Title: Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a short-term laboratory study

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Abstract: Salisbury biochar (produced from British broadleaf hardwood) with two different particle sizes (≤ 2 mm and ≤ 0.15 mm) was applied on a kaolin with three different lead (Pb^{2+}) contamination levels (50 mg/kg, 300 mg/kg and 1000 mg/kg) at the dosage of 1% in w/w. The short-term impact of biochar on the mobility and speciation of Pb^{2+} in the kaolin was investigated using attenuation periods of 1, 7 and 28 days. The leachability and extractability of Pb^{2+} in carbonic acid leaching and EDTA extraction tests as well as the sepciarion of Pb^{2+} in soils were not significantly affected by biochar treatment during all periods. The insignificant effects of biochar on Pb^{2+} immobilisation were most likely attributed to the high adsorption capacity of kaolin towards Pb^{2+} and biochar failed to competitively adsorb Pb^{2+} against kaolin. Kaolin immobilised Pb^{2+} primarily through cation exchange, which represents the readily bioavailable fractions of Pb^{2+} in soils and may still pose environmental risks. This paper suggests the inefficiency of biochar treament on heavy-metal contaminated clay-rich soils. Therefore a laboratory treatablity study with respect to the soil type may be crucial when large-scale biochar applications in heavy-metal associated soil remediation are evaluated.

Keywords: Biochar, lead, kaolin, immobilise, speciation

1 Introduction

The application of biochar in soil remediation has recently attracted global interests due to its multiple environmental benefits: (1) biochar can be produced using agricultural and industrial wastes (e.g. crop residues, manure, sludge etc.) as the feedstocks [1]; (2) the co-products (syn-gas and bio-oil) during biochar production can be used as green energy and therefore offset energy use associated with producing biochar [2]; (3) biochar can immobilise contaminants in soils and therefore reduce their leachabilities and bioavailabilities [3]; (4) biochar can help retain the nutrients and improve the water holding capacity and resilience of soils, therefore aiding the greening or revegetation of the contaminated land [4]; (5) the recalcitrant form of carbon in biochar can remain in soil for hundreds to thousands of years [2].

In order to investigate the potential of biochar application in soil remediation, Salisbury biochar, derived from British broadleaf hardwood, was characterised and applied to a contaminated site in the UK in 2011 [5,6]. The biochar treatment successfully immobilised heavy metals and reduced their leachabilities in the sand-dominated site soils three years after the treatment [6]. Due to the high availability of hardwood in the UK and the encouraging performance in the field trial, Salisbury biochar has the potential to be applied in soil remediation at a large scale. As the site soil is sand based (97% of sand particles), it is necessary to investigate the impact of this biochar on the immobilisation of metals in a soil predominantly comprising clay.

Unlike sand particles (diameter range of 0.05 - 2 mm) which are relatively chemically inert, the layer structures of phyllosilicate result in active chemical properties for clay minerals such as relatively high cation exchange capacity (CEC) and surface area [7–9]. Therefore, the clay minerals have the ability to retain heavy metals on their

surfaces through cation exchange and reduce its leaching to the environment under field conditions [8]. However on the other hand, the retained heavy metals on clay particles have the risks to be uptaken by the plants grown on clay soil, bringing further hazards to human beings [8,9]. Therefore, the impact of biochar on immobilisation of heavy metals in clay-rich soils is worth being investigated. However, the majority of studies to date have investigated the performance of biochar in sand-dominated soils, as indicated in Table S1 [3,10–14]. Studies that applied biochar on clay-rich soils are very limited, leading to a poor understanding of the performance of biochar on clay soils contaminated with heavy metals and the remediation mechanisms involved.

In this study, short-term laboratory incubation tests were carried out to investigate the impact of Salisbury biochar on the immobilisation of heavy metals in kaolin, a typical clay soil. Lead (Pb^{2+}) was selected as a representative heavy metal as it is one of the most common contaminants in water and soil and represents serious concerns to human health and environment pollution [15], and demonstrated the highest sorption to Salisbury biochar in a previous study [5]. This study aims to investigate: (1) the impact of biochar on the mobility of Pb^{2+} in kaolin; (2) the impact of biochar on the speciation of Pb^{2+} in kaolin; (3) the short-term time dependence of the two impacts.

2 Materials and methods

2.1 Biochar

Salisbury biochar was purchased from Southern Woodland products (Salisbury, UK). It is produced from British broadleaf hardwood at 600 ºC under oxygen limited ambient conditions (but no additional protective gas was added) in a retort for 13.5

hours. The physical properties and adsorption characteristics of this biochar towards Pb^{2+} have been investigated in a previous study [5] and are briefly summarised in Table 1. In general, Salisbury biochar exhibited a relatively high adsorption capacity of Pb^{2+}, which was significantly affected by the biochar particle size (30.04 mg/g for samples sieved to ≤ 2 mm versus 47.66 mg/g for those sieved to ≤ 0.15 mm).

2.2 Kaolin

The kaolin, PolwhiteE, was supplied by Richard Baker Harrison LTD (Midlands, UK). Soil pH was determined in a soil:water ratio of 1:2.5 (g/mL) based on BS 1377. Its CEC was measured by a compulsive exchange method based on [16]. Kaolin (1 g) was mixed with 20 mL of 0.5 M $BaCl_2$ and shaken at 200 rpm for 2 h before filtration through a 0.45 μm filter. The concentrations of sodium, magnesium, aluminium, potassium, calcium, manganese and iron in the filtrate were tested by inductively coupled plasma/optical emission spectrometry (ICP-OES) (Perkin-Elmer, 7000DV) after acidification. CEC was calculated by the sum of the concentrations of the measured cations. The other physicochemical properties of the kaolin were obtained from the datasheet provided by the supplier and are summarised in Table 2 together with pH and CEC.

2.3 Experimental design and sample preparation

The experimental design is shown in Table S2. After considering the adsorption capacity and dosage (1% in w/w) of biochar, three soil contamination levels were designed: 50 mg/kg to represent lightly contaminated land (less than the adsorption capacities of biochar); 300 mg/kg to represent medium contaminated land (comparable to the adsorption capacities of biochar); and 1000 mg/kg to represent severely contaminated land (exceeds the adsorption capacities of biochar). A

previous study demonstrated that particle size has a significant impact on the sorption of Pb^{2+} by this biochar [5], therefore two particle sizes of ≤ 2 mm and ≤ 0.15 mm were selected for this study in order to represent coarse and fine particle sizes. Throughout this paper, the terms "2 mm" and "0.15 mm" will be used to represent the biochar samples sieved to ≤ 2 mm and ≤ 0.15 mm respectively.

The soil and biochar (or without biochar for the control samples) were dry mixed in a mixer (Kenwood, UK) and then the contaminants ($Pb(NO_3)_2$ dissolved in solution) were added and thoroughly mixed with the soil-biochar mixture. The samples were then incubated in order to maintain them at a moisture content of 40% (w/w) (between liquid and plastic limit to avoid either too dry or too wet) and a density of 1.2 g/cm^3 in polythene tubes, and the polythene tubes were then stored in moisture chambers.

In order to investigate the short-term development of the immobilisation of biochar on Pb^{2+} in kaolin, the control and treated soil samples were incubated at a constant moisture content and temperature, and the time dependence of immobilisation was investigated using attenuation periods of 1, 7 and 28 days.

2.4 Chemical analysis

At the designated time, soil samples were collected and oven dried at 60 ⁰C for 48 h. Separate 1 g dry soil samples were taken for carbonic acid leaching, Ethylenediaminetetraacetic acid (EDTA) extraction and sequential extraction tests. The remainder of the dry samples were used to test soil pH, applying the same method as presented in section 2.2.

Carbonic acid leaching (based on BS EN 12457-2) was used to indicate the release potential of hazardous and toxic elements from solid waste under slightly acidic rain

water [17]. The dry soil (1 g) was mixed with 10 mL carbonic acid (pH = 5.6) and shaken at 200 rpm for 24 h. The mixture was then filtered through a 0.45 μm filter and the Pb^{2+} concentration in the leachate was tested by ICP-OES.

EDTA extraction was carried out to determine the potential bioavailability of Pb^{2+} in kaolin as suggested in [18]. The dry soil (1 g) was mixed with 5 mL of 0.01 M Na_2EDTA and shaken at 200 rpm for 24 h. The mixture was then centrifuged at 3000 rpm for 5 minutes and filtered using a 0.45 μm filter, and the concentrations of Pb^{2+} in the leachate was measured by ICP-OES.

Sequential extraction based on [14,16,17] was used to determine the different geochemical phases (speciation) of Pb^{2+} present in the soils. The details of the procedure can be found in a previous study [6]. The metals were partitioned into five fractions through the following steps: Step 1 - exchangeable fraction (non-specific adsorption); Step 2 - fraction bound to CO_3^{2-}/PO_4^{2-} (specific adsorption); Step 3 - fraction bound to Fe/Mn oxides; Step 4 - fraction bound to organic matter; Step 5 - residual fraction. In order to investigate the speciation of Pb^{2+} on biochar, a certain amount (0.1 g) of biochar sample (0.15 mm) after reaching adsorption equilibrium in 20 mL of 5 mM Pb^{2+} solution was collected and examined by sequential extraction.

In order to investigate the adsorption capacity of Pb^{2+} on kaolin, the adsorption equilibrium study was conducted. A certain amount of kaolin (0.1 g) was added to 20 mL solutions (pH = 5) containing different Pb^{2+} concentrations (0.1, 0.2, 0.3, 0.5, 1, 2, 3 or 5 mM) and 0.01 M $NaNO_3$. The mixture was shaken at 200 rpm at 20 °C for 24 h to reach equilibrium. Then the mixture was filtered with a 0.45 μm filter and the Pb^{2+} concentration in the collected filtrate was measured by ICP-OES.

All laboratory analysis in this study was conducted in a temperature controlled lab at 20 ± 1 °C and 50 ± 2% humidity based on the department lab standard.

2.5 Statistical analysis

All experiments were carried out in triplicates. The means and standard deviations were calculated and presented for each experiment. The normality of the data were tested and the Shapiro-Wilk results were used to indicate the normality of the data at the significance level (P) of 0.05. The homogeneity of the variances were checked at the significance level of 0.05. As in most cases, the data are normally distributed and a homogeneity of the variances between groups was found, the difference between two groups was evaluated by a one-way analysis of variance (ANOVA) at the significance level of 0.05. The data that were not normally distributed or without a homogeneity of the variances were indicated in the paper. The statistical analysis was conducted using SPSS 16.0.

3 Results and discussion

3.1 Soil pH

The soil pH values of all samples across all incubation periods were within 4.54 - 4.92 (Fig. 1), similar to the original pH value of the kaolin (4.78). Although the treated samples exhibited a significant increase in pH compared with the control samples at contamination levels of 300 and 1000 mg/kg (Fig. 1), the increases were only 0.08 - 0.19, suggesting that the influence of biochar treatment on soil pH was small. No significant trends in the differences associated with particle sizes and incubation time on soil pH were found (Fig. 1).

The relatively low dosage (1%) and low biochar pH values (6.78 - 6.96) may have resulted in the insignificant impact on soil pH. Puga et al. (2015) [21] employed

biochar produced from sugar cane straw (pH = 10.2) to a contaminated soil (pH = 6.1; sand: 34%, silt: 24%, clay: 43%) and observed no significant changes in soil pH after 120 days of incubation with biochar dosages from 1.5% to 5%. Houben et al. (2013) [22] observed that the soil pH increased with biochar dosage when adding a miscanthus straw biochar (pH = 10.24) to a contaminated soil (pH = 6.57; 64% sand, 24% silt and 12% clay) at dosages of 1 - 10% after 56 days of incubation, however increases were no more than 0.5 pH units. The pH value of Salisbury biochar was even smaller than the biochars in the studies of Puga et al. (2015) [21] and Houben et al. (2013) [22], therefore considering the low dosage, the insignificant influence of biochar on soil pH in this study was reasonable.

The increase of soil pH can enhance the adsorption capacity of biochar due to deprotonation processes [23], however it requires a greater addition of biochar which will increase the cost in purchasing and transportation. A balance between performance and cost must therefore be seek during engineering application when considering the impact of biochar on soil pH.

3.2 Carbonic acid leaching and EDTA extraction tests results

The extracted concentrations of Pb^{2+} from carbonic acid leaching were low (≤ 1.04 mg/L) compared with those from EDTA extraction (7.72 - 176.87 mg/L) (Fig. 2). The Pb^{2+} concentrations in both carbonic acid leachate and EDTA extraction were strongly affected by the contamination levels, whereas no time-related dependencies associated with biochar treatments were observed over the 28 days (Fig. 2).

The Pb^{2+} leachability (extractability) for each extraction test can be obtained by dividing the amount extracted by the total amount in the soil. As shown in Fig. 3, the Pb^{2+} leachabilities in carbonic acid leaching tests were all ≤ 1.04% (Fig. 3a), whereas

those in EDTA extraction tests range from 76.74% to 97.28% (Fig. 3b). The influences of biochar treatment on Pb^{2+} leachability were not significant. Similarly, no significant trends associated with contamination levels and incubation time were found.

The low Pb^{2+} leachabilities in carbonic acid leaching tests indicate a strong adsorption or immobilisation of Pb^{2+} by the soil itself, which is highly resistant to acidic rain water. The low soil pH values may have also contributed to this low leachability. As shown in Fig. 1, all the sample pH values were within 4.54 - 4.92, which were lower than that of the carbonic acid (5.6), making the carbonic acid unlikely to reverse the deprotonation process and release adsorbed Pb^{2+}. The carbonic acid leaching results suggest that the kaolin itself has successfully immobilised the Pb^{2+} and the effect of biochar was negligible.

The 0.01 M Na_2EDTA solution extracted a high amount of Pb^{2+} from all samples, suggesting that a high proportion of Pb^{2+} is potentially bioavailable and therefore presents an ecological risk. EDTA extracts Pb^{2+} through chelation between its ligands and Pb^{2+} ions. The high amount of Pb^{2+} extracted indicates that high proportion of Pb^{2+} was bound to the soil through binding which is weaker than chelation. The high EDTA extractability (Fig. 3b) in this study is in line with the findings of Kim et al. (2003) [24]. They observed Pb^{2+} leachability values higher than 80% at EDTA:Pb^{2+} mole ratios of 10 - 100 for one field soil (6238 mg/kg of Pb^{2+}) and one artificial soil (oxidized glacial till contaminated with 2413 mg/kg of Pb^{2+}). Kim et al. (2003) [24] also noted that the Pb^{2+} leachability was closely related to the EDTA:Pb^{2+} mole ratios in 0.1 - 10; while it did not significantly increased with EDTA:Pb^{2+} ratios in 10 - 100 for the artificially contaminated soil. The EDTA:Pb^{2+} mole ratios for the samples at contamination level of 1000, 300 and 50 mg/kg were

10, 35 and 207 in this study and did not increase the EDTA extractability, which coincides with the findings of Kim et al. (2003) [24] at high EDTA:Pb^{2+} mole ratios (10 - 100). This is most likely due to the excessive addition of EDTA: all Pb^{2+} bound weaker than chelation to the soils had been extracted while the residual Pb^{2+} which was stronger bound than chelation cannot be extracted even when EDTA was excessive.

The EDTA extraction results indicate that although the release potential of Pb^{2+} under simulated acidic rain was low, the potential bioavailability of Pb^{2+} was high and the effect of biochar treatment on this was insignificant.

3.3 Sequential extraction results

3.3.1 Recovery

The total recovery from sequential extraction tests can be obtained by dividing the total extracted Pb^{2+} in sequential extraction by the totally designated amount of Pb^{2+} in the soil and is shown and compared with that from EDTA extraction in Table S3. The total recovery from sequential extraction tests was within 61.50 - 89.30% and decreased with the increase of contamination level. No significant trend between biochar addition and the recovery was found. The recovery from sequential extraction was lower than that from EDTA extraction (76.92 - 97.28%) for most samples. Few studies have been carried out using sequential extraction tests to investigate the speciation of heavy metals in kaolin [25]. It is difficult to find the recovery of Pb^{2+} in kaolin in sequential extraction from literatures and make a relevant comparison with that in this study. The most similar one probably comes from Reddy et al., (2001) [26]. They used acid digestion method to determine the total concentrations of Chromium (Cr^{3+} and Cr^{6+}), Nickel (Ni^{2+}) and Cadmium (Cd^{2+})

in an artificially contaminated kaolin. The recovery of the heavy metals were within ~ 78 - 113%. The recovery of Cd^{2+} and Ni^{2+} from one of the two samples were ~ 78% and ~ 88% respectively, which were comparable to the recovery of Pb^{2+} in this study.

3.3.2 Speciation of Pb^{2+} in soils

The speciation of Pb^{2+} in soils is shown in Table S4 and Fig. 4. Pb^{2+} was mainly bound to the exchangeable fraction (36.12 - 42.93%), CO_3^{2-}/PO_4^{2-} (19.82-25.70%) and Fe/Mn oxides (21.63 - 26.71%) in soils at the contamination level of 50 mg/kg. At contamination levels of 300 mg/kg and 1000 mg/kg, the exchangeable fraction (64.05 - 76.26%) dominated the existence of Pb^{2+} in soils whereas the fractions bound to CO_3^{2-}/PO_4^{2-} and Fe/Mn oxides decreased (to 15.00-19.53% and 5.97 - 12.59% respectively) compared with those at 50 mg/kg. The fraction bound to organics and the residual fraction were low (5.11 - 6.70% and 6.93 - 9.85% respectively) at a contamination level of 50 mg/kg while these fractions were negligible at contamination levels of 300 mg/kg and 1000 mg/kg (≤ 2.44%). The biochar treatment did not have a significant influence on Pb^{2+} speciation in soil over the 28 day periods. It is difficult to find studies using biochar to remediate contaminated kaolin and make a relevant comparison. One similar study comes from Houben and Sonnet. (2015) who applied 5% miscanthus straw biochar to a contaminated soil (texture not shown) and used the same sequential extraction method to analyse Pb^{2+} speciation in the soil [27]. Only the cation exchangeable fraction was slightly reduced while the other four factions showed no significant changes 56 days after biochar treatment, although the soil pH was slightly increased from 5.66 to approximately 6.7 [27].

The solubility and bioavailability of heavy metals decrease with each step in sequential extraction and represent an increased binding strength with each step sequence [28,29]. Fractions from steps 2 to 5 account for more than 60% of the total Pb^{2+} at initial concentrations of 50 mg/kg. At higher contamination levels (300 and 1000 mg/kg), the relatively tightly bound fractions (steps 2 - 5) approach saturation and therefore the weakly bound fraction (step 1: cation exchange) increases and dominates the overall fraction (64.05 - 76.26%), in part due to the high cation exchange capacity of kaolin itself. The high proportions in fraction 1 represented a high readily available lead to the environment [25].

3.4 Biochar impact on the mobility and speciation of Pb^{2+}

The kaolin itself immobilises Pb^{2+} well and the experiments in this study provide no evidence that biochar affects its speciation. Similarly, biochar did not have a significant impact on Pb^{2+} leachability in carbonic acid leaching and EDTA extraction tests. This could be caused by several reasons: (1) the addition of biochar was not sufficient to have significant influence; (2) the incubation period was too short and immobilisation by biochar had not fully developed; or (3) competitive adsorption: the adsorption capacity of kaolin itself was comparable to or higher than that of biochar.

The 1 g samples of kaolin contaminated at 50 mg/kg, 300 mg/kg and 1000 mg/kg will contain 0.05 mg, 0.3 mg and 1 mg of Pb^{2+} respectively. The maximum adsorption capacity of Salisbury biochar (1% in the soil) towards Pb^{2+}, calculated based on Shen et al. (2015) [5], was 0.30 mg and 0.48 mg for 2 mm and 0.15 mm samples respectively. Therefore, although 300 mg/kg and 1000 mg/kg contamination levels were comparable to or in excess of the adsorption capacities of biochar, a 1% addition of biochar is theoretically capable of fully treating 1 g of soil contaminated at

50 mg/kg Pb^{2+}. However the impact of biochar on the mobility and speciation of Pb^{2+} at a contamination level of 50 mg/kg was insignificant, indicating reason 1 is unlikely to be the most significant factor.

Rees et al. (2014) applied biochar (originated from 80% coniferous and 20% hardwood) to two soils (Soil A: 33% sand, 47% silt, 20% clay; soil B: 24% sand, 60% silt, 16% clay) contaminated with 1120 mg/kg and 1080 mg/kg of Pb^{2+} respectively, and observed that the extractabilities of Pb^{2+} in $Ca(NO_3)_2$ were reduced by ~ 70% and ~ 10% respectively one week after biochar treatment [30]. Further, Uchimiya et al. (2012) applied several biochars to a slightly acidic soil (pH 6.27) containing 14847 mg/kg of Pb^{2+} and observed that the soluble Pb^{2+} was significantly reduced one week after biochar treatment [31]. These findings suggest that insufficient contact time (reason 2) may not be a significant factor in the low impact of biochar. However, the soil used in this study is different from the soils Rees et al. (2014) and Uchimiya et al. (2012) used, therefore the long-term influence of biochar on immobilisation of heavy metals in kaolin is still suggested to investigate to form a comparison with the short-term findings in this study.

In order to test reason 3, the equilibrium isotherm for Pb^{2+} adsorption onto kaolin was determined and the results are shown in Fig. S1. Kaolin exhibited high adsorption of Pb^{2+} at the initial adsorbate concentration of 0.1 - 5 mM (0.1 g kaolin in 20 mL solution). Linear Langmuir and Freundlich models were adopted to fit the data (Table S5). The poor regression for the Linear Langmuir model (R^2 = 0.64) and good regression for the Linear Freundlich model (R^2 = 0.96) suggest heterogeneously chemical adsorption dominates kaolin adsorption of Pb^{2+} rather than monolayer adsorption (Table S5). This is in line with the finding from the sequential extraction tests, which indicate that Pb^{2+} was bound to biochar through 5

different fractions. The high sorption of lead by the kaolin, together with the low carbonic acid leachability, suggests kaolin itself was able to immobise Pb^{2+} in the soils in this study.

In a previous study, oak wood biochar was found to transfer the readily bioavailable fraction (exchangeable: step 1 in this study) of Pb^{2+} to more stable residual fraction (step 5) in a sandy loam soil [32]. Likewise, wine lees biochar was found to significantly increase the residual fraction (step 5) while decrease the reducible (step 2) and oxidizable (step 4) Pb^{2+} in a paddy soil [33]. In these two studies, biochar may either have adsorbed competitively against the soil and transferred the weakly bound Pb^{2+} to stable fractions by itself; or enhanced the bonds of Pb^{2+} into soil lattice through increased soil pH and other mechanisms [28,29].

The speciation of Pb^{2+} in salisbury biochar was investigated and shown in Table 3. The Pb^{2+} was adsorbed to biochar mainly through bond to carbonates/phosphates, which is an acidic soluble fraction [25]. Although it represents a slightly tighter bond than cation exchange, this bond is highly pH dependent [25] and it is difficult to win the competitive adsorption of Pb^{2+} against kaolin at such low soil pH values (4.54-4.92). The X-ray absorption fine structure (XAFS) analysis in [32] observed that 62.7% Pb^{2+} was adsorbed on kaolinte 175 days after amending the contaminated soil with 5% oak wood biochar, indicating the affinity of kaolinite for Pb^{2+}. The biochar itself failed to adsorb Pb^{2+} in a more stable form in this study and its influence on the soil pH was insignificant or small. Therefore, no significant impact of biochar on the speciation of Pb^{2+} in kaolin was observed.

Hence, the insignificant influence of biochar on the mobility and speciation of Pb^{2+} in kaolin was most likely due to the fact that kaolin itself has an adsorption capacity

comparable to that of the biohcar and biochar failed to competitively adsorb Pb^{2+} againt kaolin or alter its speciation by enhancing soil pH values.

It is of note that kaolin is mainly made of kaolinite which is a variable charge mineral with a relatively low CEC (which is confirmed in Table 1) due to its 1:1 phyllosilicate layer structure [9,34]. Soils dominated by clay minerals with 2:1 phyllosilicate layer structure (illite, smectite, vermiculite, palygorskite etc.) and permanently charged commonly have much higher CECs [9,34]. Since Salisbury biochar failed to competitively adsorb Pb^{2+} againt kaolin, it could be expected that this biochar may not be able to affect the mobility or specation of Pb^{2+} in soils dominated by 2:1 clay minerals.

4 Conclusions

In this study, it was found that biochar did not have a siginificant effect on the mobility or speciation of Pb^{2+} in a kaolin, suggesting that the performance of biochar in immobilising heavy metals in soils is related to the soil types and that biochar may not perform well on contaminated soils with high clay content. The reasons may be due to the high adsorption capacity (mainly CEC) of Pb^{2+} on kaolin itself and the failure of biochar to competitively adsorb Pb^{2+} against kaolin. As other clay minerals such as illite, smectite, vermiculite, palygorskite etc. usually have higher CECs than kaolinite which forms the basis of kaolin, biochar may also fail to affect the mobility or speciation of heavy metals in soils rich in these clay minerals. This paper suggests the inefficiency of biochar treament on heavy-metal contaminated clay-rich soils. According to the suggestions in this study, field applications of biochar in heavy-metal associated soil remediation need to take the soil type into account, and a

laboratory treatablity study with respect to the soil type is crucial when large-scale biochar applications are evaluated.

It is of note that this was a short-term study carried out under laboratory conditions. Treatments on clay soils under field conditions and in the long term are needed in order to make a comparison with the findings in this study.

Although this study found that the release potential of Pb^{2+} in kaolin under simulated acidic rain water was low, it existed primarily as the exchangeable fraction and the EDTA extractability was high. This suggests that the readily and potentially bioavailability of Pb^{2+} in kaolin was high. As biochar was found to reduce the bioavailable fractions and enhance the non-bioavailable fractions of metals in soils [25,28], it may still have the potential to be applied to reduce the bioavailability of metals in clay soils. Therefore, biochar derived from other feedstocks using different production methods (slow and fast pyrolysis) are suggested to apply on clay soils and investigate their performances in immobilising heavy metals.

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Table 1 Physicochemical properties of Salisbury biochar.

	2 mm	0.15 mm
BET surface area (m^2/g)	2.46 ± 0.03[a]	5.30 ± 0.06
Cation exchange capacity (cmol/kg)	5.62 ± 0.15	7.20 ± 0.17
pH	6.78 ± 0.01	6.96 ± 0.01
C (%)	79.91 ± 2.33	
N (%)	0.73 ± 0.02	
Pb (%)	0.01 ± 0.0004	

Adsorption capacity of Pb (mg/g)	30.04	47.66

("2 mm" and "0.15 mm" represent the biochar samples sieved to ≤ 2 mm and 0.15 mm respectively; a - mean ± standard, n=3)

Table 2 Physicochemical properties of kaolin.

Properties	Value
pH	4.78 ± 0.02^a
CEC (cmol/kg)	5.49 ± 0.03
BET surface area (m^2/g)	8
Specific gravity	2.6
Water soluble salt content (%)	0.15
SiO_2 (%)	50
Al_2O_3 (%)	35

Liquid limit (%)	47
Plastic limit (%)	31
Sand (0.05-2 mm) (%)	0
Silt (0.002-0.05 mm) (%)	65
Clay (0-0.002 mm) (%)	35

(a - mean ± standard, n=3)

Table 3 Speciation of Pb^{2+} in biochar (0.1 g biochar sample (0.15 mm) after reaching adsorption equilibrium in 20 mL of 5 mM Pb^{2+} solution).

	Pb^{2+} amount in biochar (mg)	%
Step 1	0.18 ± 0.01	4.29
Step 2	3.53 ± 0.47	85.31
Step 3	0.40 ± 0.11	9.66
Step 4	0.02 ± 0.007	0.41
Step 5	0.01 ± 0.0002	0.33

Fig. 1. Soil pH values. The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time (P < 0.05).
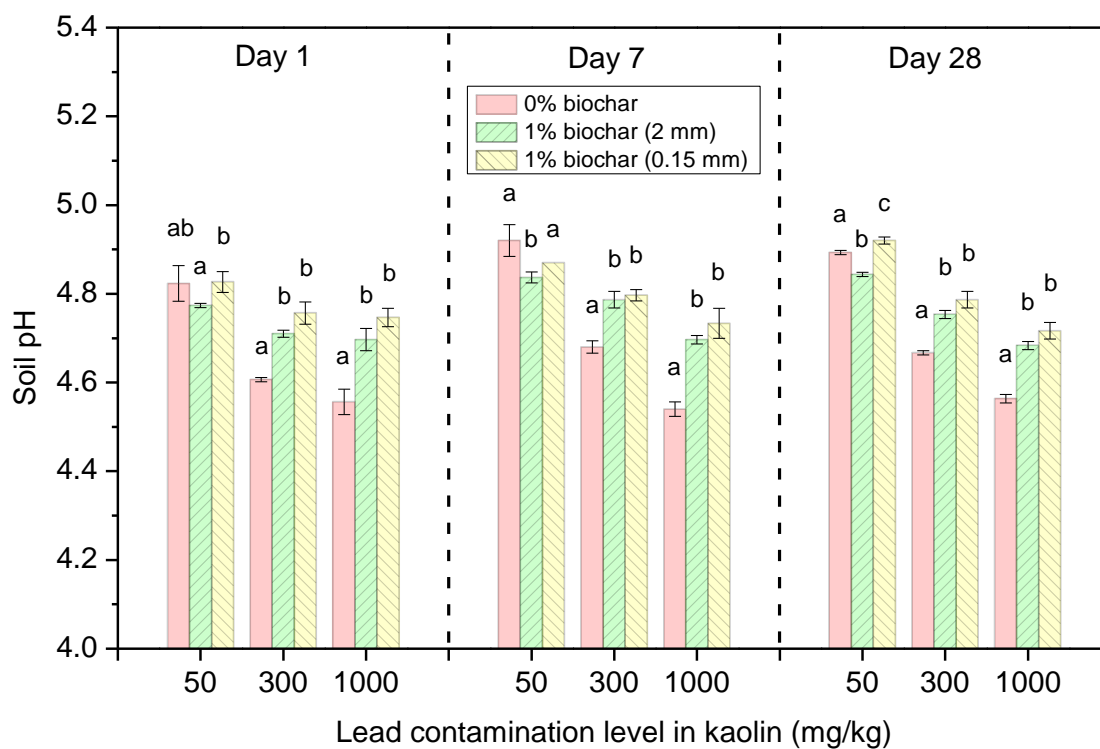
Fig. 2. Pb^{2+} concentrations in (a) carbonic acid leachate and (b) EDTA extraction. Data not shown indicates below limit of detection (0.010 mg/L). The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time ($P < 0.05$). N.N.D = not normally distributed. N.H.V = not homogeneity of variance.
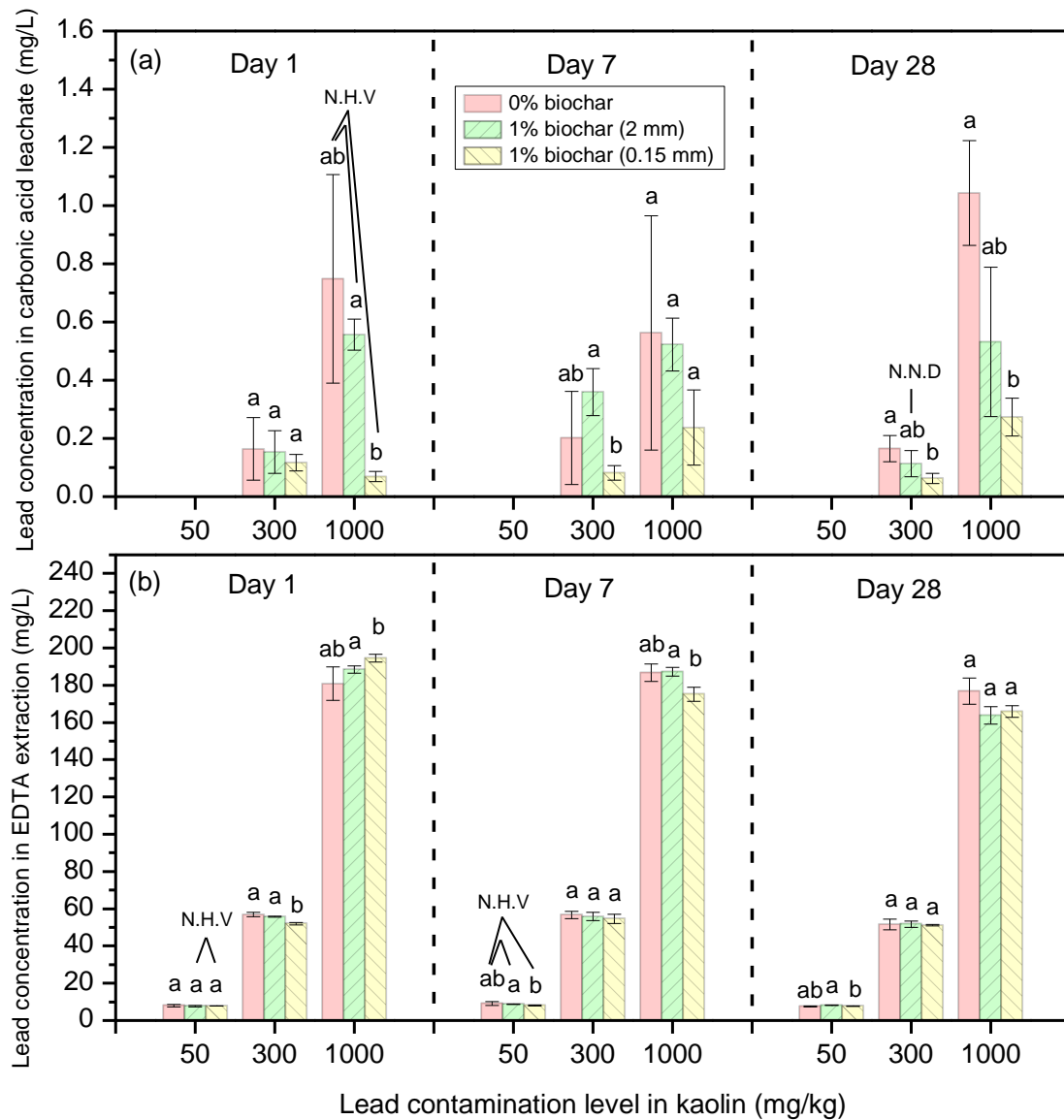
Fig. 3. Pb^{2+} leachabilities in carbonic acid leaching test (a) and EDTA extraction test (b). The different lower case letters indicate a significant difference between the treatments in each experiment with a specific contamination level at a specific time ($P < 0.05$). N.N.D = not normally distributed. N.H.V = not homogeneity of variance.
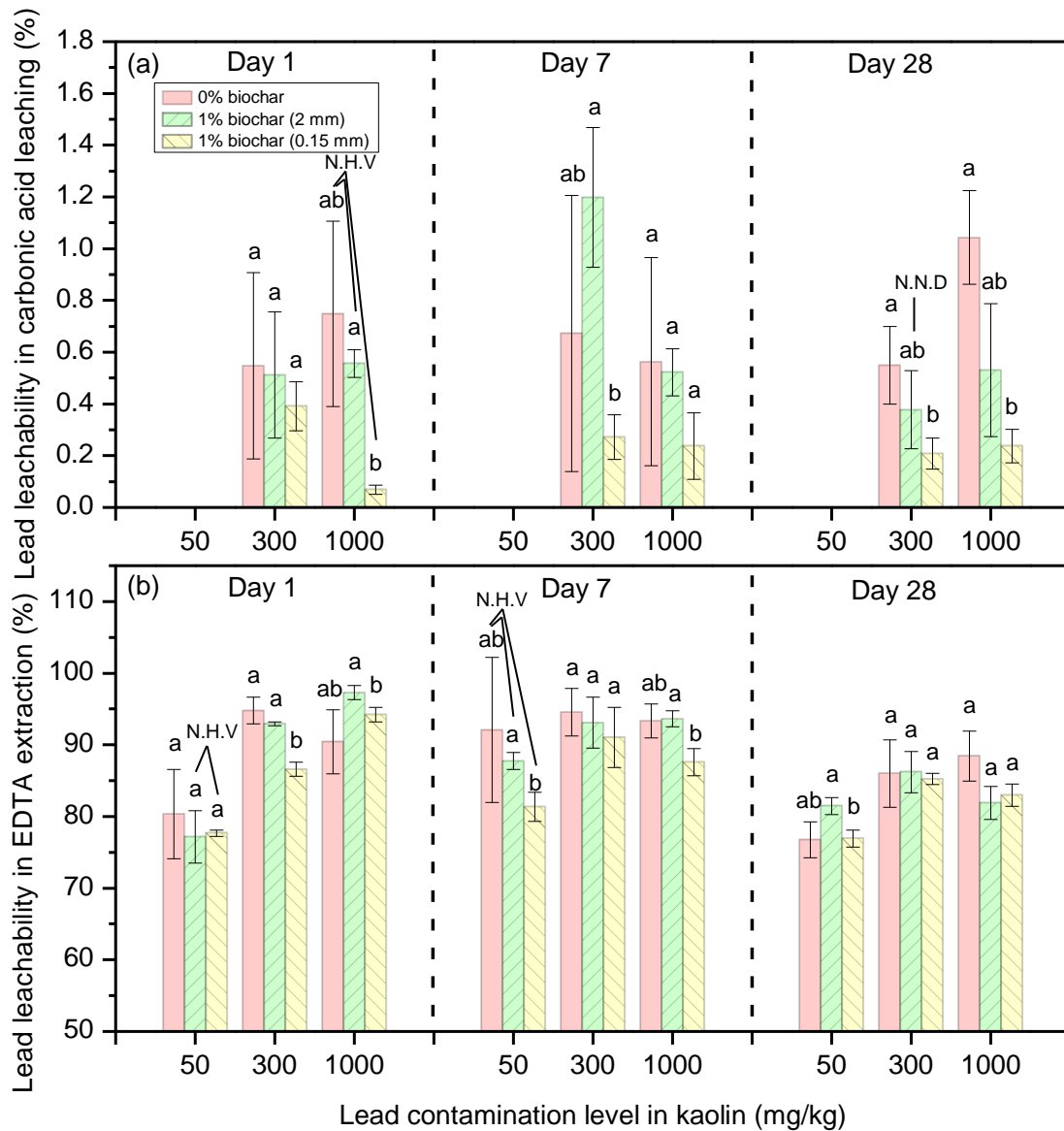
Fig. 4. Sequential extraction results. The horizontal axis indicates the contamination
level (mg/kg) + the dosage of biochar treatment (0% or 1% in w/w).

Fractions (%)

Day 1　　　Day 7　　　Day 28

Step 1
Step 2
Step 3
Step 4
Step 5

50 + 0%
50 + 1% (2 mm)
50 + 1% (0.15 mm)
300 + 0%
300 + 1% (2 mm)
300 + 1% (0.15 mm)
1000 + 0%
1000 + 1% (2 mm)
1000 + 1% (0.15 mm)
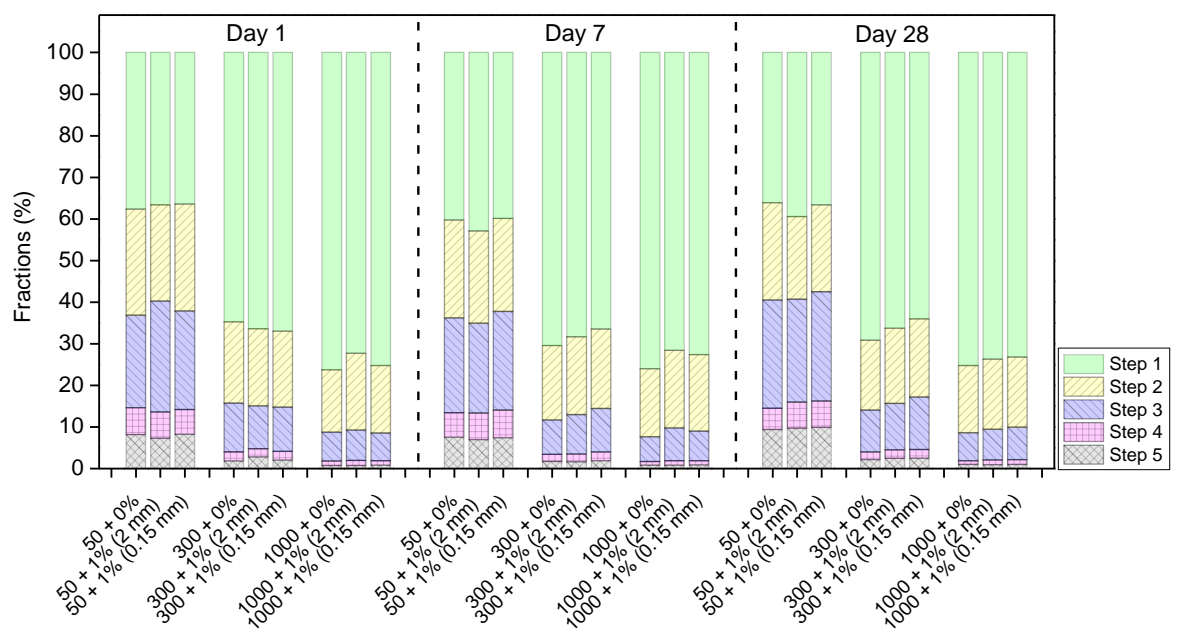
Table S1 Soil constitutes in existing biochar research associated with heavy-metal contaminated land

Sand (%)	Silt (%)	Clay (%)	Reference
87.7	4.8	7.5	(Balwant and Singh 2010)
83	16	1	(Beesley and Dickinson 2011)
43	48	8	(Beesley and Marmiroli 2011)
46		17	(Bian et al. 2013)
42		18	
49		20	
52		16	
59		10	
54	39	7	(Brennan et al. 2014)
92	8		(Cao et al. 2011)
88	12		
83	6	12	(Hartley et al. 2009)
83.4	9.1	7.5	
48.3	22.3	29.3	
64	24	12	(Houben et al. 2013)
78	10	12	(Kargar et al. 2015)
90		9.8	(Liang et al. 2014)
85	12	3	(Moon et al. 2013)
34	24	43	(Puga et al. 2015)
33	47	20	(Rees et al. 2014)
24	60	16	
42	38	20	(Riedel et al. 2015)

Table S2 Experimental design

Specimens	Biochar dosage (w/w)		Biochar particle size (mm)		Lead contamination level (mg/kg)			Incubation time (day)		
	0%	1%	< 2	< 0.15	50	300	1000	1	7	28
S1-3	×				×			×		
S4-6	×					×		×		
S7-9	×						×	×		
S10-12		×	×		×			×		
S13-15		×	×			×		×		
S16-18		×	×				×	×		
S19-21		×		×	×			×		
S22-24		×		×		×		×		
S25-27		×		×			×	×		
S28-30	×				×				×	
S31-33	×					×			×	
S34-36	×						×		×	
S37-39		×	×		×				×	
S40-42		×	×			×			×	
S43-45		×	×				×		×	
S46-48		×		×	×				×	
S49-51		×		×		×			×	
S52-54		×		×			×		×	
S55-57	×				×					×
S58-60	×					×				×

S61-63	×						×		×
S64-66		×	×		×				×
S67-69		×	×			×			×
S70-72		×	×				×		×
S73-75		×		×	×				×
S76-78		×		×		×			×
S79-81		×		×			×		×

Table S3 Recovery of sequential extraction and EDTA extraction

| Soil sample (Contamination level + biochar dosage)	Day 1 (%)		Day 7 (%)		Day 28 (%)	
	Sequential extraction	EDTA extraction	Sequential extraction	EDTA extraction	Sequential extraction	EDTA extraction
50 + 0%	87.95 ± 9.19	80.33 ± 6.25	88.18 ± 6.48	92.08 ± 10.10	89.30 ± 5.18	76.74 ± 2.53
50 + 1% (2 mm)	77.13 ± 0.90	77.17 ± 3.65	72.75 ± 0.70	87.74 ± 1.18	76.96 ± 0.16	81.46 ± 1.20
50 + 1% (0.15 mm)	82.63 ± 6.02	77.67 ± 0.43	76.56 ± 3.17	81.34 ± 2.01	78.20 ± 5.66	76.92 ± 1.20
300 + 0%	69.31 ± 0.85	94.78 ± 1.85	70.14 ± 4.16	94.54 ± 3.30	74.45 ± 6.35	86.02 ± 4.70
300 + 1% (2 mm)	69.75 ± 4.07	92.92 ± 0.27	72.13 ± 4.58	93.08 ± 3.57	70.50 ± 4.52	86.22 ± 2.88
300 + 1% (0.15 mm)	74.89 ± 1.14	86.59 ± 0.96	71.92 ± 1.67	91.03 ± 4.22	72.21 ± 1.68	85.24 ± 0.76
1000 + 0%	64.29 ± 0.64	90.42 ± 4.48	66.62 ± 3.32	93.35 ± 2.38	68.32 ± 2.04	88.43 ± 3.50
1000 + 1% (2 mm)	63.72 ± 2.11	94.22 ± 1.00	61.50 ± 2.33	93.62 ± 1.12	67.41 ± 2.22	81.90 ± 2.31
1000 + 1% (0.15 mm)	71.53 ± 5.78	97.28 ± 1.02	63.66 ± 1.28	87.57 ± 1.88	66.97 ± 0.52	82.98 ± 1.57

Table S4 Sequential extraction results.

Soil sample (Contamination level + biochar dosage)	Step	Day 1		Day 7		Day 28	
		mg/kg	%	mg/kg	%	mg/kg	%
50 + 0%	1	17.56 ± 0.05	37.66	17.75 ± 1.68	40.26	16.13 ± 0.52	36.12
	2	11.20 ± 1.82	25.47	10.37 ± 0.85	23.53	10.45 ± 1.49	23.41
	3	9.80 ± 1.10	22.28	10.07 ± 0.39	22.83	11.60 ± 0.82	25.98
	4	2.84 ± 0.35	6.47	2.59 ± 0.11	5.88	2.28 ± 0.31	5.11
	5	3.57 ± 0.13	8.13	3.31 ± 0.35	7.50	4.19 ± 0.11	9.38
50 + 1% (2 mm)	1	14.12 ± 0.01	36.61	15.61 ± 0.06	42.93	15.18 ± 0.16	39.46
	2	8.92 ± 0.77	23.12	8.05 ± 0.04	22.14	7.63 ± 0.04	19.82
	3	10.30 ± 0.79	26.71	7.87 ± 0.04	21.63	9.53 ± 0.19	24.77
	4	2.44 ± 0.09	6.34	2.32 ± 0.14	6.38	2.42 ± 0.14	6.28
	5	2.79 ± 0.28	7.23	2.52 ± 0.15	6.93	3.72 ± 0.11	9.67
50 + 1% (0.15 mm)	1	15.05 ± 0.05	36.44	15.28 ± 0.72	39.90	14.32 ± 0.18	36.61
	2	10.62 ± 1.47	25.70	8.56 ± 0.52	22.36	8.19 ± 0.16	20.94
	3	9.80 ± 0.50	23.72	9.07 ± 0.14	23.69	10.27 ± 0.25	26.26
	4	2.46 ± 0.13	5.95	2.57 ± 0.16	6.70	2.48 ± 0.07	6.34
	5	3.39 ± 0.18	8.20	2.81 ± 0.15	7.35	3.85 ± 0.25	9.85
300 + 0%	1	134.61 ± 0.04	64.74	149.23 ± 8.99	70.45	153.76 ± 14.57	69.15
	2	40.60 ± 1.67	19.53	37.92 ± 2.58	17.90	37.44 ± 3.49	16.84
	3	24.47 ± 0.57	11.77	17.53 ± 0.17	8.28	22.33 ± 0.81	10.04
	4	4.56 ± 0.40	2.19	3.66 ± 0.21	1.73	4.06 ± 0.28	1.83
	5	3.68 ± 0.21	1.77	3.49 ± 0.02	1.65	4.76 ± 0.03	2.14
300 + 1% (2 mm)	1	138.93 ± 0.79	66.39	147.89 ± 11.13	68.35	140.19 ± 10.07	66.29
	2	38.82 ± 0.72	18.55	40.53 ± 1.94	18.73	38.27 ± 2.02	18.09
	3	21.61 ± 0.56	10.33	20.40 ± 0.17	9.43	23.53 ± 1.27	11.13

	4	4.13 ± 0.26	1.97	4.06 ± 0.41	1.88	4.35 ± 0.31	2.06
	5	5.76 ± 0.34	2.75	3.49 ± 0.28	1.61	5.15 ± 0.10	2.43
300 + 1% (0.15 mm)	1	150.56 ± 0.18	67.02	143.52 ± 3.54	66.52	138.75 ± 4.25	64.05
	2	40.93 ± 1.08	18.22	41.12 ± 0.53	19.06	40.69 ± 0.55	18.79
	3	24.00 ± 1.45	10.68	22.60 ± 0.19	10.47	27.27 ± 0.66	12.59
	4	4.72 ± 0.27	2.10	4.54 ± 0.28	2.11	4.63 ± 0.16	2.14
	5	4.45 ± 0.27	1.98	3.99 ± 0.16	1.85	5.28 ± 0.36	2.44
1000 + 0%	1	490.40 ± 0.06	76.27	506.43 ± 28.03	76.01	514.40 ± 15.45	75.29
	2	96.43 ± 6.01	15.00	109.07 ± 3.96	16.37	110.00 ± 3.33	16.10
	3	44.60 ± 2.83	6.94	39.80 ± 0.23	5.97	46.00 ± 1.72	6.73
	4	6.86 ± 0.43	1.07	5.62 ± 0.15	0.84	6.28 ± 0.61	0.92
	5	4.65 ± 0.59	0.72	5.33 ± 0.13	0.80	6.51 ± 0.19	0.95
1000 + 1% (2 mm)	1	460.62 ± 0.05	72.29	446.88 ± 13.75	71.59	496.93 ± 17.15	73.71
	2	117.89 ± 18.42	18.50	113.07 ± 7.42	18.70	113.89 ± 4.36	16.89
	3	46.53 ± 1.60	7.30	43.67 ± 0.37	7.82	49.60 ± 1.23	7.36
	4	7.53 ± 0.99	1.18	6.29 ± 0.48	1.09	7.79 ± 0.46	1.16
	5	4.60 ± 0.10	0.72	5.13 ± 0.19	0.97	5.93 ± 0.25	0.88
1000 + 1% (0.15 mm)	1	538.27 ± 3.45	75.25	455.68 ± 15.62	72.66	490.40 ± 2.67	73.22
	2	116.16 ± 7.73	16.24	119.07 ± 4.25	18.38	112.67 ± 2.17	16.82
	3	47.60 ± 2.86	6.65	49.80 ± 0.14	7.10	52.73 ± 1.09	7.87
	4	7.95 ± 0.48	1.11	6.96 ± 0.46	1.02	7.72 ± 0.07	1.15
	5	5.35 ± 0.11	0.75	5.05 ± 0.14	0.83	6.23 ± 0.39	0.93

Table S5 Isotherm model parameters

Isotherm models		Parameters	
Linear Langmuir: $\dfrac{C_e}{q_e} = \dfrac{1}{Q_0 b} + (\dfrac{1}{Q_0})C_e$	Q_0 (mmol/g) and b (L/mmol) are the Langmuir constants related to the maximum adsorption capacity and rate of adsorption; q_e (mmol/g) is the adsorbed amount of adsorbate per unit mass of adsorbent at the equilibrium aqueous concentration of C_e (mM).	Q_0 (mmol/g)	0.19
		b (mM^{-1})	0.45
		R^2	0.64
Linear Freundlich: lnq_e $= lnK_F + \dfrac{1}{n}lnC_e$	K_F (mmol/g) and n are Freundlich constants; and q_e and C_e are the same as Linear Langnmuir	K_F (mmol/g)	0.05
		$1/n$	0.58
		R^2	0.96

Figure S1. Equilibrium isotherm for Pb^{2+} adsorption onto kaolinite (0.1 g kaolinite in 20 mL solution (0.01 M $NaNO_3$), initial Pb^{2+} concentration 0.1-5 mM; reaction temperature 20 °C; initial solution pH 5; contact time 24 h).
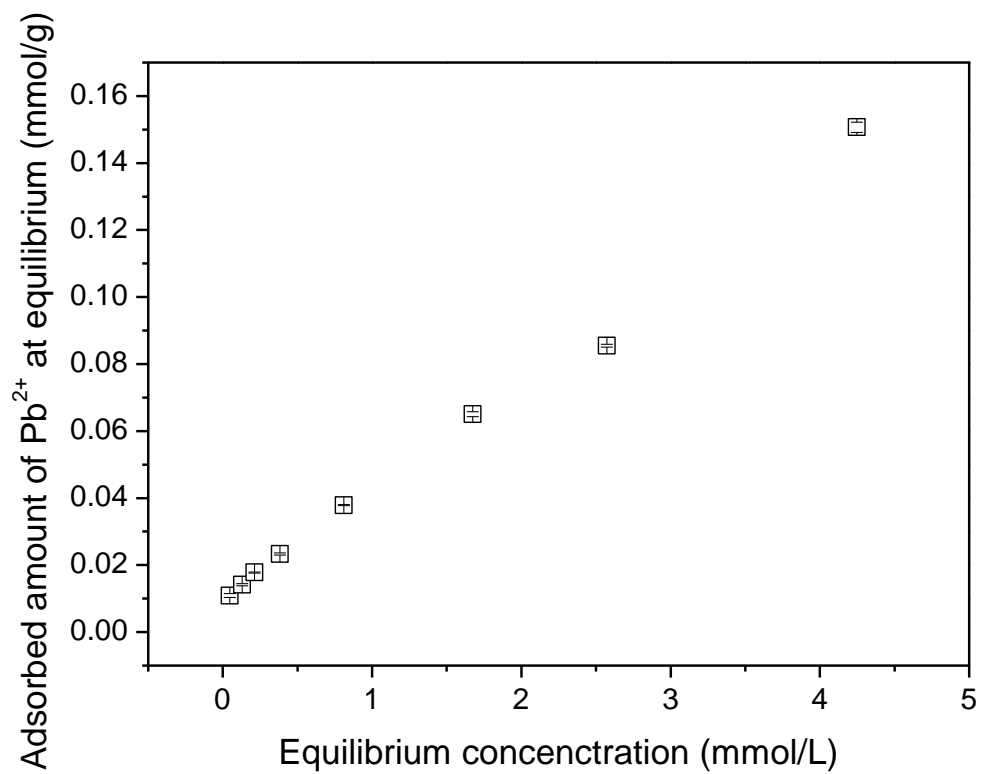
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The immobilisation of biochar on heavy metals in clay soils has been yet or limited investigated compared with sand-based soils. The short-term laboratory incubation study found that biochar failed to affect the mobility or speciation of lead in kaolin. Further chemical analysis suggests it was very likely due to that the biochar failed to competitively adsorb the lead against kaolin. The findings in this study offer a new view towards the biochar potential in soil remediation.

Abstract: Salisbury biochar (produced from British broadleaf hardwood) with two different particle sizes (≤ 2 mm and ≤ 0.15 mm) was applied on a kaolin with three different lead (Pb^{2+}) contamination levels (50 mg/kg, 300 mg/kg and 1000 mg/kg) at the dosage of 1% in w/w. The short-term impact of biochar on the mobility and speciation of Pb^{2+} in the kaolin was investigated using attenuation periods of 1, 7 and 28 days. The leachability and extractability of Pb^{2+} in carbonic acid leaching and EDTA extraction tests as well as the sepciarion of Pb^{2+} in soils were not significantly affected by biochar treatment during all periods. The insignificant effects of biochar on Pb^{2+} immobilisation were most likely attributed to the high adsorption capacity of kaolin towards Pb^{2+} and biochar failed to competitively adsorb Pb^{2+} against kaolin. Kaolin immobilised Pb^{2+} primarily through cation exchange, which represents the readily bioavailable fractions of Pb^{2+} in soils and may still pose environmental risks. This paper suggests the inefficiency of biochar treament on heavy-metal contaminated clay-rich soils. Therefore a laboratory treatablity study with respect to the soil type may be crucial when large-scale biochar applications in heavy-metal associated soil remediation are evaluated.