in bagasse biochars with concentration as high as 1.33 mg g⁻¹. Hence, besides cation exchange, Pb precipitation also occurred on the surface of biochars, especially for biochars with high P content, resulting in the decrease of both Pb and P concentrations in solution. In this study, based on the reduced amounts of P and assuming a P/Pb molar ratio of 3:5, the amounts of Pb sorbed onto biochars through P–Pb precipitation ranged from 0.35–1.43 mg g⁻¹, accounting for 5.8–9.7% of sorption capacity

Table 2

Net cations release from Pb sorption onto biochar BC250 and BC500 (0.1 g biochar was shaken with 20 or 105 mg L⁻¹ Pb for 24 h).

Biochar	Initial Pb conc. (mg L ⁻¹)	Pb sorbed (mol kg ⁻¹)	pH		Net cations released (mol kg ⁻¹)			
			Initial	Equilibrium	Ca ²⁺	2K ⁺	2Na ⁺	Total
BC250	20	42 ± 1.3	5.8	5.8	15 ± 1.7	0.00	2.3 ± 0.8	17 ± 2.5
	105	64 ± 1.6	4.8	4.4	33 ± 1.2	1.4 ± 0.8	2.7 ± 2.3	37 ± 4.2
BC500	20	28 ± 0.8	5.0	4.9	57 ± 1.2	4.1 ± 0.2	0.00	61 ± 0.9
	105	43 ± 2.9	4.8	4.9	60 ± 3.2	3.6 ± 0.5	0.00	64 ± 3.7

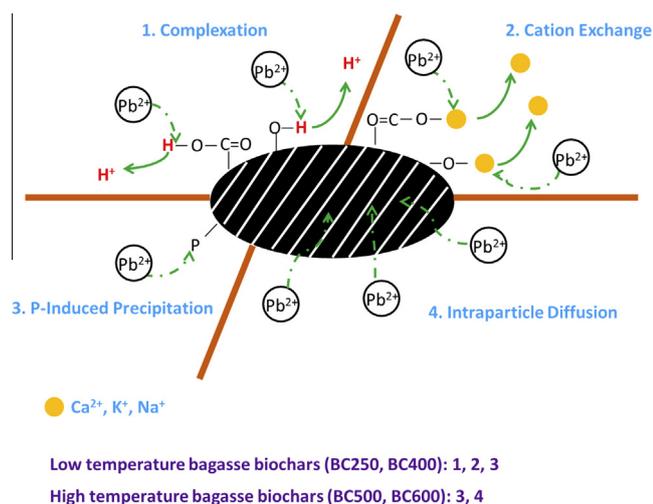


Fig. 5. Mechanisms of Pb sorption by bagasse biochars.

(Chen et al., 2003). This was the most conservative projection, since maximum Pb sorption capacity was ideal situation, for most sorption experiments, it could not be achieved. In short, P-induced Pb precipitation might be responsible for Pb sorption on bagasse biochar, which contain high P content.

4. Conclusions

Sugarcane bagasse biochar was effective to remove Pb from aqueous solution. The sorption process was best described by the Langmuir isotherm model and pseudo-second-order kinetic model. Experimental and modeling results showed that Pb sorption onto bagasse biochar was controlled by multiple mechanisms including complexation, cation exchange, precipitation, and intraparticle diffusion (Fig. 5). Most of the Pb could be desorbed by HCl indicating reversible reactions. Based on our data, bagasse biochar may serve as a potential alternative for removal of toxic Pb from aqueous solution. Our data also demonstrated that pyrolysis temperatures significantly affected the biochar properties and thus played an important role in controlling the sorption characteristics of lead onto biochars.

Acknowledgements

This work was partially supported by USDA-TSTAR, University of Florida and the scholarship from China Scholarship Council received by the senior author. We would like to thank Mr. Orlando L. Lanni for his assistance in the development of the pyrolysis reactor.

References

- Amin, N.K., 2008. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalination* 223, 152–161.
- Asadullah, M., Rahman, M.A., Ali, M.M., Rahman, M.S., Motin, M.A., Sultan, M.B., Alam, M.R., 2007. Production of bio-oil from fixed bed pyrolysis of bagasse. *Fuel* 86, 2514–2520.
- Baucum, L.E., Rice, R.W., Schueneman, T.J., 2009. An overview of Florida sugarcane. Institute of Food and Agricultural Sciences (UF/IFAS), Report Publication #SS-AGR-232, Gainesville, FL.
- Bilba, K., Ouensanga, A., 1996. Fourier transform infrared spectroscopic study of thermal degradation of sugar cane bagasse. *J. Anal. Appl. Pyrol.* 38, 61–73.
- Bolan, N.S., Adriano, D.C., Naidu, A.R., 2003. Role of phosphorus in (Im)mobilization and bioavailability of heavy metals in the soil–plant system. *Rev. Environ. Contam. Toxicol.* 117, 1–44.

- Bonelli, P.R., Buonomo, E.L., Cukierman, A.L., 2007. Pyrolysis of sugarcane bagasse and co-pyrolysis with an argentinean subbituminous coal. *Energy Sour. Part A* 29, 731–740.
- Cao, X.D., Ma, L.N., Gao, B., Harris, W., 2009a. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* 43, 3285–3291.
- Cao, X.D., Wahbi, A., Ma, L.N., Li, B., Yang, Y.L., 2009b. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. *J. Hazard. Mater.* 164, 555–564.
- Chen, B.L., Chen, Z.M., Lv, S.F., 2011. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour. Technol.* 102, 716–723.
- Chen, M., Ma, L.Q., Singh, S.P., Cao, R.X., Melamed, R., 2003. Field demonstration of in situ immobilization of soil Pb using P amendments. *Adv. Environ. Res.* 8, 93–102.
- Darmstadt, H., Garcia-Perez, M., Chaala, A., Cao, N.Z., Roy, C., 2001. Co-pyrolysis under vacuum of sugar cane bagasse and petroleum residue – properties of the char and activated char products. *Carbon* 39, 815–825.
- Das, P., Ganesh, A., Wangikar, P., 2004. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. *Biomass Bioenergy* 27, 445–457.
- Deng, L.P., Su, Y.Y., Hua, S., Wang, X.T., Zhu, X.B., 2007. Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. *J. Hazard. Mater.* 143, 220–225.
- Dias, M.O.S., Ensinas, A.V., Nebra, S.A., Maciel, R., Rossell, C.E.V., Maciel, M.R.W., 2009. Production of bioethanol and other bio-based materials from sugarcane bagasse: Integration to conventional bioethanol production process. *Chem. Eng. Res. Des.* 87, 1206–1216.
- EPA, 1986. Test methods for evaluating solid waste. Laboratory Manual Physical/Chemical Methods. Environmental Protection Agency, United States Department of Agriculture Office, Washington, DC.
- EPA, 2009. National Primary Drinking Water Regulations. Environmental Protection Agency, EPA 816-F-09-004.
- Garcia-Perez, M., Chaala, A., Roy, C., 2002. Vacuum pyrolysis of sugarcane bagasse. *J. Anal. Appl. Pyrol.* 65, 111–136.
- Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., 2008. Removal of nickel(II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresour. Technol.* 99, 1325–1331.
- GomezSerrano, V., PastorVillegas, J., PerezFlorindo, A., DuranValle, C., 1996. FT-IR study of rockrose and of char and activated carbon. *J. Anal. Appl. Pyrol.* 36, 71–80.
- Hawari, A.H., Mulligan, C.N., 2006. Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. *Bioresour. Technol.* 97, 692–700.
- Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34, 735–742.
- Johnson, P.R., Sun, N., Elimelech, M., 1996. Colloid transport in geochemically heterogeneous porous media: modeling and measurements. *Environ. Sci. Technol.* 30, 3284–3293.
- Karnitz, O., Gurgel, L.V.A., de Melo, J.C.P., Botaro, V.R., Melo, T.M.S., Gil, R.P.D.F., Gil, L.F., 2007. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresour. Technol.* 98, 1291–1297.
- Katyal, S., Thambimuthu, K., Valix, M., 2003. Carbonisation of bagasse in a fixed bed reactor: influence of process variables on char yield and characteristics. *Renew. Energy* 28, 713–725.
- Kilic, M., Keskin, M.E., Mazlum, S., Mazlum, N., 2008. Hg(II) and Pb(II) adsorption on activated sludge biomass: effective biosorption mechanism. *Int. J. Miner. Process.* 87, 1–8.
- Liu, Z., Zhang, F.S., 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *J. Hazard. Mater.* 167, 933–939.
- Lourie, E., Gjengedal, E., 2011. Metal sorption by peat and algae treated peat: kinetics and factors affecting the process. *Chemosphere* 85, 759–764.
- Lu, H.L., Zhang, W.H., Yang, Y.X., Huang, X.F., Wang, S.Z., Qiu, R.L., 2012. Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar. *Water Res.* 46, 854–862.
- Ma, L.Q., Rao, G.N., 1999. Aqueous Pb reduction in Pb-contaminated soils by Florida phosphate rocks. *Water Air Soil Pollut.* 110, 1–16.
- Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interf. Sci.* 310, 57–73.
- Neves, M.F., Trombin, V.G., Consoli, M.A., 2010. Measurement of sugarcane chain in Brazil. *Int. Food Agribus. Man.* 13, 37–54.
- Noeline, B.F., Manohar, D.M., Anirudhan, T.S., 2005. Kinetic and equilibrium modelling of lead(II) sorption from water and wastewater by polymerized banana stem in a batch reactor. *Sep. Purif. Technol.* 45, 131–140.
- Qiu, Y.P., Cheng, H.Y., Xu, C., Sheng, D., 2008. Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. *Water Res.* 42, 567–574.
- Rao, M.M., Rao, G.P.C., Seshiah, K., Choudary, N.V., Wang, M.C., 2008. Activated carbon from Ceiba pentandra hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions. *Waste Manage.* 28, 849–858.

- Sublet, R., Simonnot, M.O., Boireau, A., Sardin, M., 2003. Selection of an adsorbent for lead removal from drinking water by a point-of-use treatment device. *Water Res.* 37, 4904–4912.
- Sud, D., Mahajan, G., Kaur, M.P., 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - A review. *Bioresour. Technol.* 99, 6017–6027.
- Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. ASCE* 89, 31–59.
- Xu, X.Y., Cao, X.D., Zhao, L., 2013. Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: role of mineral components in biochars. *Chemosphere* 92, 955–961.
- Zhang, W.H., Mao, S.Y., Chen, H., Huang, L., Qiu, R.L., 2013. Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. *Bioresour. Technol.* 147, 545–552.