Sorption of lead by Salisbury biochar produced from British broadleaf hardwood

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Abstract: In this study, the physicochemical properties of Salisbury biochar produced from British broadleaf hardwood and its adsorption characteristics towards lead was investigated. The biochar particle size has a significant effect on its BET surface area, cation exchange capacity and sorption of lead. The kinetics data were well fitted by the Pseudo second order model. The increase of biochar dosage increased the percentage of lead removal in solutions. The increase of initial solution pH increased the percentage of lead removal across the pH range of 2 - 10. The calculated maximum adsorption capacity of lead by Langmuir model were 47.66 and 30.04 mg/g for 0.15 mm and 2 mm samples. The adsorption capacities of different metals decreased in the order of lead > nickel > copper > zinc calculated in mmol/g. This study suggests a great potential of biochars derived from British broadleaf hardwood to be applied in soil remediation.

Keywords: Adsorption, Lead, Salisbury biochar, British hardwood, Heavy metals

1. Introduction

Biochar, as a carbon storage material, is produced by heating biological residues with the exclusion of air (Sohi, 2012). Recently, the potential application of biochar in soil remediation has been investigated. When applied in contaminated soils, the benefits of biochar are: 1) the high sorption capacity helps to immobilise the heavy metals and organic pollutants (Beesley et al., 2011) 2) the enhancement of fertility and resilience of soil by biochar addition can help the greening and restoration of the contaminated land (Sohi, 2012) 3) the sequestration of CO_2 by storing carbon in a more recalcitrant form (Sohi, 2012).

Before undertaking field trials, it is necessary to identify a feedstock that is readily available and renewable, and to investigate its performance in removing contaminants from soil and water. Biochar from hardwood is able to treat both organic and inorganic contaminants according to the principles proposed by Beesley et al. (2011). In a previous study, Salisbury biochar, which is made from British broadleaf hardwood, was applied to an industrial contaminated site in Yorkshire, UK in 2011 (Shen et al., 2015). The three-year study that followed observed a good performance for Salisbury biochar in immobilising heavy metals in soils (Shen et al., 2015). Likewise, Gomez-Eyles et al. (2011) applied Salisbury biochar to calcareous contaminated-soil and observed that the treatment successfully reduced the bioavailability of organic contaminants as well as the concentration of water soluble Cu^{2+}. In the UK, 31% of the total productive woodland, which covers 10.6% of the entire land area, is broadleaved (Thurkettle, 1997). According to a recent forecast, the average

annual hardwood availability for the UK forest estate is at least 1.6 million m^3 over the next 50 years and may be up to 6.25 million m^3 (National Forest Inventory, UK, 2014).

Based on this evidence, British hardwood is potentially a suitable feedstock both in terms of its high efficiency in removing contaminants from soil and its reliable future availability. However a systematic adsorption characterisation for this kind of biochar has not been carried out yet; this is important for understanding the sorption mechanisms involved and will aid the design of future field-scale remediation projects.

This study focused on the adsorption characterisation for heavy metals to Salisbury biochar. Lead was selected for the sorption studies as it is among the most serious concerns for water and soil pollution (Yang et al., 2014). The kinetics, the influence of biochar dosage, particle size and the pH of the solution on adsorption of lead on biochar, the adsorption isotherms and the comparison of the adsorption capacity of lead with those of copper, nickel and zinc were investigated. The aims of this study were to highlight the potential application of Salisbury biochar in soil remediation and to give validation for its future practical application.

2 Materials and methods

2.1 Physicochemical properties of biochar

Salisbury biochar was obtained from Southern Woodland products (Salisbury, UK). It was produced from British broadleaf hardwood at a pyrolysis temperature of 600 °C. The biochar was dried at 40 °C for 48 h in an oven and sieved to smaller than 0.15 mm and 2 mm respectively for further analysis.

Throughout this paper, the terms “0.15 mm” and “2 mm” will be used to represent the biochar samples sieved to smaller than 0.15 mm and 2 mm respectively.

The BET surface area, cation exchange capacity (CEC), pH, carbon and nitrogen contents and the total contents of trace elements of biochar were determined. The infrared spectrum of biochar was tested by Fourier transform infrared spectroscopy (FTIR) spectrometer. The surface morphology of biochar was examined by scanning electron microscopy (SEM). The details of these test methods are presented in Appendix A.

2.2 Sorption studies

The kinetics of Pb^{2+} adsorption, the influence of biochar dosage and solution pH on Pb^{2+} adsorption and the isotherms of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} adsorption onto biochar were studied by laboratory batch tests. The details of these test methods are presented in Appendix A.

2.3 Statistical analysis

All the experiments in this study were carried out in duplicates. The means and standard deviations were calculated and presented for each experiment. The significance of the influence of the particle size on BET surface area, CEC and pH of biochar and the influence of biochar dosage, solution pH and particle size on Pb^{2+} adsorption were evaluated by a one-way analysis of variance (ANOVA) at the significance level of 0.05 using SPSS 16.0. Regression was used to evaluate the models predicting the kinetics and equilibrium using Origin 8.5. R square were used to indicate the fitness of the models.

3 Results and discussion

3.1 Physicochemical properties of biochar

The physicochemical properties of biochar are shown in Table B.1. The BET surface area and CEC were 54% and 22% lower respectively for the 2 mm biochar (2.46 m^2/g and 5.62 cmol/kg) compared with the 0.15 mm biochar (5.30 m^2/g and 7.20 cmol/kg), indicating that particle size significantly ($P < 0.001$ for BET surface area and $P < 0.05$ for CEC) influenced the physicochemical properties of the biochar. Whereas the influence of particle size on the pH of biochar was not significant ($P > 0.05$). The pH of biochar in water was slightly lower than 7. The slightly acidic pH values (6.96 and 6.78) of Salisbury biochar in this study may indicate that this biochar retained relatively more carboxyl and acidic groups (Ronsse et al., 2013). The CN analysis revealed that Salisbury biochar mainly contained carbon (79.97%). Elemental analysis showed that the biochar contained less than 0.01% of nickel, copper, zinc and lead, therefore it was assumed that this small part of metals would not affect the sorption studies. The FTIR spectra of Salisbury biochar is shown in Fig. B.1. The biochar has a C-C stretching peak at 1578 cm-1 wavenumbers and a C-H/O-H bending peak at 1428 cm^{-1} due to the cellulose and hemicellulose in the raw material as well as C-H out-of-plane bending peaks at 1172 and 745 cm^{-1} wavenumbers due to either lignin or cellulose/hemicellulose in the raw material. SEM images of Salisbury biochar are shown in Fig. B.2 and indicate a porous surface structure on the biochar.

3.2 Adsorption studies

3.2.1 Kinetics

The influence of contact time on the adsorbed amount of Pb^{2+} on biochar is shown in Fig. 1. Approximately 66% and 73% of the sorption occurred in the first 3 hours for the 0.15 mm and 2 mm samples respectively. The adsorption rates subsequently reduced as the equilibrium concentrations were approached. 24 hours was deemed sufficient to ensure the adsorption to reach equilibrium (Fig. 1).

In order to investigate the adsorption mechanism, a pseudo first order model and a pseudo second order model (Table B.2) were used to describe the kinetics of Pb^{2+} adsorption onto biochar. The regression coefficients (R square) using pseudo first order model were low (0.70 and 0.60) (Table B.3) and the fitted model observed a poor fit with the experimental data. The pseudo second order equation fitted the kinetics data well and the regression coefficient was greater than 0.99 (Table B.3). The calculated q_e matched the experimental value well, indicating the Pb^{2+} adsorption on Salisbury biochar follows the pseudo second order model which assumes chemisorption. The Weber and Moris model was used to describe the intraparticle diffusion mechanism. In this study, a linear relationship was observed for both 0.15 mm and 2 mm biochar within the first 3 hours but the trends did not pass through the origin (Fig. B.3), indicating that the intraparticle diffusion is not the rate limiting step during this period.

3.2.2 The influence of biochar dosages

The percentages of Pb^{2+} removal increased significantly from 72.84% to 98.56% ($P < 0.05$) for 0.15 mm samples and from 42.57% to 89.61% ($P < 0.001$) for 2 mm samples with the increase of the biochar dosage from 5 to 15 g/L and

remained almost constant beyond 25 g/L (Fig. 2a). The amount of Pb^{2+} adsorbed per unit adsorbent mass at equilibrium decreased across the biochar dosage range of 5 - 100 g/L (Fig. 2a). This trend may be caused by the aggregation between biochar particles and subsequently the unsaturation of adsorption sites on biochar surface at high solid concentrations during the experiment (Meng et al., 2014).

3.2.3 The influence of initial solution pH

The adsorbed Pb^{2+} at initial pH of 2 was the lowest among the pH values tested (26.50% and 21.77% removal degrees for the 0.15 m and 2 mm samples respectively) (Fig. 2b). The increase of solution pH can enhance the deprotonation process on biochar surface and create more negative sites that enhance the adsorption of Pb^{2+} (Mohan et al., 2014). Hence the amount of Pb^{2+} adsorbed was significantly greater at higher initial pH values (99.92% and 92.83% removal degrees for the 0.15 mm and 2 mm samples respectively at initial pH of 10, $P < 0.001$ compared with removal degrees at pH of 2 for both samples) (Fig. 2b).

Yang et al. (2014) and Kołodyńska et al. (2012) each observed a decrease in Pb^{2+} sorption to biochar when the initial pH was greater than 5. In the study of Kołodyńska et al. (2012), the equilibrium pH values were higher than 8 when the initial pH value was 5 or higher due to the alkalinity of the biochar while Yang et al. (2014) did not report the pH of the biochar or the equilibrium pH values of the solutions. It was suggested that this decrease in sorption was a result of lead precipitation or the formation of lead complex ions at high pH values. In this study, a decrease of adsorption capacity of Pb^{2+} onto biochar

was not observed up to an initial pH value of 10 (Fig. 2b). This is most likely due to the equilibrium pH values of the solution staying below 7.17 due to the acidity of the biochar (Fig. 2b). Precipitation of Pb^{2+} to $Pb(OH)_2$ occurs at a pH of approximately 7.70 and was therefore unlikely to be present in significant quantities. The finding that the amount of Pb^{2+} adsorbed is greater at higher pH values is in line with Mohan et al. (2014) who ensured that precipitation did not occur by maintaining the initial and equilibrium solution pH at less than 7.70.

3.2.4 Adsorption equilibrium

Pb^{2+} batch adsorption studies were conducted and experimental data were fitted by the Langmuir and Freundlich isotherm models. The linear forms of the two models (Table B.2) were used in this study because linear forms, rather than nonlinear forms, of adsorption isotherms had been applied in over 95% of the liquid-phase adsorption systems (Foo and Hameed, 2010). The results are shown in Fig. B.4 and Table B.4. The experimental data was well fitted by the Langmuir model with an R^2 value of 0.988 for 0.15 mm samples and 0.978 for 2 mm samples (Table B.4). The equilibrium parameter R_L was used to express the essential characteristics of a Langmuir isotherm (Hameed and Ahmad, 2009). The R_L values in this case were 0.017 for 0.15 mm biochar and 0.049 for 2 mm biochar, confirming that adsorption of Pb^{2+} to Salisbury biochar is favourable under conditions of this study.

The Freundlich model was also applied which assumes multilayer adsorption to a heterogeneous adsorbent surface (Foo and Hameed, 2010). The Freundlich model fit the experimental data closely with R^2 values greater than 0.98 for both 0.15 and 2 mm samples; the regression constants are given in Table B.4. The

1/n values were 0.742 and 0.713 for the 0.15 mm and 2 mm samples respectively indicating some degree of heterogeneity in the Salisbury Biochar.

The calculated adsorption capacity for Pb^{2+} is compared with that of biochars in other studies in Table B.5. Although the BET surface area of this biochar (section 3.1) was lower than sugarcane bagasse biochar (14.1 m^2/g), its adsorption capacity of lead was much higher, indicating that physical adsorption did not dominate the sorption of lead on biochar. Cation exchange or surface complexation may have dominated the sorption process as Salisbury biochar has a higher CEC capacity and probably more carboxyl groups (which was suggested by the lower pH) that favours the formation of complexation with lead (Cao et al., 2009). Although some manure-derived biochars reveal a higher adsorption capacity than this biochar (Table B.5), their availability was much lower compared with the large annual production of hardwood (National Forest Inventory, UK, 2014). Therefore, hardwood biochar is a good choice in field-scale remediation projects in the UK for its considerable adsorption capacity and reliable future availability.

3.2.5 Influence of particle size

0.15 mm biochar adsorbed more Pb^{2+} than 2 mm biochar at all times during the kinetics study (Fig. 1). 0.15 mm biochar exhibited significantly ($P < 0.001$) higher sorption capacity than 2 mm biochar at biochar dosage of 5 g/L (Fig. 2a). At initial biochar dosages greater than 25 g/L, the percentages of lead removal were very close to 100% for both samples (Fig. 2a). Sorption of Pb^{2+} was higher for 0.15 mm biochar than 2 mm biochar across all pH values tested (Fig. 2b). The samples with smaller particle size exhibited a higher adsorption capacity

(Table B.4). The better performance of 0.15 mm biochar at Pb^{2+} sorption is attributed to both the significantly higher surface area which creates more active sites for the sorption of Pb^{2+} and the significantly higher CEC which gives better capacity to exchange the metals (Table B.1).

3.2.6 Adsorption capacity of copper, nickel and zinc

The adsorption capacity of Cu^{2+}, Ni^{2+} and Zn^{2+} on Salisbury biochar were also investigated in order to form a basis for comparison with Pb^{2+}. The experimental data were fitted to the Langmuir and Freundlich isotherm models using the same methodology as described for Pb^{2+} and the results are shown in Fig. B.5 and Table B.6. The calculated adsorption capacity by Langmuire model for Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} were 0.230, 0.101, 0.105 and 0.098 mmol/g respectively for 0.15 mm samples (Table B.6), equal to 47.66, 6.42, 6.16 and 6.41 mg/g respectively. The higher adsorption capacity of Pb^{2+} by this biochar may be due to the stronger surface electrostatic attraction, since the electronegativity constant of Pb^{2+} is high (2.33) and plays a significant role in its adsorption (Caporale and Pigna, 2014). The formation of surface complexation between biochar's carboxyle groups and lead can also contribute to its higher adsorption capacity. The release of negatively charged ions such as CO_3^{2-} and PO_4^{3-} may also favour the precipitation of lead on the biochar's surface (Cao et al., 2009; Liu and Zhang, 2009) which would incerase apparent sorption of Pb^{2+}. However, the manure-derived biochars in Kołodyńska et al. (2012) may also contain a considerable amount of CO_3^{2-} and PO_4^{3-}. As Kołodyńska et al. (2012) did not present the P contents in the biochars, it is hard to make a comparison.

4 Conclusions

It was found that biochar particle size, dosage and the solution pH significantly affect the sorption of lead on biochar. The kinetics data were well fitted by the pseudo second order model. The Salisbury biochar in this study exhibited high adsorption capacity of lead in aqueous solutions compared with both other studies on lead sorption on biochar and other metals in this study. Therefore, given the abundant and renewable source of its feedstock in the UK, biochar derived from British broadleaf hardwood has the potential to be produced on a large scale and applied in soil remediation.

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Fig. 1. The Influence of contact time on Pb^{2+} adsorption onto biochar and the fit of the data by Pseudo first order and Pseudo second order models (0.1 g biochar in 20 mL solution (0.01 M $NaNO_3$), initial Pb^{2+} concentration 1mM; reaction temperature 20 ºC; initial solution pH 5).

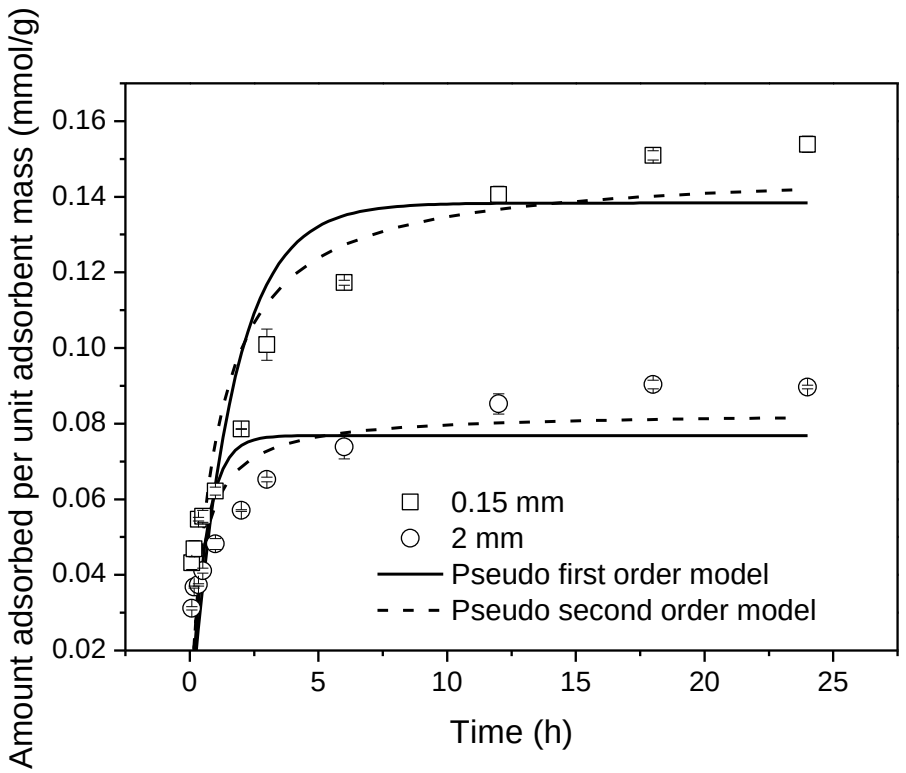

Fig. 2. The influence of biochar dosage (a) and solution pH (b) on the percentage of lead removal (initial Pb^{2+} concentration 1mM in 20 mL solution (containing 0.01 M $NaNO_3$), reaction temperature 20 °C, initial solution pH 5, contact time 24 h), (a) also presents the influence of biochar dosage on the amount adsorbed per unit of adsorbent mass at equilibrium and (b) also presents the equilibrium solution pH.