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Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH

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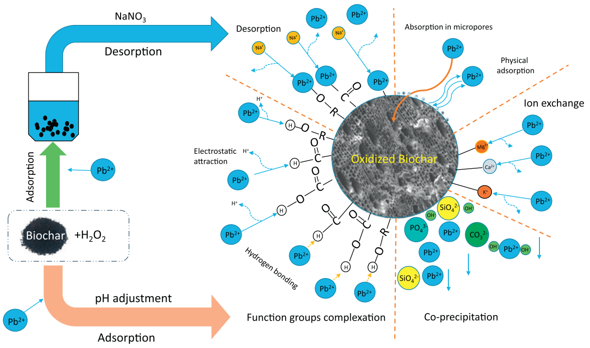
HIGHLIGHTS

- Adsorption is largely affected by oxygen-containing surface functional groups and pH.
- Oxidation increases the affinity of Pb(II) to biochar and decreases the desorption in water.
- Pb(II) adsorption is not fully reversible using $NaNO_3$ irrespective of oxidation.
- Oxidized biochar has the potential for Pb(II) immobilization.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of biochar for the removal of heavy metals from water has environmental benefits. In order to elucidate the potential application of highly functionalized biochar for the removal of Pb(II) in aqueous solution, maple wood biochar was oxidized using hydrogen peroxide. The pH values of oxidized biochar ranged from 8.1 to 3.7, with one set being adjusted to a pH of 7 as a comparison. It was found that oxidizing the biochars increased their Pb(II) adsorption capacity if the pH remained below 6 (strong oxidation), but decreased their Pb(II) adsorption ability above pH 6 (weak oxidation). After adjusting the pH of oxidized biochar to pH 7, the Pb(II) adsorption capacity further increased two to sixfold for oxidized biochars originally at pH 3.7–6. The adsorption characteristics of Pb(II) were well described by the Langmuir equation. Adsorption of Pb(II) was not fully reversible in water. Less than 6% of Pb(II) desorbed in water in two consecutive steps than was previously adsorbed, for biochars with a pH below 7, irrespective of oxidation. Recovery using an extraction with 0.1 M $NaNO_3$ increased from 0.7% to 32.7% of Pb(II) undesorbed by both preceding water extractions with increasing oxidation, for biochars with a pH below 7. Unextractable Pb(II) was lower at low oxidation but increased to 99.0% of initially adsorbed amounts at low pH, which indicated that the adsorption of Pb(II) on oxidized biochar is pH independent.

1. Introduction

Water pollution caused by heavy metals poses a major threat worldwide with a cumulative, chronic and harmful effect on the environment

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and human health (Fu and Wang, 2011). Toxic elements such as lead, cadmium, chromium, and nickel are classified as heavy metals and are associated with water pollution. Among these heavy metals, Pb(II) is considered to be one of the most toxic elements to humans and can be found at high concentrations in liquid industrial waste (Abdel-Halim et al., 2003). Lead enters the human body through the water and food chains, causing respiratory, digestive, nervous, blood, urinary and immune system symptoms of acute or chronic poisoning, and even death (Järup, 2003). Different processing techniques have been adopted to treat heavy metals pollution, such as precipitation, flotation, ion exchange, solvent extraction, cementation onto iron, membrane filtration, chemical oxidation, coagulation, flocculation and electrochemical treatment (Fu and Wang, 2011; Hua et al., 2012). Compared with other techniques, adsorption of heavy metal ions onto solid materials has been found to be advantageous in treating wastewater due to its simplicity, making it often the most economical solution (Bailey et al., 1999; Cao et al., 2011).

Biochar refers to a carbonaceous organic matter prepared by pyrolysis of biomass in a closed system under oxygen-limited conditions (Laird, 2008; Lehmann and Joseph, 2009). Because of its negative surface charge, charge density, high degree of porosity, and extensive surface area, biochar has been considered as a low-cost material with sufficient suitability and selectivity for removal of toxic heavy metal ions in various aqueous environments (Saeed et al., 2005; Liu and Zhang, 2009; Chen et al., 2011; Venkata Ramana et al., 2012; Hina, 2013; Tan et al., 2015). Biochar application to water has been shown to increase heavy metal immobilization through electrostatic and non-electrostatic forces (Xu and Zhao, 2013; Kim et al., 2015). However, untreated biochars usually have a relatively low ability to adsorb cations compared to activated carbon or engineered biochar (Takaya, 2016). Therefore, biochar modification may become more common in the future (Ahmed et al., 2016; Rajapaksha et al., 2016; Wang et al., 2017).

Currently, different biochar modification/activation technologies have been developed to improve its adsorption capacity (Shen et al., 2015; Rajapaksha et al., 2016; Trakal et al., 2016). These methods include chemical, physical and magnetic modification methods (Ahmed et al., 2016; Rajapaksha et al., 2016). Different modification methods have different advantages and disadvantages depending on the purpose of application. Chemical modification can alter the surface chemistry of biochar, thereby leading to enhanced sorption capacity compared with pristine biochar. Hydrogen peroxide (H_2O_2), as a strong and clean oxidant, has been shown to increase oxygen-containing functional groups on the surface of biochar and enhance its ability to remove heavy metals from wastewater (Xue et al., 2012; Huff and Lee, 2016). Previous studies have examined adsorption kinetics on H_2O_2-modified biochar (Xue et al., 2012; Fang et al., 2014; Huff and Lee, 2016). However, few data are available on pH effects and recovery of heavy metal adsorption of oxidized biochars.

Oxidation is an important process controlling the quality of biochars in the environment (Cheng et al., 2008; Qian and Chen, 2014). Oxidation introduces carboxylic and other oxygen-containing functional groups to biochar surfaces that may serve as binding sites for heavy metals. There are several ways that heavy metals interact with biochars including ion exchange, covalent bonding, surface complexation, and precipitation (Tan et al., 2015; Trakal et al., 2016). All these processes could change with pH which plays an important role in elemental solubility in soils/water (Beesley and Marmiroli, 2011). Therefore, it is unclear how the change of pH due to oxidation affects the Pb(II) adsorption capacity of oxidized biochar.

Results from our previous study show that oxidized biochar has significantly greater adsorption and retention of ammonium after neutralization, indicating that pH plays a key role in this process (Wang et al., 2015). Based on this consideration, we investigate if such a pH effect also exists in heavy metal adsorption so as to provide guidance for biochar technology used in sewage treatment. Heavy metals adsorbed by negatively charged organic functional groups on biochar surfaces should be fully desorbable (Rauret, 1998). Results of desorption of heavy metals from peanut biochar showed almost complete desorbability with HCl (Saeed et al., 2005). However, it is not clear whether oxidation of biochar surfaces would change this high desorbability, which would implicate other processes in addition to electrostatic adsorption in the retention mechanism.

The objectives of this study were (i) to quantify the extent to which biochars should be oxidized to increase their Pb(II) retention; (ii) assess the affinity of Pb(II) to oxidized biochar surfaces with increasing oxidation; and (iii) investigate whether Pb(II) adsorption to oxidized surfaces is fully reversible. We hypothesized that (i) oxidation using strong oxidants increases the affinity of Pb(II) to biochar and decreases desorption in water, and (ii) Pb(II) adsorption is not fully reversible using $NaNO_3$ irrespective of oxidation.

2. Experimental methods and materials

2.1. Preparation of biochar

The collection, handling, and pyrolysis conditions of the studied biochars are described in detail by (Wang et al., 2015). Briefly, maple wood biochars (20% sugar maple, 80% red maple) which were pyrolyzed at 500 °C using a modified muffle furnace (Thermo Scientific, Waltham, MA, USA) under argon atmosphere (sweep of 1 L min^{-1}), were ground and sieved to obtain a uniform particle size between 149 and 850 μm. In order to obtain biochars with different pH values, the biochars were oxidized using different concentrations of H_2O_2 as well as different exposure times at 30 °C, in comparison to deionized water (DIW) for 100 h. All samples were prepared using a solid-to-liquid ratio of 1:10 (w/v). Biochar was exposed to oxidant (at 33–35 °C) for 15 min (30% H_2O_2), 45 min (15% H_2O_2), 6 h (30% H_2O_2), 110 h (30% H_2O_2), 350 h (30% H_2O_2) and 100 h in DIW, respectively. Their physical and chemical properties are described in (Wang et al., 2015).

Surface morphology of biochars after water oxidization and washing with water was examined with a scanning electron microscope (SEM) (JSM-6460 LV Scanning Microscope (JEOL, Tokyo, Japan). Surface morphologies of the untreated and oxidized maple wood biochars are shown in Fig. 1. The surface functional groups of the biochars before and after oxidation were determined using a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer (Thermo Fisher Scientific, USA). Infrared spectra were obtained at room temperature in the spectral range from 400 cm^{-1} to 4000 cm^{-1}.

2.2. Adsorption experiments

Batch adsorption experiments were conducted in 50 mL PE centrifuge tubes at room temperature. Stock solutions (1000 mg L^{-1}) of Pb (II) were prepared by dissolving analytical grade $Pb(NO_3)_2$ in ultrapure water (>18.2 MΩ cm). Adsorption experiments were conducted by mixing 0.1 g of biochar with 20 mL of 50 mg L^{-1} Pb(II). The tubes were then agitated on a reciprocating shaker at room temperature at 120 rpm for 24 h. After 24 h, the solid and liquid phases were separated by centrifugation at 3000 rpm for 15 min, and the supernatant was carefully aspirated using a Pasteur pipette. The supernatant was acidified immediately with 0.2% (v/v) HNO_3 for analysis. To obtain the sorption isotherms, solutions of various Pb(II) concentrations (5, 30, 50, 150, 250, 400, 550 mg L^{-1}) were shaken with the adsorbent for 24 h. At the end of each experiment, the mixtures were immediately acidified and Pb(II) concentrations in the supernatant were determined. The concentrations of initial and final Pb(II) in the adsorption experiments were determined using atomic absorption spectrometry (AAS, Buck Scientific Model 200). All experiments were conducted in triplicate including the blank and calibration control.

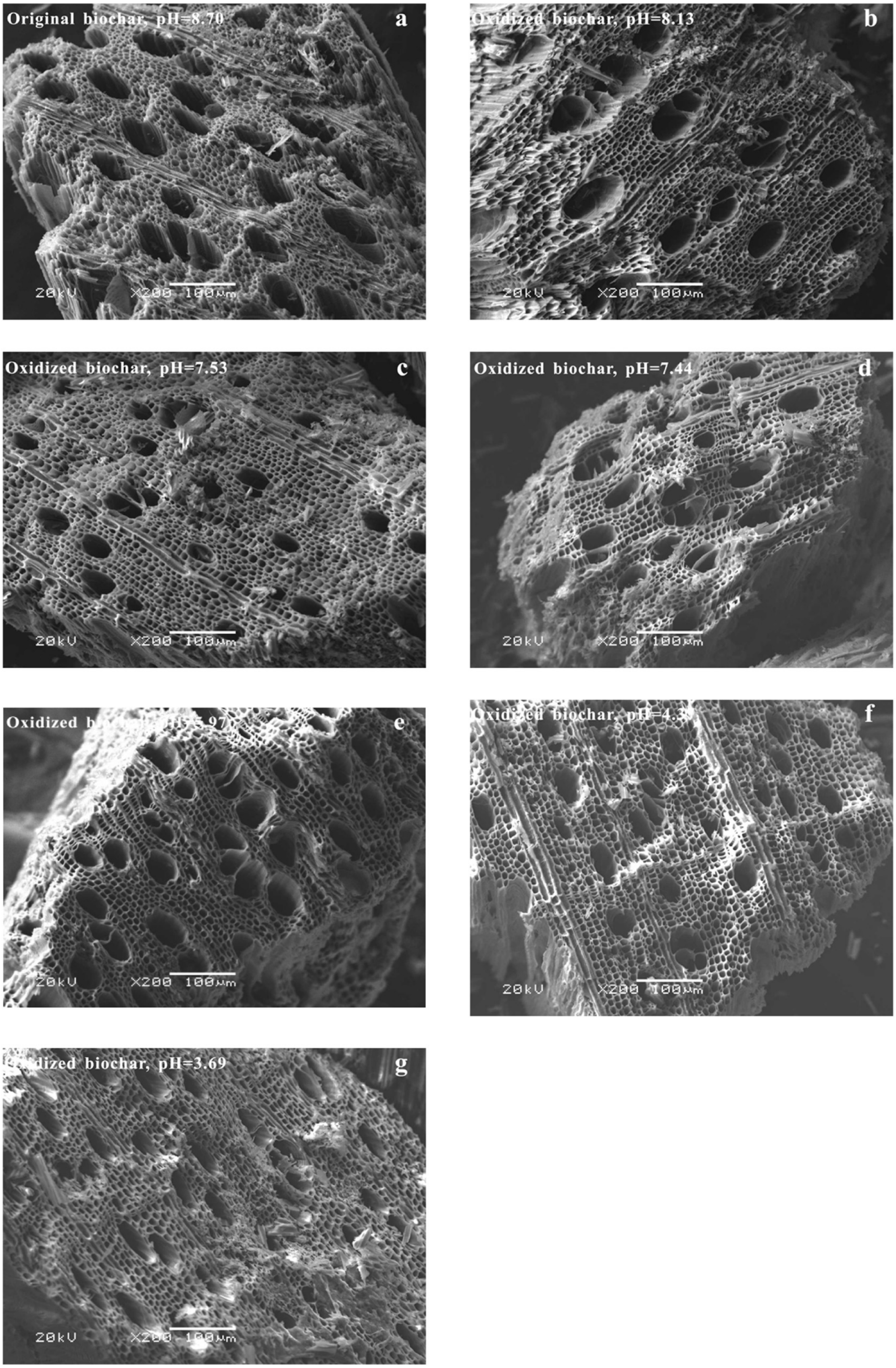

Fig. 1. Scanning electron microscope (SEM) images showing macroporosity of maple wood-derived biochars before and after oxidation using H_2O_2 at the different duration of exposure. The biochar samples were imaged with a beam energy of 20 kV on a JSM-6460LV SEM.

2.3. Desorption experiments

Desorption experiments were carried out to investigate if biochar adsorption of Pb(II) was reversible and evaluated the Pb(II) immobilization ability of biochar. Both water and $NaNO_3$ solution were used to examine the desorption of lead. After the adsorption, the solution remaining in the tubes was decanted and 20 mL of ultrapure water which was prepared by a MINI-Q pure water purifier was added as described in the adsorption experiment above. This procedure was repeated twice, generating two desorption steps. Pb(II) concentration in the supernatant was determined within 24 h by using atomic absorption spectrometry (AAS, Buck Scientific Model 200).

2.4. $NaNO_3$ extraction experiments

After desorption with ultrapure water, all the liquids in the tubes were decanted and 20 mL 0.1 M $NaNO_3$ were added into the centrifuge tubes to extract the absorbed heavy metals from the biochar. This procedure was repeated once as mentioned above for the desorption using initial concentrations of 50 mg L^{-1} Pb(II) solution.

2.5. Data analyses

Adsorption data were fitted to both Freundlich and Langmuir isotherm models using the following equations:

$$\text{Langmuir isotherm}: q_e = Q_o k_L C_e / (1 + k_L C_e) \tag{1}$$

$$\text{Freundlich isotherm}: q_e = k_f \cdot {C_e}^{1/n} \tag{2}$$

where q_e (g kg^{-1}) is the adsorption capacity; C_e (mg L^{-1}) is the equilibrium concentration after the adsorption or desorption; 1/n (dimensionless) is the intensity of adsorption or affinity; k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) is the Freundlich constant; Q_o (g kg^{-1}) is the maximum sorption capacity; k_L (L mg^{-1}) is a Langmuir constant. The data were fitted to these equations using non-linear regression and the goodness of fits, the sum of squares (R_{sqr}) associated with the model results were calculated using SigmaPlot 12.5 (SAS, Cary, NC).

3. Results and discussion

3.1. Characterization of the biochars

The physical and chemical properties of both oxidized and unoxidized biochars are described in our previous work (Wang et al., 2015). Surface morphology of the maple wood-derived biochars and their oxidized biochars is shown in Fig. 1. As illustrated in Fig. 1a–g, the surface morphology of maple wood-derived biochar was changed after H_2O_2 oxidation. Remarkably, oxidation did not only change the micropore surface area and micropore volume but also affected the ratio of micropores to mesopores, as confirmed by the specific surface area decreasing from 257 (Fig. 1a) to 225 m^2 g^{-1} (Fig. 1g) (Han et al., 2013; Wang et al., 2015). This indicated that micropore structure and chemical composition may vary among different oxidized biochars. As shown in Fig. 2, the FTIR spectra of pristine and oxidized biochars indicated changes in the carboxyl and hydroxyl groups. The primary changes of the FTIR spectra between the pristine biochar and oxidized biochar occurred at around 1634 cm^{-1} and 1315 cm^{-1}. The peaks at 1634 and 1315 cm^{-1} corresponded to carbonyl groups, which increased with oxidation, consistent with previous studies (Xue et al., 2012; Huff and Lee, 2016). Additionally, the peak around 1580 cm^{-1} is indicative of C═C stretching of the aromatic carbons of biochar. With an increase in oxidation, this peak gradually decreased, due to oxidized functional groups becoming proportionally more important.

3.2. Adsorption isotherms and pH effects

3.2.1. Adsorption isotherms

In the study of adsorption behavior, solutions of various Pb(II) concentrations (5, 30, 50, 150, 250, 400, 550 mg L^{-1}) were shaken with the adsorbent for 24 h. Longer contact times did not show significant changes in equilibrium concentration as the adsorption phase had already reached equilibrium. The Freundlich and Langmuir equations are the most commonly used models for describing adsorption isotherms. The Langmuir model assumes that adsorptions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions and is used successfully in many monolayer adsorption processes. The Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface and multilayer sorption. Although the Langmuir and Freundlich models cannot provide conclusive proofs of the adsorption mechanisms, they are commonly used in the literature as an indirect tool to interpret isotherms to better understand the adsorption processes (Xue et al., 2012; Ifthikar et al., 2017). Table 1 shows that the adsorption isotherms are better described by the Langmuir model, suggesting that the adsorption process might be monomolecular. For the Freundlich constant, 1/n is the concentration index, which represents the degree of linearity of the isotherm. The 1/n constants of both biochar and oxidized biochar are <1, suggesting that the adsorption process might be an easy and fast adsorption process.

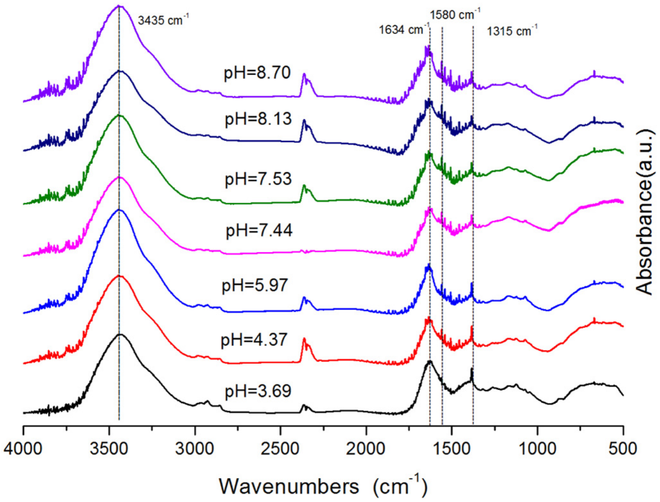

Fig. 2. FTIR spectra of biochar before and after oxidation.

The maximum adsorption capacity Q_o reached 43.3 g kg^{-1} for the greatest oxidation after pH adjustment, in comparison to 1.38 g kg^{-1} for the weakly oxidized or unoxidized biochars (Table 1). The reason for this difference was that the oxidized biochar had more oxygen-containing functional groups than the weakly oxidized or unoxidized biochar. After pH adjustment, the carboxyl and phenolic groups at low pH were deprotonated, and the negatively charged organic functional groups became the main adsorption sites of Pb(II). The adsorption capacities in this study were comparable with other studies using carbon

Table 1
Fitted parameter values using different adsorption isotherm models for the adsorption of Pb(II).

pH of oxidized biochar	Langmuir adsorption model			Freundlich adsorption model		
	Q_o (g kg^{-1})	k_L	R_{sqr}	k_f	1/n	R_{sqr}
pH = 3.69	10.7	0.500	0.975	4.232	0.221	0.968
pH = 4.37	5.92	1.480	1.000	3.054	0.177	0.912
pH = 5.97	2.92	2.705	0.950	1.432	0.217	0.991
pH = 7.44	3.41	0.269	0.986	1.060	0.304	0.924
pH = 7.53	3.28	0.611	1.000	1.288	0.263	0.976
pH = 8.13	4.36	0.474	0.984	1.420	0.328	0.996
pH = 3.69 → 7.00	43.3	0.269	0.941	13.811	0.231	0.831
pH = 4.37 → 7.00	13.8	2.400	0.930	6.282	0.186	0.942
pH = 5.97 → 7.00	6.84	2.750	0.998	3.865	0.198	0.881
pH = 7.44 → 7.00	2.73	0.220	0.972	0.693	0.359	1.000
pH = 7.53 → 7.00	2.38	0.308	0.954	0.898	0.240	0.875
pH = 8.13 → 7.00	1.38	0.308	0.991	0.554	0.221	0.955

Q_o: maximum adsorption capacity; k_L: Langmuir constant; k_f: Freundlich adsorption constant; 1/n: intensity of adsorption or affinity.

materials or other adsorbents (Table 2). Compared with other adsorbents, the oxidized biochar exhibited superior Pb(II) adsorption capacity, which reached a considerable level compared to carbon nanotubes, and in some cases even higher compared to activated carbon (Kadirvelu et al., 2000; Li et al., 2002). In comparison to nanotubes or activated carbons, biochars are less expensive to produce, which suggests that maple wood biochars prepared under oxidation and pH adjustment may have an economic advantage for the removal of Pb(II) from aqueous solutions.

3.2.2. Oxidation and pH effects

Generally, Pb(II) adsorption onto biochars strongly depends on pH. The effect of pH can be explained by the surface charge of the biochars. With increasing oxidation and a consequent lowering of pH, the Pb(II) adsorption capacity remained almost unchanged when the pH was above 7, but increased Pb(II) adsorption from 2.92 g kg^{-1} to 10.69 g kg^{-1} was observed for biochars at pH below 6 (Fig. 3a). The fact that Pb(II) adsorption did not increase with oxidation when the pH was above 7 can be explained by the formation of soluble hydroxyl complexes or surface precipitation. By increasing the pH value, the deprotonation of functional groups provided the opportunity to coordinate with Pb(II) ions. However, neutralizing the oxygen-containing surface functional groups on oxidized biochar increased the Pb(II) adsorption capacity, the most strongly oxidized biochar increased adsorption more than forty-fold after pH adjustment (Fig. 3b). Several mechanisms could be invoked to explain the interactive effects of oxidation and pH on Pb(II) sorption/desorption behavior of biochar, which included ion exchange with Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, surface complexation with carboxyl functional groups and surface precipitation with CO_3^{2-}, PO_4^{3-} and SiO_4^{2-} (Ifthikar et al., 2017).

Pb(II) adsorption was nearly unchanged at low Pb(II) concentrations with increasing oxidation, irrespective of pH adjustment. However, Pb (II) adsorption capacity decreased first from pH 8.13 to 5.97 and then increased from pH 5.97 to 3.69 at high concentration of Pb(II). The lowest adsorption appeared at pH 5.97 (Fig. 4a). The reason for this is hydroxide or carbonate precipitation at higher pH (Tünay and Kabdaşli, 1994). The higher degree of oxidation formed more oxygen-containing functional groups on the biochar surface resulting in a lower pH. Therefore, the Pb(II) adsorption capacity at lower pH was higher than that at higher pH. On the other hand, adjusting the pH to a common pH of 7, caused a significant increase in adsorption with increasing oxidation (Fig. 4b). The reason for this was that after pH adjustment, carboxyl and phenolic groups at low pH were deprotonated and the negatively charged organic functional groups became the main adsorption sites for Pb(II) (Brady and Weil, 2008).

3.3. $NaNO_3$-extractable Pb(II) and total Pb(II) recovery

The proportion of $NaNO_3$-extracted Pb(II) for biochars with an initial addition of 50 mg L^{-1} without pH of biochar adjustment ranged from 14% to 59% of Pb(II) undesorbed by the two preceding water extractions. This was higher than the proportion of 0.67–41% of Pb(II) undesorbed when the pH of biochar was adjusted (Fig. 5). In general, with increasing pH of biochar, more Pb(II) was extracted irrespective of pH of biochar adjustment.

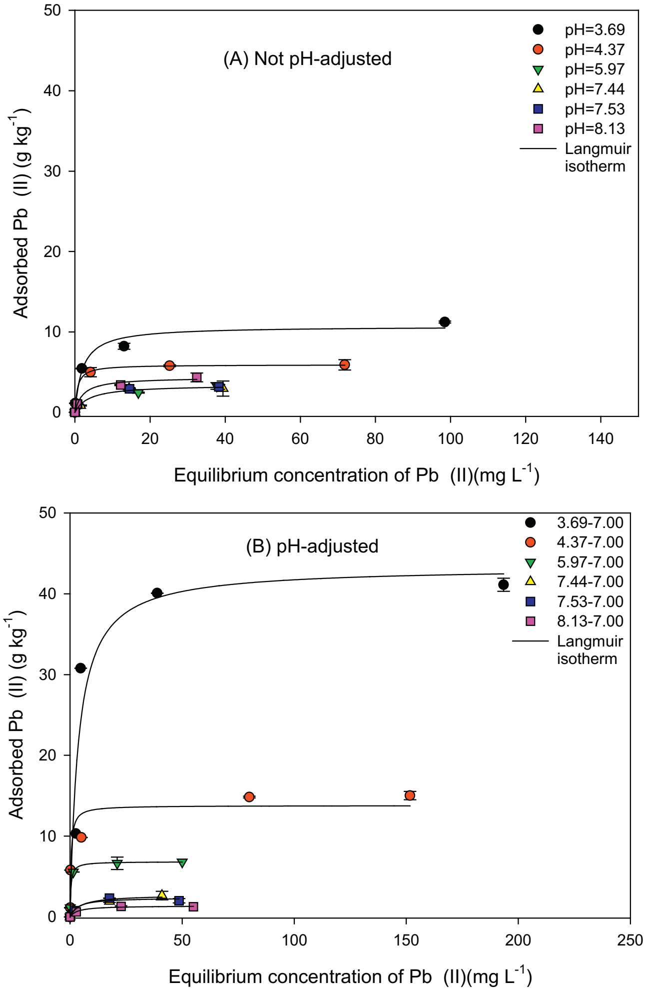

Fig. 3. Adsorption isotherms of Pb(II) at pH values (not pH-adjusted and pH-adjusted) after oxidation. Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars. C_{eq} is the equilibrium concentration of Pb(II) in aqueous solution (mg L^{-1}). Initial Pb(II) concentration 5–250 mg L^{-1}, contact time 24 h, dose 100 mg/20 mL.

Compared with the Pb(II) adsorption in water, the Pb(II) desorption in water was very low for the biochar with a pH of biochar below 7, accounting for <6% of adsorbed Pb(II) if the pH of biochar was not adjusted and <0.91% if the pH of biochar was adjusted (Fig. 6). Both pH-adjusted biochars, as well as pH not-adjusted biochars, have significant Pb(II) retention potential, indicating that biochar has a strong affinity for Pb(II).

Table 2
Comparison of the Pb(II) adsorption capacities of oxidized biochar and different absorbents.

Adsorbent	Temperature (°C)	pH of solution	Adsorption capacities (g kg^{-1})	References
Biochar from maple wood	25	–	43.3	This study
Biochars from pine wood	25	5.0	3.89	(Liu and Zhang, 2009)
Biochar from rice husk	25	5.0	1.84	(Liu and Zhang, 2009)
Pigeon peas hulls	20	4.0	20.83	(Venkata Ramana et al., 2012)
Modified hydrochar from peanut hull	22	–	22.82	(Xue et al., 2012)
Modified cotton	20	–	69.5	(Ding et al., 2014)
Carbon nanotubes	Room T	5.0	17.44	(Li et al., 2002)
Sweetgum biochar supported with GO	22	–	40	(Liu et al., 2016)
Activated carbon	20	5.0	30.46	(Kadirvelu et al., 2000)
Biochar from digested sugarcane bagasse	22	–	132.9	(Inyang et al., 2011)

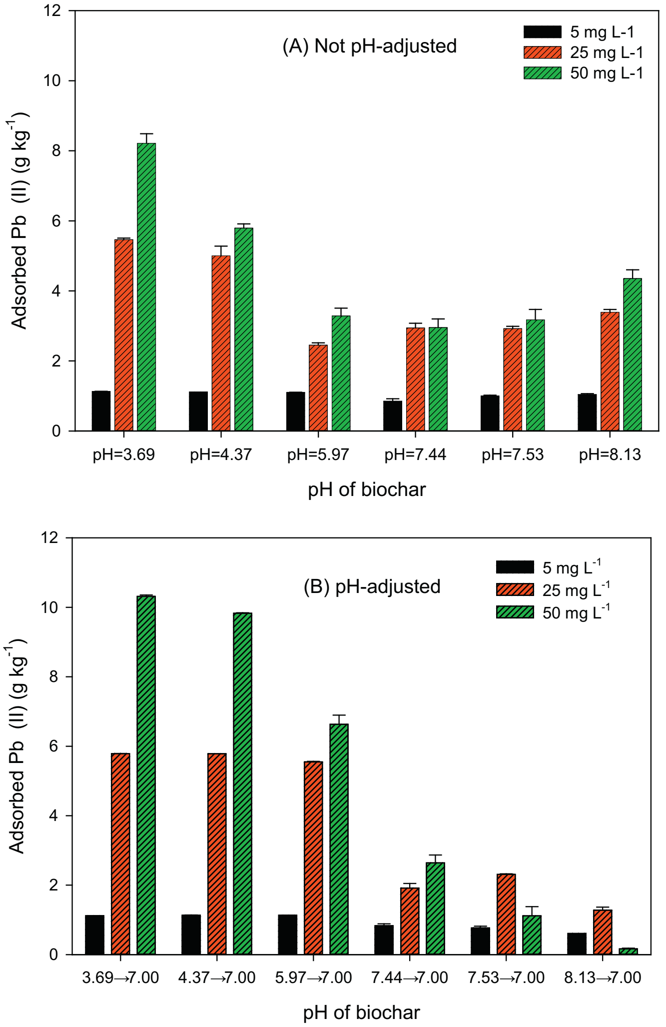

Fig. 4. Effect of biochar pH on the adsorption of Pb(II). Initial Pb(II) concentration 5, 25, 50 mg L^{-1}, contact time 24 h, dose 100 mg/20 mL.

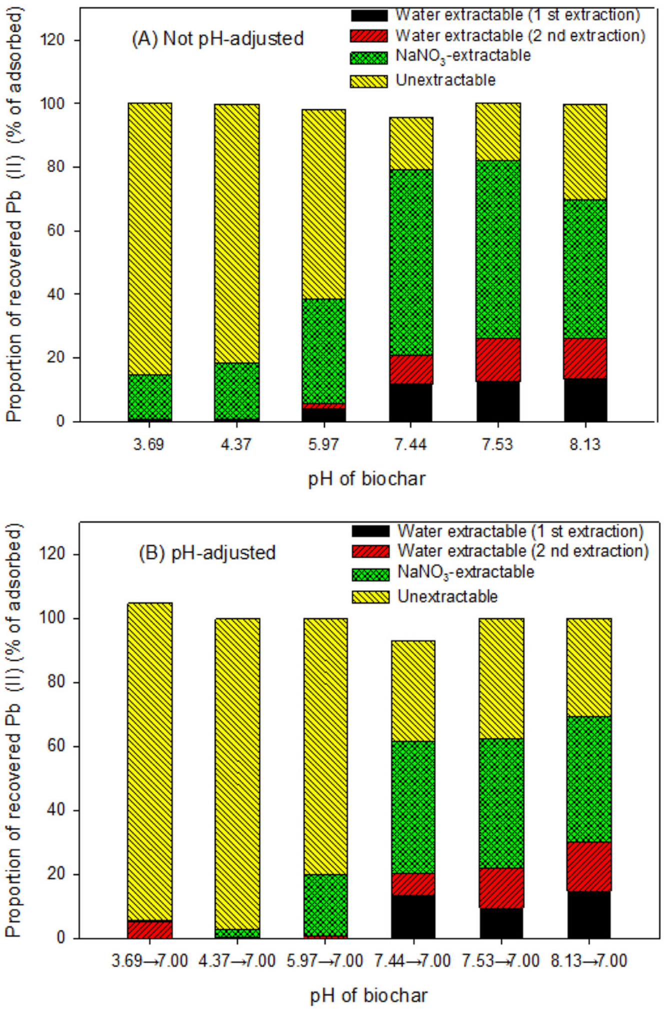

Fig. 6. Proportion of recovered Pb(II) in relation to pH values (with biochars either not pH-adjusted or pH-adjusted) after oxidation only for biochars with an initial Pb(II) concentration of 50 mg L^{-1}.

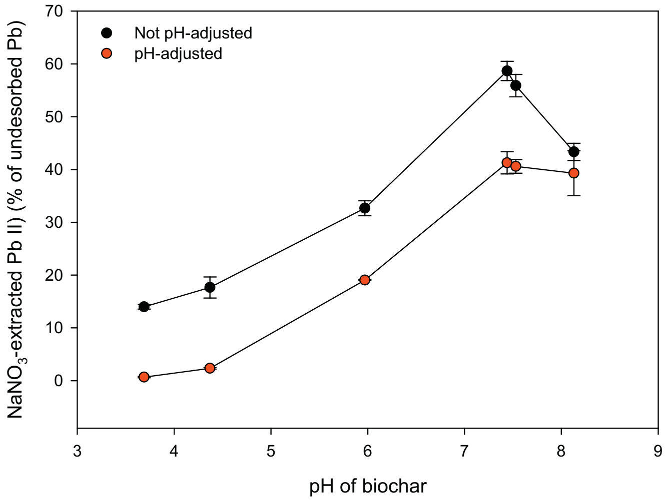

Fig. 5. Extracted Pb(II) usingNaNO$_3$ as a proportion of adsorbed Pb(II) not being desorbed by water for biochars either not pH-adjusted (A) or pH-adjusted (B) only for the initial Pb (II) concentration of 50 mg L^{-1}. Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars.

The incomplete recovery of the remaining adsorbed Pb(II) (after both water extractions; Figs. 5 and 6) by NaNO$_3$ conforms with expectations that biochar application reduced Pb(II) availability to plants. At lowest oxidation, irrespective of pH of biochar adjustment, NaNO$_3$ extraction only recovered another 41–89% of previously adsorbed Pb(II). This incomplete recovery of adsorbed Pb(II) in the biochar after all extractions could be explained by surface complexation reactions (Namgay et al., 2010). Our study, therefore, suggests that this often observed incomplete extraction using NaNO$_3$ may be a result of strong bonds to biochar surfaces that would make adsorbed Pb(II) unavailable to plants.

4. Conclusions

Oxidation using strong oxidants increased the affinity of Pb(II) to biochar and decreased its desorption in water. Neutralizing the ensuing acidity dramatically increased Pb(II) retention. The Pb(II) adsorption process was pH independent and not fully reversible using NaNO$_3$ irrespective of oxidation. This may indicate that oxidized biochar has the potential for Pb(II) immobilization and passivation and open up possible utility of chemical oxidation of biochars for practical applications for Pb(II) contamination. Further studies including its application in soils are necessary to explore the competitive adsorption of heavy metals.

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