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**Graphical Abstract**

Lead on high temperature rice straw biochars is generally more stable
Higher temperature biochars remove Pb faster and have higher removal capacity.

Precipitation was a mechanism by which all three biochars immobilized Pb.

RSB300 has 11.34% of total immobilized Pb attributed to the exchangeable fraction.

Exchangeable Pb was less than 1% on RSB500 and RSB700.

High temperature rice straw biochars may be more suitable for soil remediation.
Effect of production temperature on lead removal mechanisms by rice straw biochars

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Abstract: Production temperature significantly affects biochar properties and consequently the removal mechanisms of heavy metals. In this study, rice straw biochars were produced at 300, 500 and 700 °C (RSB300, RSB500 and RSB700). The influence of production temperature on the adsorption characteristics and removal mechanisms of lead on this set of rice straw biochars were investigated by batch adsorption tests, micro-structural analyses and sequential metal extractions. Biochars produced at higher temperatures had significantly higher pH values and surface areas, resulting in higher metal removal capacities and faster uptake kinetics. Precipitation was a key mechanism for lead removal from solution for all biochars: lead oxalate was precipitated on RSB300, and hydrocerussite was precipitated on RSB500 and RSB700. The immobilized lead fraction on the biochars could be divided into exchangeable, acid soluble and non-available fractions. RSB300 had 11.34% of the total immobilized Pb attributed to the exchangeable fraction, whereas for RSB500 and RSB700, it was less than 1%. Immobilized Pb on RSB500 and RSB700 was almost exclusively attributable to the acid soluble and non-available fractions (>99%). Based on our results, RSB500 and RSB700 are likely much more appropriate for soil remediation of Pb as compared with RSB300.

Keywords: soil remediation, biochar, lead immobilization, adsorption, precipitation, production temperature
Soil contamination is becoming an increasing threat to human health in China.

Polluted agricultural land (19% of total sampling points in China’s national soil survey) may produce crops with elevated heavy metals concentrations, which may enter into the human body through ingestion and ultimately damage organ systems (Zhao et al., 2015; Hou and Li, 2017). For these reasons, there is an urgent need to seek effective and sustainable technologies to remediate contaminated agricultural land (Hou and Al-Tabbaa, 2014). Biochar is regarded as a promising material that can reduce the bioavailability/mobility of heavy metals after its addition into contaminated soils (Sohi, 2012). In addition, biochar amendment can promote soil fertility and enhance crop yields, which promotes its use as a green and sustainable remediation material (Hou et al., 2017a; Zhao et al., 2017).

Extensive studies have been carried out recently, to investigate the potential application of biochar in remediation of heavy metal contaminated soils (O’Connor et al., 2018b). Biochar reduces the bioavailability/mobility of heavy metals in soils through various mechanisms, including: physical adsorption, cation exchange, electrostatic interaction, precipitation and complexation (Inyang et al., 2015). Heavy metals immobilized on biochar in soils via these various mechanisms result in different mobility and environmental risks. Physically adsorbed and exchangeable heavy metals on biochar are readily bioavailable and pose immediate risks to the environment (Shen et al., 2017). The stability of the metals immobilized on biochar through electrostatic interaction and precipitation depends on environmental
conditions. For instance, they may be stable in the short term; however, if the environmental conditions change (e.g., significant reduction of soil pH), they may be desorbed/dissolved from the biochar surface and thereby pose risks to the environment (Filgueiras et al., 2002). Complexed metals on biochar are generally regarded as stable and environmentally benign (Filgueiras et al., 2002).

For the reasons discussed above, immobilization mechanisms are very important for biochar application in soil remediation/stabilization. Although some biochars show high adsorption capacities of heavy metals, if the adsorption mechanisms are mainly physical adsorption or cation exchange, these biochars may not be suitable for soil remediation as these weakly bound metals may pose elevated environmental risks in soil. On the other hand, if the immobilization is via precipitation and/or complexation, relatively higher long-term stability is expected compared to physical adsorption and cation exchange.

The mechanisms for biochar removal of heavy metals depend on biochar chemical properties, which is significantly affected by the biochar production process (e.g., production temperature). Although a range of studies have investigated the characteristics and mechanisms of heavy metal adsorption to biochar (Shen et al., 2015; Shen et al., 2017; Shen et al., 2018b), the influence of biochar production temperature on the removal mechanisms remains unclear. It is important to link biochar production temperature and removal mechanisms of heavy metals, for optimal production and application of biochar in soil remediation.
To address this knowledge gap, rice straw biochars were produced at differing temperatures and the effect of production temperature on adsorption characteristics and immobilization mechanisms of lead on the biochars was investigated. Rice straw was selected as a feedstock due to its high availability in China, as one of the most abundant agricultural wastes (Wang et al., 2017), and lead was selected as a representative heavy metal due to its high concentrations in contaminated soils in China (Zhao et al., 2015) and high health risks (especially to children) (Shen et al., 2018a) (O'Connor et al., 2018c). The hypothesis to be verified in this study is that lead retention on the rice straw biochars produced at various temperatures will have different mechanisms, and therefore understanding these differences is critical in producing appropriate biochar for soil remediation.

2 Materials and methods

2.1 Biochar production and characterization

The rice straws used in this study were obtained from Taicang, Suzhou, China. After reception, they were oven dried at 60 °C to reach constant weight. The resulting dried feedstock was then used to produce biochars at 300, 500 and 700 °C (RSB300, RSB500 and RSB700). During production, the rice straw was pyrolyzed in a furnace (under limited air) with a heating rate of 10 °C/min and held at the target terminal temperature for 1 h. After preparation, the biochars were sieved through a #100 mesh sieve (< 0.15 mm) and stored in sealed sample bags.

The pH of the biochars was determined based on the works of Alam et al. (2018 a and
b) and von Gunten et al. (2017). Briefly, a certain amount (0.1 g) of biochar was mixed with 10 mL of deionized water and shaken at 250 rpm for 24 h. After centrifugation, the pH of the supernatant was measured. The Brunauer–Emmett–Teller (BET) surface area of the biochar was determined by a Tristar II 3020 (Micromeritics) instrument. The C, H, O, N contents of biochar were tested using a CE-440 Elemental Analyzer (Perkin Elmer).

The fundamental vibrations and associated rotational-vibrational structure of the biochars were tested using a VERTEX 70v Fourier-transform infrared spectroscopy (FT-IR) spectrometer (BRUKER) between wavenumbers 4000 to 600 cm$^{-1}$. The crystalline phases in the biochar were examined using a D8 ADVANCE X-ray diffractometer (XRD) (Bruker). To do so, dry samples were mounted on a flat holder and examined with a Cu K$\alpha$ source operating at 40 kV and 40 mA, emitting radiation at a wavelength of 1.5406 Å. The scanning regions were between 2θ values of 10-60° at a step rate of 0.1 s/step and a resolution of 0.01°/step. The surface morphology of the biochars (coated with Pt) was tested using a SU8010 Ultra-High Resolution (1.0 nm) Scanning Electron Microscope (SEM) (Hitachi, Japan).

2.2 Adsorption tests

Batch adsorption tests were carried out to reveal the characteristics of Pb adsorption on the rice straw biochars. In order to assess the adsorption kinetics, a certain amount of biochar (0.1 g) was added to 20 mL solution of 5 mM Pb(NO$_3$)$_2$ containing 0.01 M NaNO$_3$ (for a relatively stable solution ionic strength) in 50-mL polyethylene tubes.
The mixtures were shaken at 250 rpm for 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 6 h, 12 h, 18 h or 24 h in a temperature-controlled shaker (SHA-CA, Kexi Instrument CO., Ltd.). After the designated shaking time, a mixture was filtered through a 0.45 μm membrane. The Pb concentration in the collected filtrate was measured by inductively coupled plasma/optical emission spectrometry (ICP-OES) (Perkin-Elmer, Optima 8300) after dilution (if necessary) and acidification. The kinetics tests confirmed that the equilibrium adsorption time for all biochars was less than 24 hours.

In order to construct a sorption isotherm for each biochar, 0.1 g of biochar was added to 20 mL solutions containing different Pb concentrations (0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10 or 20 mM) and 0.01 M NaNO₃. The mixture was shaken at 200 rpm for 24 h to reach equilibrium before filtration and ICP-OES testing as described above.

Pseudo first order, pseudo second order and intraparticle diffusion models are three of the most commonly used kinetics models to reveal the time-dependence of adsorption (Cui et al., 2016; Inyang et al., 2011), and were used to simulate the kinetics data:

\[ q_t = q_e (1 - e^{-k_1 t}) \]  
(1)

\[ q_t = \frac{k_2q_e^2t}{1+k_2q_e^2t} \]  
(2)

\[ q_t = k_i t^{0.5} + C \]  
(3)

where \( k_1 \) (h⁻¹) is the rate constant of pseudo first order adsorption, \( k_2 \) (g/mg h) is the pseudo second order rate constant, and \( k_i \) (mg/g h⁻⁰.⁵) is the coefficient of intraparticle diffusion. In equation (2), \( q_e \) (mg/g) is the equilibrium adsorption capacity, and \( q_t \) (mg/g)
in each equation is the adsorbed Pb at time $t$.

Langmuir and Freundlich models are two of the most commonly used isotherm models and were used to describe the equilibrium sorption data (Foo and Hameed, 2010):

$$q_e = \frac{Q_{\text{max}} b C_e}{1 + b C_e}$$  \hspace{1cm} (4)$$

$$q_e = K_f C_e^{1/n}$$  \hspace{1cm} (5)

where $Q_{\text{max}}$ (mg/g) is the maximum monolayer adsorption capacity, $b$ is the Langmuir isotherm constant (L/mg), $K_f$ (mg/g) is the Freundlich isotherm constant, $n$ represents the adsorption intensity, $q_e$ is the adsorbed Pb (mg/g) at equilibrium and $C_e$ (mg/L) is the equilibrium Pb concentration in solution.

2.3 Mechanistic analysis

The biochar samples after Pb adsorption were tested by FT-IR and XRD to reveal the mineralogical and molecular changes, using the same testing procedure described in section 2.1. In order to investigate the fractions of immobilized Pb on the biochars, a simplified sequential extraction test was carried out (Shen et al., 2017): (1) approximately 0.1 g solid sample was extracted with 8 mL of 0.5 M MgCl$_2$ (adjust to pH 7.0 using NaOH or HCl) and shaken for 20 min at room temperature; (2) another 0.1 g solid sample was extracted with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc) and shaken for 5 h at room temperature. After shaking, the mixtures were centrifuged and the supernatants collected and filtered through 0.45 μm membranes, and then tested for Pb concentrations by ICP-OES test after dilution (if necessary).
and acidification. The exchangeable Pb on biochar can be calculated from extraction (1); the exchangeable + acid soluble Pb on biochar can be calculated from extraction (2), and therefore the acid soluble Pb can be obtained by subtracting (1) from (2) (Shen et al., 2017). The stable Pb on biochar can be calculated by subtracting the exchangeable and acid soluble Pb from the total adsorbed Pb (obtained from the adsorption studies).

2.4 Statistical analysis

The pH, adsorption and sequential extraction tests were conducted in duplicates, and the mean and standard deviation was reported for each experiment. The micro-structural and other tests were conducted once, and so no statistical analysis appears for these measurements.

3 Results and discussion

3.1 Biochar characterization

<table>
<thead>
<tr>
<th>Table 1 Characteristics of the rice straw biochars</th>
</tr>
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<tbody>
<tr>
<td></td>
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<tr>
<td>---</td>
</tr>
<tr>
<td>Yield</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
</tr>
<tr>
<td>Average pore size (nm)</td>
</tr>
</tbody>
</table>
Biochar properties are shown in Table 1. Biochar yield decreases as production temperature increases, however the decreases diminished at high temperatures (from 500 to 700 °C), because most of the volatile components had been removed at lower temperatures (Zhao et al., 2017). RSB300 is slightly alkaline with a pH of 7.89. In comparison, higher production temperature for RSB500 and RSB700 results in much higher pH values (10.40 and 10.68), because higher production temperature leads to the decomposition of acidic functional groups (e.g., carboxyl and phenol) of biochar and the formation of alkaline minerals (e.g., K₂O) (Dodson, 2011). The carbon content of the three biochars were all near 45%. In contrast, H, N, and O contents in the biochars all decreased with increasing production temperature due to the loss of the volatile component and dehydration of organic compounds (Zhao et al., 2017). Correspondingly, H:C and O:C of the biochars decreased with increasing production temperature, suggesting the surface of the biochars were more aromatic and less hydrophilic (Zhao et al., 2017).

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>44.66 ± 0.14</td>
<td>3.06 ± 0.01</td>
<td>1.62 ± 0.02</td>
<td>19.29 ± 0.53</td>
</tr>
<tr>
<td></td>
<td>44.53 ± 0.36</td>
<td>1.88 ± 0.01</td>
<td>1.35 ± 0.02</td>
<td>9.75 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>44.91 ± 0.75</td>
<td>1.24 ± 0.01</td>
<td>1.03 ± 0.02</td>
<td>5.91 ± 0.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>H:C</th>
<th>O:C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.07</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0.13</td>
</tr>
</tbody>
</table>
The BET surface area of the rice straw biochars was also significantly affected by production temperature. The surface area of RSB300 (6.766 m$^2$/g) was relatively low, however, it climbs to 22.383 for RSB500 and dramatically increases to 115.465 m$^2$/g for RSB700. The increased surface area suggests that pores in biochar gradually developed with increased production temperature in 300-700°C, which was also observed in previous studies (Keiluweit et al., 2010; Yang et al., 2015). The increase in surface area from 300 to 500 °C was due to the degradation and destruction of cellulose, which results in the formation of amorphous carbon structure and micropores (Chen et al., 2012; Zhao et al., 2017). The dramatic increase in surface area from 500°C to 700°C was due to the decomposition of lignin and quick release of H$_2$ and CH$_4$, which generates significant densities of micropores (Chen et al., 2012; Zhao et al., 2017). This can also be revealed by the decrease of the average pore size with increased production temperature, whereby more and more macropores transferred to meso and micro pores (Table 1). SEM results (Figure 1) show the porous structure of the biochars at the micron scale, however, a quantitative comparison of the porous structure is best confirmed by the BET results discussed above.
Figure 1 Surface morphology of the rice straw biochars at different magnifications and cross sections under SEM (a) RSB300; (b) RSB500 and (c) RSB700

The FT-IR spectra of the biochars are shown in Figure 2. The peaks at ~1575 and ~800 cm\(^{-1}\) that appear in each spectrum are typically found for biochars, representing aromatic carbon (Keiluweit et al., 2010). The peaks at ~1080 cm\(^{-1}\) are attributable to the stretching of C-O bonds (Wang et al., 2017). A range of peaks (O-H, C=O and C-H) between 1440-1300 cm\(^{-1}\) were observed for RSB300, which originate from the cellulose, hemicellulose and lignin (Keiluweit et al., 2010). With higher production
temperature, these raw materials decomposed and a more active aromatic structure
formed, resulting in the disappearance of the peaks between 1440-1300 cm\(^{-1}\) and the
appearance of peaks representing aromatic C=C stretching (1414 cm\(^{-1}\)) for RSB500
(Keiluweit et al., 2010; Wu et al., 2012). At a production temperature of 700 °C, the
C=C stretching peak declined due to the progressive condensation of the aromatic
structure at high temperatures (Keiluweit et al., 2010; Wu et al., 2012). The XRD
patterns are shown in Figure 3, and indicate that the biochars are highly amorphous
and contain only KCl as the crystalline phase, which is in line with previous findings on
rice straw biochars (Qian et al., 2016; Tan et al., 2017).

Figure 2 FT-IR spectra of the rice straw biochars before and after lead adsorption
Figure 3: XRD patterns of the rice straw biochars before and after lead adsorption.

3.2 Adsorption kinetics and isotherms

The adsorption kinetics of lead on the rice straw biochars are shown in Figure 4 and Table 2. The kinetics data were better described using a pseudo second order model ($R^2$ of 0.88-0.97), which was originally created to describe the kinetics of heavy metal removal by zeolites (Blanchard et al., 1984), as compared with a pseudo first order model ($R^2$ of 0.71-0.95) for all three biochars. The adsorption capacity ($q_e$) and $k_2$ values obtained from the pseudo second order model were both in the order of RSB700>RSB500>RSB300. This suggests that higher production temperature can both aid in higher Pb adsorption capacity and faster adsorption kinetics (Plazinski et al., 2009). Nearly all of the Pb (94%) was removed by RSB700 within 1 h. In
comparison, RSB500 and RSB300 only removed 73% and 65% of the total Pb at 1 h, respectively, and required 6 h to reach >90% total Pb removal from solution.

Figure 4 Adsorption kinetics of lead on rice straw biochars (0.1 g biochar in 20 mL of 5mM Pb solution)

Table 2 Kinetics parameters for lead adsorption to the rice straw biochars (0.1 g biochar in 20 mL of 5mM Pb solution).

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Pseudo first order</th>
<th></th>
<th>Pseudo second order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_e (mg/g)</td>
<td>k_1 (h^{-1})</td>
<td>R^2</td>
<td>q_e (mg/g)</td>
</tr>
<tr>
<td>RSB300</td>
<td>100.50±3.76^a</td>
<td>1.36±0.21</td>
<td>0.95</td>
<td>109.59±3.42</td>
</tr>
<tr>
<td>RSB500</td>
<td>144.25±7.42</td>
<td>3.82±0.93</td>
<td>0.71</td>
<td>153.81±5.46</td>
</tr>
</tbody>
</table>
The kinetics were further analyzed by intraparticle plotting (Figure 5 and Table S1). The three biochars exhibit the same three stages of adsorption. The first fast stage is due to the movement of Pb across the external liquid film boundary layer to the external surface sites of biochars (Choy et al., 2004). The second, slower stage is attributed to the migration of Pb within the pores of the biochars by intraparticle diffusion (Choy et al., 2004). The third stage, which appears nearly flat, occurs because the final stage of Pb adsorption was at internal surface sites, which is rapid (Choy et al., 2004). Equilibrium sorption was complete by approximately 6 h, and therefore remained unchanged from 6 to 24 h. The majority of total adsorbed Pb had been adsorbed on RSB700 after the first stage. This was because RSB700 has the largest surface area (Table 1) amongst the three biochars, and therefore has the most accessible surface sites to seat the Pb ions. The data additionally indicate that intraparticle diffusion is the main rate-limiting step for lead adsorption on all the three biochars.
Figure 5 Plots of intraparticle diffusion for lead adsorption on the rice straw biochars

The adsorption isotherms are shown in Figure 6 (equilibrium pH shown in Table S2).

The Langmuir model generally shows better goodness of fitness for the equilibrium data, except RSB700, for which Freundlich resulted in a slightly better fit. The calculated maximum monolayer adsorption capacities for RSB300, RSB500 and RSB700 were 100.27, 164.62 and 198.18 mg/g respectively. This finding was in line with the kinetics findings that the rice straw biochars with higher production temperatures tend to have higher Pb adsorption capacities. The observed maximum monolayer adsorption capacities of the rice straw biochars in this study were higher than most of the reported adsorption capacities of biochars reported in existing literature (Inyang et al., 2015; Li et al., 2017), suggesting that rice straw is a promising biochar feedstock for heavy metal adsorption.
Figure 6 Adsorption isotherms of lead on rice straw biochars (0.1 g biochar in 20 mL solution)

Table 3 Parameters for Langmuir and Freundlich modelling (0.1 g biochar in 20 mL solution)

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>RSB300</td>
<td>100.27±2.88$^a$</td>
<td>1.30±0.22</td>
</tr>
<tr>
<td>RSB500</td>
<td>164.62±21.81</td>
<td>2.26±1.10</td>
</tr>
<tr>
<td>RSB700</td>
<td>198.18±25.40</td>
<td>1.96±1.08</td>
</tr>
</tbody>
</table>

(a – mean ± standard error)
3.3 Adsorption mechanisms

After batch adsorption experiments, the rice straw biochars were tested by XRD, FT-IR and sequential extractions to investigate the immobilization mechanisms. The XRD results (Figure 3) show that lead oxalate (PbC$_2$O$_4$) was formed on RSB300, whereas hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) was formed on RSB500 and RSB700.

Low-temperature rice straw biochars (100-300 °C) favor the formation of calcium oxalate (CaC$_2$O$_4$) (Qian et al., 2016). With the increase of production temperature (to 500 and 700 °C), the calcium oxalate decomposes and forms calcite (CaCO$_3$) (Qian et al., 2016). This explains the formation of lead oxalate for RSB300 and hydrocerussite for RSB500 and RSB700 after Pb adsorption. The XRD results generally suggest that precipitation was a mechanism for Pb removal by the rice straw biochars. The FT-IR results (Figure 2) also show the presence of CO$_3^{2-}$ for RSB500 and RSB700 after Pb adsorption, which is likely due to the newly-formed hydrocerussite.

The fractions of Pb immobilized by the biochars are shown in Figure 7 and Figure S1. The stable Pb concentrations on RSB300, RSB500 and RSB700 were 61.50, 91.59 and 99.11 mg/g, accounting for 60.01%, 57.55% and 59.00% of their total Pb loadings, respectively. The acid soluble Pb on RSB300, RSB500 and RSB700 was 29.33, 66.18 and 68.40 mg/g, accounting for 28.62%, 41.58% and 40.72% of their total Pb loadings respectively. These results clearly show that the increased Pb removal capacity by increased production temperature for the rice straw biochars (Table 3) comes from the increased acid soluble and stable Pb. In contrast, the exchangeable Pb significantly decreased for the high-temperature rice straw biochars. RSB300 has 11.64 mg/g
exchangeable Pb, accounting for 11.34% of its total immobilized amount, however, RSB500 and RSB700 only have 1.39 and 0.47 mg/g exchangeable Pb, which are 0.87% and 0.28% of their total immobilized amount respectively.

The higher exchangeable Pb concentration for RSB300 was due to its having more exchangeable cations (H⁺, K⁺) that exchanged with Pb²⁺, as compared with RSB500 and RSB700. These cations come from carboxylic and phenolic groups on RSB300 (Dodson, 2011). With the increase of production temperature, the carboxylic and phenolic groups decompose, and H⁺ and K⁺ form H₂O and K₂O (Dodson, 2011). Therefore, RSB500 and RSB700 have less exchangeable cations for Pb exchange, but higher pH due to the loss of H⁺ and formation of alkaline minerals (e.g., K₂O) (Dodson, 2011). The higher pH of RSB500 and RSB700 thereby aids the formation of hydrocerussite.

3.4 Implications for soil remediation

Soil contamination by heavy metals is a great environmental concern in China and globally (Hou et al., 2017a). It is important to seek greener and more sustainable technological solutions to address contaminated land (Hou et al., 2017b; O'Connor et al., 2018a). The rationale for biochar application in soil remediation is to immobilize the heavy metals within the soil and thereby reduce environmental risks that result from their presence. As mentioned in the introduction section, biochar can immobilize/adsorb heavy metals through a range of mechanisms, and each mechanism results in different binding strengths and environmental risks in the
context of the soil environment.

In this study, the majority of Pb immobilized by the biochars are generally stable according to sequential leaching results (Filgueiras et al., 2002), suggesting that the majority of Pb on rice straw biochars are of low risk in the context of the soil environment. RSB300 has 11.34% of total immobilized Pb attributing to exchangeable fraction, which is highly mobile and of high risks. Therefore, if applied in soil remediation, a certain amount of immobilized Pb on RSB300 may easily leach to the environment, suggesting that RSB300 may not be as appropriate for Pb decontamination as compared with RSB500 and RSB700, which have very low exchangeable fractions. RSB500 and RSB700 have ~40% of the total immobilized Pb attributed to the acid soluble fraction. This Pb may be stable in the short-term, however, when applied in soil, may pose risks after field ageing (e.g., acidic rain exposure) in the long term.

The XRD results show that a certain amount of lead was precipitated to lead oxalate on RSB300 and hydrocerussite on RSB500 and RSB700. Lead oxalate is slightly soluble (e.g., $K_{sp}$ of $10^{-9}$, and 4.5 mg/L Pb$^{2+}$ for saturated solution of lead oxalate in water at 26 °C (Kolthoff et al., 1942)). In addition, higher oxalate concentrations (e.g., $\geq 0.05$ M) can significantly dissolve lead oxalate due to complexation (Kolthoff et al., 1942). Lower solution pH (e.g., < 4) can also dramatically dissolve lead oxalate (Sayer et al., 1999). Therefore, lead oxalate is unstable in the soil environmental under aggressive environmental conditions and may pose risks in the long term.
In comparison, hydrocerussite has a much lower solubility (e.g., $K_{sp}$ of $10^{-47}$, and ~ 0.08 mg/L Pb$^{2+}$ for saturated solution at 20 °C (Mohammadzadeh et al., 2015)). RSB500 and RSB700 have significantly higher pH values (Table 1) as compared to RSB300, and consequently have much stronger buffering capacities against conditions such as acidic rain in the context of the soil environment. Therefore, RSB500 and RSB700 are more applicable for soil remediation of divalent metals such as Pb.
4 Conclusions

Rice straw biochars were produced at 300, 500 and 700 °C. The influence of production temperature on the adsorption characteristics and mechanisms of lead on rice straw biochars were investigated. Biochars produced at higher temperatures have significant higher pH values and surface areas, resulting in higher Pb removal capacities and faster adsorption kinetics. Precipitation was a mechanism by which all three biochars immobilized Pb: lead oxalate was precipitated on RSB300 and hydrocerussite was precipitated on RSB500 and RSB700. The immobilized lead on the biochars can be divided into exchangeable, acid soluble and non-available fractions. RSB300 has 11.34% of total immobilized Pb attributed to the exchangeable fraction, whereas for RSB500 and RSB700, this fraction was less than 1%. The immobilized Pb on RSB500 and RSB700 is attributable to acid soluble and non-available fractions (>99%). Based on the mechanistic analyses discussed above, RSB500 and RSB700 are much more appropriate for soil remediation as compared with RSB300. Field-scale applications of rice straw biochars for heavy metal stabilization in soil are suggested for future research, to verify the laboratory findings of the present study.

Acknowledgements

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doi:10.1016/j.chemosphere.2017.03.072


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