

Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals

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Abstract The objectives of this study were to determine the selected physicochemical properties of two biochars, one commercially produced from rice husks and the other from oil palm empty fruit bunches, and to evaluate their adsorption capacities for Zn, Cu, and Pb using a batch equilibrium method. The results showed that there was no significant difference between the carbon content of biochars formed from empty fruit bunches (EFBB) and rice husks (RHB). However, the EFBB did present higher quantities of O, H, S, N, and K, compared to the RHB. Although the EFBB had a much lower surface area than the RHB, the former adsorbed much more Zn, Cu, and Pb than the RHB. The higher adsorption capacity of the EFBB over the RHB was a result of the EFBB having higher amounts of oxygen-containing functional groups, a higher molar ratio of O/C, and a higher polarity index $[(O + N)/C]$. This suggests that the biochar's chemical properties were more important than its surface area in the adsorption of Zn, Cu, and Pb.

Keywords Heavy metals · Adsorption · Functional groups · Surface area

Introduction

Biochars derived from organic waste have received a lot of attention lately from environmental management because of

their ability to decrease methane emissions coming from landfills, reduce industrial energy use and emissions through recycling and waste reduction, recover energy from waste, enhance carbon sequestration in soils, decrease energy use for the long-distance transport of waste, reclaim infertile soils and remove inorganic and organic contaminants from soil, sediment and water (Lehmann 2007; Lehmann and Joseph 2009; Roberts et al. 2010; Knowles et al. 2011; Trakal et al. 2011).

The adsorption of heavy metals by biochars from aqueous environments has been explored by numerous studies (Rao et al. 2009; Uchimiya et al. 2010). Chen et al. (2011) studied the ability of two different biochars, derived from hardwood and corn straw, to adsorb Cu(II) and Zn(II) from an aqueous solution. Their results have indicated that these biochars were effective as adsorbents of these heavy metals. Liu and Zhang (2009) investigated the removal of Pb from water using biochars prepared from the hydrothermal liquefaction of pinewood and rice husks, and they found that the two biochars were quite effective at removing Pb from water. Biochars produced from rapid pyrolysis of the wood and barks of oaks were reported to adsorb Pb and Cd better than a commercial activated carbon per unit surface area (Mohan et al. 2007). Barker et al. (2011) showed that charcoal in soils has a distinct and important role in controlling As, Pb, Zn, Fe, and Mn speciation and their subsequent fates in the environment. Black carbon derived from wheat residues has been successfully used as a low-cost adsorbent for the removal of Cr(VI) from an aqueous solution (Wang et al. 2010). The adsorption of Cr(VI) to this black carbon led to the formation of carboxylic and hydroxyl moieties, which were attributed to the oxidation of the wheat residue-derived black carbon, in turn reducing Cr(VI) to Cr(III).

In Malaysia, the presence of heavy metals in the soil and water raises serious concerns, principally due to the acidic

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nature of the soil and water in the country, as heavy metals in acidic conditions are highly mobile (Matos et al. 2001).

The adsorption capacities of biochars for organic and inorganic contaminants are controlled by the biochar's characteristics (Lehmann and Joseph 2009), which in turn are influenced by both the feedstocks (Sohi et al. 2009) and the processing conditions under which they are made (Chen et al. 2011). The characterization of biochars has generally been performed on samples produced by small-scale laboratory reactors under controlled conditions with little feedstock. However, studies on the characterization and adsorption capacities of commercially produced biochars for heavy metals are scarce. Commercially produced biochars can potentially be used as low-cost adsorbents (Chun et al. 2004; Qiu et al. 2008). A large-scale biochar manufacturing plant using a modern engineering system has been built by Universiti Putra Malaysia (UPM), in collaboration with a private company (Nasmech Technology Sdn. Bhd). The plant was built to produce biochar from oil palm empty fruit bunches and is capable of producing 20 tons of biochar daily (Biochar Malaysia 2010). Additionally, biochar derived from rice husks has been produced commercially in Malaysia to avert wastage of large quantities of rice husks (Fauziah et al. 2010). However, as far as we know, there is no available data on the physicochemical properties of these two biochars or on their ability to adsorb heavy metals from aqueous solutions. The objectives of this study were, therefore, to determine the selected chemical properties of both a commercially produced empty fruit bunch biochar (EFBB) and a rice husk biochar (RHB) and to evaluate their adsorption capacities for Zn(II), Cu(II), and Pb(II).

The batch equilibrium adsorption and precipitation studies were carried out at the Soil Chemistry Laboratory of Department of Land Management, Universiti Putra Malaysia (UPM). The surface area, functional groups analysis, C, H, N, S, and O elemental analysis of biochar samples were determined at the Department of Chemistry, UPM. The surface morphology study was carried out at the Institute of Bioscience, UPM. The experiments and analysis were conducted from September to December 2011.

Materials and methods

Chemicals

Millipore[®] water was used to prepare all solutions throughout this study. Zinc(II) chloride, copper(II) chloride, and lead(II) nitrate were purchased from Sigma-Aldrich, and stock solutions (2,000 mg L⁻¹) of each metal were prepared by dissolving an appropriate amount of

analytical grade metal compound in Millipore[®] water. Solution pHs were adjusted to six with concentrated nitric acid. All other chemicals used were of analytical reagent grade purchased from Sigma-Aldrich (Seelze, Germany).

Biochar characterization

Both the EFBB and the RHB were purchased locally. The EFBB was purchased from Nasmech Technology Sdn. Bhd., located in Puchong, while the RHB was purchased from Kedah. The biochar moisture content was measured by drying 5 g of a sample in oven at 80 °C for 24 h, and the moisture content was calculated by the difference between the weights of fresh and oven-dried samples. The pH was measured in a 0.5:100 (w/v) biochar:water suspension. The concentrations of K, Ca, Mg, P, Mn, Fe, Cu, and Na were determined using the ASTM D5142 method (D5142 2009). Ash contents were determined by combusting the EFBB and RHB at 700 °C for 12 h in open crucibles. The carbon, hydrogen, nitrogen, sulfur, and oxygen components of biochar samples were determined using a CHNSO elemental analyzer (Perkin Elmer 2400 Series II CHNSO Elemental Analyzer).

Zeta potential

The zeta potential of a biochar was determined by placing a 0.02-g sample in a 250-mL conical flask and then adding 100 mL of 0.1 M NaCl solution. The suspension pH was adjusted within the range of 2–9, using 0.1 M NaOH or 0.1 M HCl. The suspensions were ultrasonically dispersed in a bath-type sonicator at 40 kHz, with a 300-W power supply, for 2 h at 30 °C. The suspensions were kept standing for 24 h, after which electrophoresis mobility was measured using the JS94G+ micro electrophoresis apparatus (Zetasizer Nano Z).

Surface area analysis

The surface areas of biochar samples were measured with N₂ adsorption at 77.3 K, using a Quantachrome version 2.01 (Quantachrome AS1WinTM) surface area analyzer. The biochar samples were degassed at 100 °C for 9 h prior to N₂ adsorption. The multipoint Brunauer–Emmett–Teller (BET) method was employed to calculate total surface area. The pore volumes, pore radii and internal surface areas (pore surface areas) were obtained from their desorption isotherms, using the Barrett–Joyner–Halenda (BJH) method. Four data points with relative pressures of 0.05–0.3 were used to construct the monolayer adsorption capacity. The total pore volume was estimated from a single N₂ adsorption point at a relative pressure of approximately 0.97.



Functional groups analysis

Fourier transform infrared (FTIR) spectroscopy analysis was carried out to determine the surface functional groups of the biochar samples before and after the adsorption of heavy metals, using a Perkin Elmer FTIR-2000 spectrometer. The oxygen-containing functional groups of EFBBs and RHBs were determined by the Boehm titration method. Briefly, a known amount of biochar was added to alkaline solutions (Na_2CO_3 , NaHCO_3 , and NaOH), and the mixture was agitated for 24 h. The supernatant was then drawn and back titrated with HCl (Boehm 1966; Bandosz et al. 1993).

Surface morphology

The surface morphology of the EFBB and RHB before and after adsorption of heavy metals was examined using a scanning electron microscope at 15 keV, equipped with energy dispersive X-ray spectroscopy (JEOL, JSM-6400V, Japan). The scanning electron microscopy (SEM) analysis was carried out before and after the adsorption of different heavy metals. The biochar samples used for this study were obtained from the batch equilibrium adsorption experiment in which 0.2 g of biochar was shaken in 40 mL of buffer solution (pH 6) containing 100 mg L^{-1} of heavy metal.

The effects of pH on heavy metal precipitation

To distinguish between the adsorption and the precipitation process of heavy metals in solutions, the precipitation of heavy metals was examined in four different solutions. These solutions were (1) derived from a supernatant solution with 1.25, 2.5, 5, 10 or 15 g L^{-1} of EFBB; (2) derived from a supernatant solution with 1.25, 2.5, 5, 10 or 15 g L^{-1} of RHB; (3) non-buffered solutions with pHs between 2 and 9; and (4) buffered solutions with pHs between 2 and 9.

All solutions further received 100 mg L^{-1} of Zn, Cu, or Pb and were then shaken for 24 h, after which the solutions were centrifuged at 1,000 rpm for 10 min. The supernatant solutions were then analyzed for their concentrations of heavy metals using a PerkinElmer AA analyst 400 atomic absorption spectrometer.

The effects of solution pH on heavy metal adsorption

The adsorption of Zn, Cu, and Pb was studied using a buffer solution at different pHs. The adsorption of Zn, Cu, and Pb was studied at pHs between 2 and 8, 2 and 7, and 2 and 6, respectively. The procedure was the same as that used for the batch equilibrium experiment, except that only one concentration of heavy metal (50 mg L^{-1}) was used.

The concentration of the remaining heavy metals in the solution was measured after 24 h of equilibration.

Batch equilibrium adsorption

This experiment was carried out at $25 \pm 1.5^\circ\text{C}$. Exactly 0.2 g of the EFBB or RHB was transferred to centrifuge tubes containing 40 mL of either Zn, Cu or Pb, at $4\text{--}400 \text{ mg L}^{-1}$, prepared in a buffer solution at a pH of 6. The optimum equilibrium time and the concentration of the biochar for the batch equilibrium method have been determined to be 24 h and 5 g L^{-1} , respectively, prior to the experiment. The centrifuge tubes were shaken on a rotary shaker at 40 rpm for 24 h and then centrifuged at 10,000 rpm for 10 min. The supernatants were analyzed for their concentrations of heavy metals by the Perkin Elmer AA analyst 400 atomic absorption spectrometer. All experiments were conducted in triplicate. Control samples without biochar were included to determine the degrees of adsorption of Zn, Cu, and Pb, from solutions without the EFBB or RHB. To evaluate and compare the adsorption capacities of the EFBB and RHB for Zn(II), Cu(II), and Pb(II), the Langmuir and Freundlich adsorption models were used to fit the sorption data. The equations of Langmuir and Freundlich's adsorption models are as follows:

$$\text{Langmuir, } q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (1)$$

$$\text{Freundlich, } q_e = K_f C_e^n \quad (2)$$

where q_e is the amount of the metal adsorbed per unit weight of biochar (mg g^{-1}); C_e is the equilibrium concentration of metal in solution (mg L^{-1}); Q_{\max} is the maximum adsorption capacity (mg g^{-1}) and b is the constant related to the affinity. The K_f and n are the Freundlich constants, which are related to the adsorption capacity and intensity, respectively. The values of Q_{\max} , b , K_f , and n were determined from the linearized form in the Langmuir and Freundlich equations.

Results and discussion

Physicochemical properties of the EFBB and RHB

The selected physicochemical properties of the EFBB and RHB are shown in Table 1. There was no significant difference between the carbon content of the EFBB and RHB; however, the concentrations of O, H, S, N, and K in the EFBB were much higher than in the RHB. In contrast, the amount of Si was higher in the RHB. The concentrations of Zn, Cu, and Pb were very low in both biochars. The molar ratios of hydrogen to carbon (H/C) for the EFBB and RHB



Table 1 The selected physiochemical characteristics of the EFBB and RHB

Parameters	EFBB	RHB
Moisture content (%)	2.00	3.70
Ash content (%)	13.9	27.2
pH	9.4	8.50
C (%)	48.0	45.0
O (%)	30.0	17.0
H (%)	3.80	2.30
S (%)	0.50	0.20
N (%)	1.30	0.17
K (%)	5.40	0.09
Si (%)	0.80	11.00
H/C molar ratio	0.08	0.05
O/C molar ratio	0.61	0.37
(O + N)/C molar ratio	0.64	0.38
Al (mg kg ⁻¹)	350	189
Ca (mg kg ⁻¹)	792.00	671.00
Mg (mg kg ⁻¹)	414.00	357.00
Na (mg kg ⁻¹)	63.00	75.00
P (mg kg ⁻¹)	587.00	638.00
Fe (mg kg ⁻¹)	23.00	45.00
Mn (mg kg ⁻¹)	8.00	13.00
Zn (mg kg ⁻¹)	0.73	0.50
Cu (mg kg ⁻¹)	0.19	0.10
Pb (mg kg ⁻¹)	0.16	0.11
OH group (mEq g ⁻¹)	0.33	0.09
CO group (mEq g ⁻¹)	0.34	0.27
COOH group (mEq g ⁻¹)	0.31	0.24
Total oxygen-containing functional groups (mEq g ⁻¹)	0.98	0.60
Total surface area (m ² g ⁻¹)	1.890	25.161
Pore surface area (m ² g ⁻¹)	1.085	7.469
Pore volume (cm ³ g ⁻¹)	0.011	0.018
Pore radius (Å)	24.818	18.068

were 0.08 and 0.05, respectively. These amounts are much lower than the reported value obtained from an activated carbon, which was 0.256 (Chen et al. 2008). The degree of carbonization can be estimated from the H/C molar ratio (Kuhlbusch 1995). The low H/C molar ratios for both biochars suggest that they contained low amounts of the original plant organic residues, such as cellulose, but high carbonization (Chun et al. 2004). The molar ratio of oxygen to carbon (O/C) of biochars has been used as an indicator for surface hydrophilicity because it is indicative of the polar group content derived from carbohydrates (Chun et al. 2004). The molar ratio of O/C for the EFBB (0.67) was higher than for the RHB (0.37). The O/C molar ratios of both biochars were high in comparison to the reported values in the literature (Chen et al. 2011),

suggestive of the hydrophilic nature of the EFBB and RHB. The EFBB had a higher polarity index [(O + N)/C] than the RHB, which indicates a higher concentration of surface polar functional groups in the EFBB (Chen et al. 2008). The total concentration of oxygen-containing groups in the EFBB (0.98 mEq g⁻¹) was higher than in the RHB (0.60 mEq g⁻¹). The presence of high concentrations of oxygen-containing groups has been demonstrated as an indicator of a biochar's ability to adsorb heavy metals (Tan et al. 1993). The total surface area of the RHB (25.161 m² g⁻¹) was much higher than that of the EFBB (1.898 m² g⁻¹). The pore surface area and pore volume were also higher in the RHB than in the EFBB. However, the pore radius in the RHB was smaller than in the EFBB, and there was not much difference between in the pore volumes of both biochars.

Zeta potential of the EFBB and RHB

The zeta potentials of EFBB and RHB at different pHs are shown in Fig. 1. In the pH range of 2–9, the zeta potentials of both biochars were negative. The zeta potential of the EFB at pH 2 was −7 mV and became drastically more negative with increasing pH, reaching −24 mV at a pH of 4. Thereafter, the zeta potential was not significantly affected by increasing pH. The zeta potential of the RHB also dropped with increasing solution pH but less drastically than was observed for the EFBB. The zeta potential of the RHB dropped significantly, from −5 mV at pH 2 to −14.3 mV at pH 6, after which no further significant decline was observed. The zeta potential of the EFBB was more negative than of the RHB's at all pHs. The negative values of the zeta potentials of both biochars at all pHs suggest that the surfaces of both biochars are negatively charged. With increasing pH, more functional groups become deprotonated and the biochar surfaces become more negatively charged. The EFBB were more negatively charged than RHB due to the presence of higher amount of OH-containing functional groups in the EFBB than the RHB (Table 1).

The effect of pH on heavy metal precipitation in different solutions

Figure 2 shows the amounts of Zn, Cu, and Pb at 100 mg L⁻¹ remained in four different solutions at different pHs, after being equilibrated for 24 h. Figure 2a shows that the concentrations of Zn, Cu, and Pb were quite low in buffered solutions at pHs of 7, 8, and 9, respectively, suggesting that most of the heavy metals were precipitated at these pHs. The precipitation densities of these heavy metals at a pH of 9 were 55, 38, and 20 mg L⁻¹ for Pb, Cu, and Zn, respectively. The percentages of heavy metals



precipitated were lower in the non-buffered solution (Fig. 2b). The heavy metals were also precipitated in a solution made up of an EFBB and RHB supernatant and Millipore® water mixture (Fig. 2c, d). The amounts of heavy metals precipitated in the solution derived from the EFBB supernatant were higher than for the solution made up of RHB. This may be because the EFBB supernatant was able to raise the solution pH higher than the RHB supernatant. For instance, solution derived from supernatant solution with $1.25\text{--}15\text{ g L}^{-1}$ of EFBB were increased from pH 7.8 to 10.3, while solution derived from supernatant solution with $1.25\text{--}15\text{ g L}^{-1}$ of RHB increased only from pH 7.3 to 9 (Fig. 2c, d). The main mechanism for the precipitation of heavy metals is the complexation of metals with hydroxyl ions in solutions (Sciban et al. 2006). The addition of heavy metals to the non-buffered solution ($\text{pH} > 6$) and the solutions made up of the EFBB and RHB supernatant decreased the solution's pH. The pH of these solutions after adding the heavy metals dropped from pH 5.3 to 6.2. Therefore, the hydroxyl ions may have coordinated with the metals ions and precipitated as metal-(OH)₂. However, the hydroxyl ions can be continually supplied in the buffered solution. As a result, greater precipitation will occur in the buffered solution (Fig. 2a), compared to the non-buffered solution (Fig. 2b). The solutions made up of the EFBB and RHB supernatants had alkaline pHs, and the heavy metals may have been precipitated by the same mechanism.

The results indicate that the addition of biochar to a non-buffered solution will increase the solution pH in an adsorption study; hence, it would be difficult to differentiate metal adsorption with precipitation in the non-buffered solution. Therefore, in the study on the effect of pH on heavy metal adsorption to the EFBB and RHB, testing was conducted within the pH range at which no precipitation of heavy metals would be expected, i.e., at pHs of 2 through 8, 2 through 7, and 2 through 6 for Zn, Cu and Pb, respectively.

The effect of pH on heavy metal adsorption

The amounts of heavy metals adsorbed at different pHs by the EFBB and RHB are presented in Fig. 3. The amount of heavy metals adsorbed increased with increasing solution pH for all metals. At low pHs, the heavy metals compete with hydrogen ions for the sorption sites. As the solution pHs increased, the amount of negative charge on the EFBB and RHB surfaces also increased (Fig. 1), making more adsorption sites available for heavy metals. The adsorption of heavy metals by the EFBB was higher than by the RHB at all pHs for all heavy metals, with the adsorption of Pb being highest, followed by Cu and Zn for both biochars at all pHs.

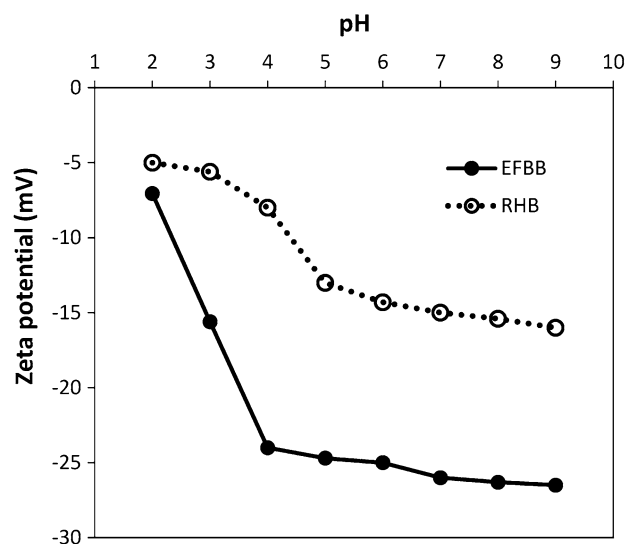


Fig. 1 Zeta potential of the EFBB and RHB measured at different pHs

Batch equilibrium adsorption

The isotherm adsorption data were fitted to the Langmuir and Freundlich adsorption models, and the values of the adsorption isotherm parameters are shown in Table 2. The Langmuir adsorption model fits all adsorption data better than the Freundlich adsorption model, as shown by the higher R^2 values. The EFBB had higher Langmuir affinity values (b) and a maximum adsorption capacity (Q_{\max}) for all heavy metals, compared with the RHB. In general, the adsorption affinity and maximum adsorption capacities of both biochars for all heavy metals were in the order of $\text{Pb} > \text{Cu} > \text{Zn}$, similar to the results of the effect of pH on adsorption. The Freundlich adsorption coefficient values also indicate a higher heavy metal adsorption by the EFBB over the RHB for all metals, and the adsorption of Pb was highest, followed by Cu and Zn. The adsorption capacities of the EFBB and RHB for the heavy metals were higher than the values reported in the literature for other biochars (Liu and Zhang 2009; Chen et al. 2011). Therefore, it can be concluded that these commercially produced EFBBs and RHBs have the potential for use as adsorbents for Zn, Cu, and Pb from aqueous solutions. The adsorption of Pb was highest for both biochars, followed by Cu and Zn. This can be explained by the fact that both Pb and Cu can easily react with functional groups containing unshared pairs of electrons such as those in O, N, P, and S. Additionally, Pb and Cu have a greater affinity for carboxyl groups than does Zn (Thirumavalavan et al. 2011). Hence, Pb and Cu can easily coordinate with both the carboxyl and hydroxyl groups of the biochars, as the functional groups have valence shell electrons in the outer orbital. However, it is hard for Zn to coordinate with carboxyl and hydroxyl



Fig. 2 Concentrations of heavy metals remaining in **a** buffer solution at pHs of 2 through 9, **b** non-buffer solution at pHs 2 through 9, **c** solution containing supernatant of the EFBB and Millipore® water at pHs 7.8 through 10.3, **d** solution containing supernatant of the RHB and Millipore® water at pHs 7.3 through 9, after equilibration

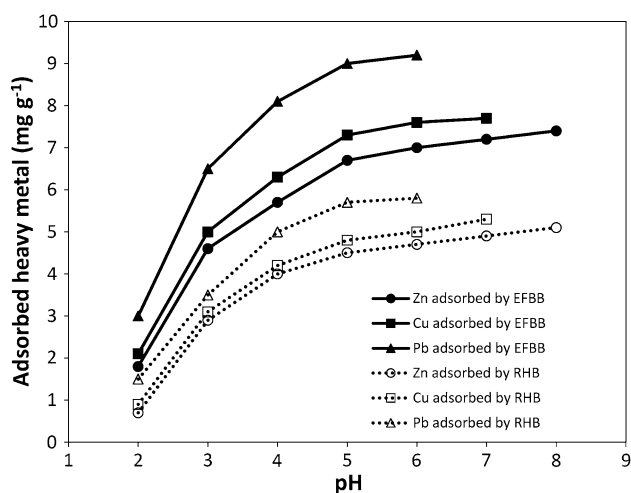
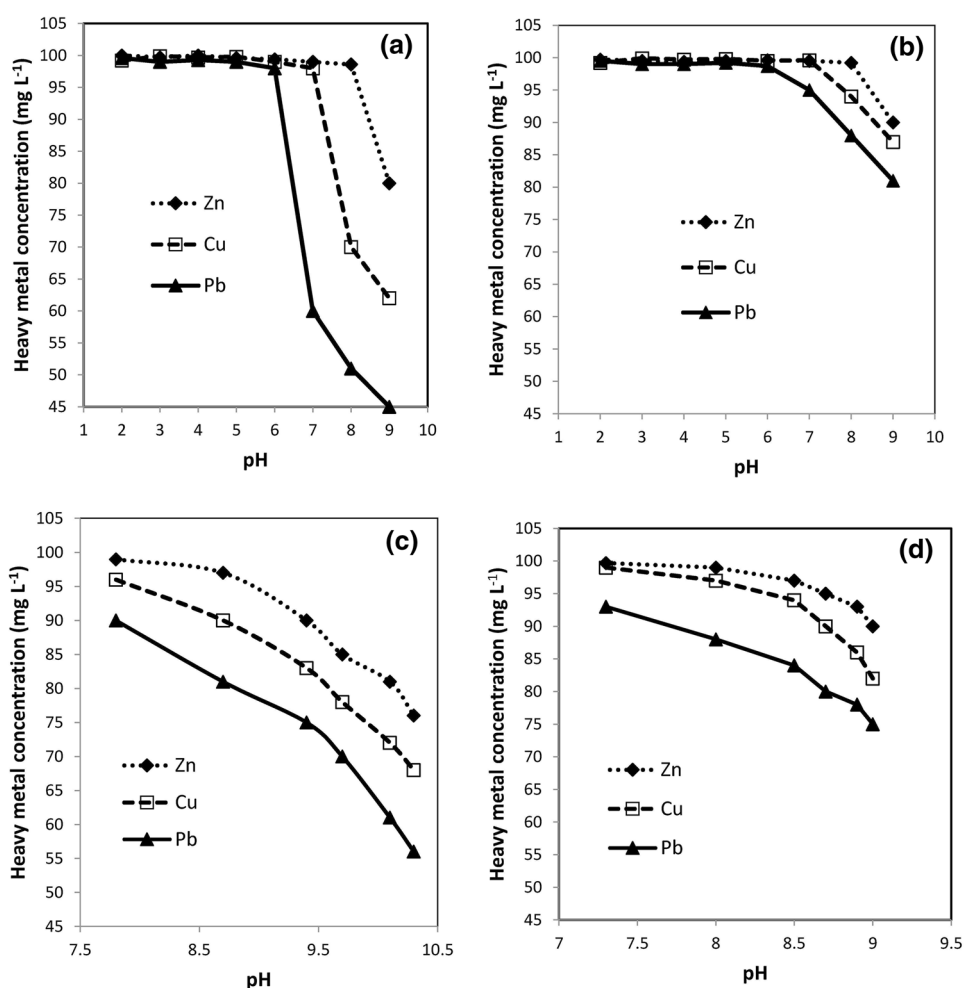


Fig. 3 The amounts of Zn, Cu, and Pb adsorbed by the EFBB and RHB from solutions buffered at different pHs

groups because its outer orbital electrons are completely filled—hence the decreased adsorption of Zn by the biochars. Pb has the fewest electrons in its outermost valence shell among the heavy metals studied; thus, it can bind with

functional groups with donor sites better than Cu and Zn (Thirumavalavan et al. 2011). The result of this study is in agreement with the result of Zhua et al. (2012) who reported that metals adsorption onto xanthate-modified magnetic chitosan followed the order of Pb(II) > Cu(II) > Zn(II). They speculated that electron pair of the nitrogen atom of the adsorbent was donated to the shared bond between the nitrogen and the heavy metals.

Functional groups analysis

The FTIR spectra of the EFBB before and after adsorption of heavy metals are shown in Fig. 4. The absorption band at 3,385.73 cm⁻¹ indicates the stretching vibration of hydroxyl groups. The spectra of these groups shifted to 3,387, 3,359 and 3,373 cm⁻¹ after adsorption of Zn, Cu, and Pb, respectively. The shift in the hydroxyl group spectrum indicates its involvement in the adsorption process. The 2,925.66 cm⁻¹ band, which is a signature of the C–H group of long-chain aliphatic components, shifted slightly after adsorption of the heavy metals. This may be due to the formation of a heavy metal–carbon bond during



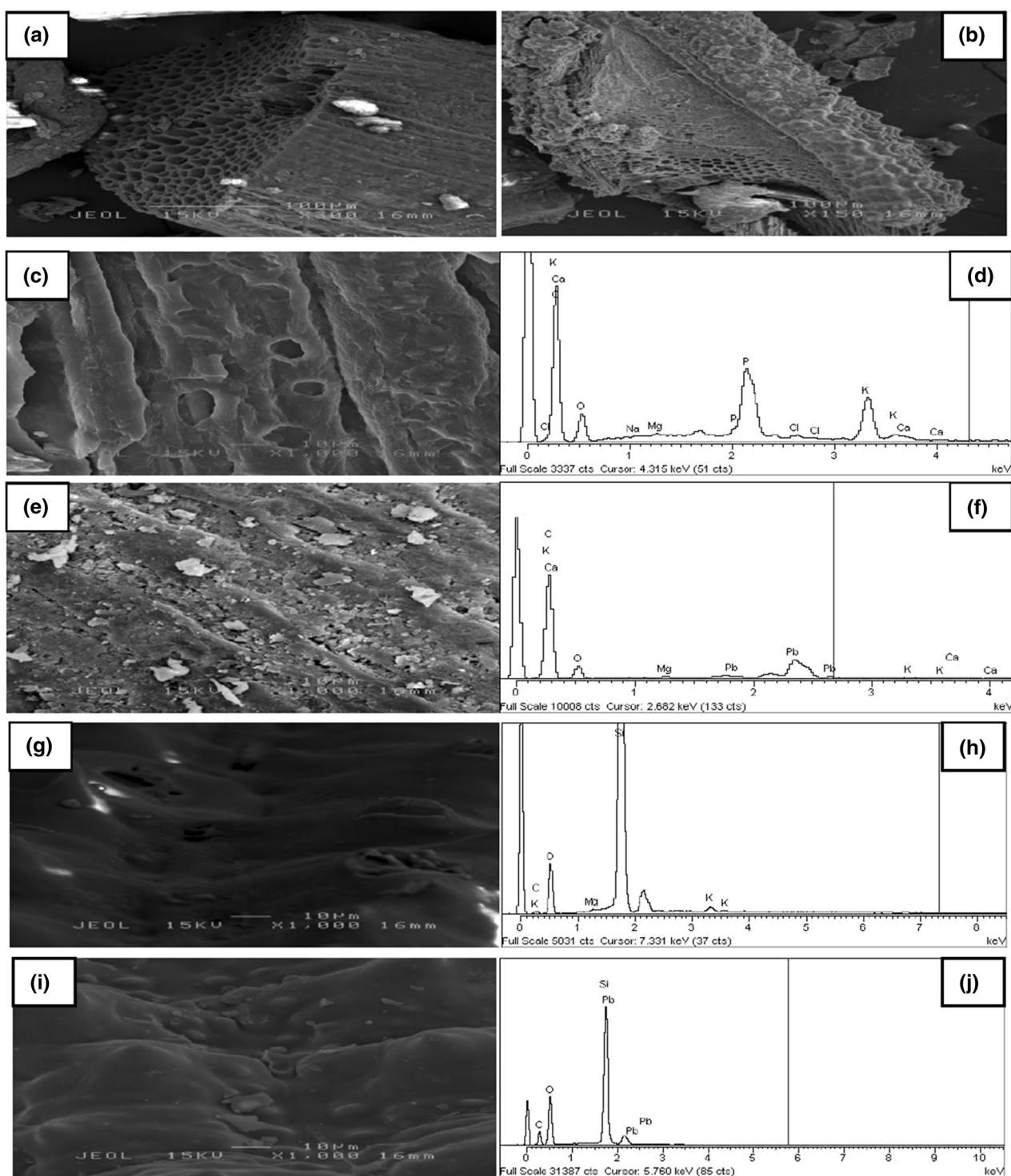


Fig. 6 The SEM micrographs of the EFBB and RHB: **a** the shape and pores of the EFBB, **b** the RHB shape and pores, **c** surface of the EFBB before adsorption of Pb, **d** EDS spectrum of the EFBB before adsorption of Pb, **e** surface of the EFBB after adsorption of Pb, **f** EDS

spectrum of the EFBB after adsorption of Pb, **g** surface of the RHB before adsorption of Pb, **h** EDS spectrum of the RHB before adsorption of Pb, **i** surface of the RHB after adsorption of Pb, **j** EDS spectrum of the RHB after adsorption of Pb

functional groups were involved in heavy metal adsorption. The spectra of EFBB (Fig. 4) shows more peaks than the RHB (Fig. 5), and this is confirmed by the higher

concentration of oxygen-containing functional groups in the EFBB (0.98 mEq g^{-1}), compared with the RHB (0.60 mEq g^{-1}) (Table 1). The zeta potential of the EFBB



was more negative than that of the RHB. The higher concentration of oxygen-containing functional groups, amounts of functional groups, O/C ratio and (O + N)/C, as well as the lower zeta potential (greater negativity) can all be the cause of the higher adsorption of heavy metals by the EFBB over the RHB. The type and concentration of surface functional groups have been reported as playing an important role in the adsorption capacities of organic adsorbents (Yenisoy-Karakas et al. 2004). Although the surface area of the RHB ($25.161 \text{ m}^2 \text{ g}^{-1}$) was much higher than that of the EFBB's ($1.890 \text{ m}^2 \text{ g}^{-1}$), it had a lower adsorption capacity for the metals, suggesting that surface area was less important than oxygen-containing functional groups, zeta potentials, the amounts of functional groups, O/C ratios, (O + N)/C ratios and polarity indices [(O + N)/C] in determining Zn, Cu, and Pb adsorption by these biochars. From these results, it can be concluded that the adsorption of Zn, Cu, and Pb by the EFBB and RHB was a charge transfer interaction and not an intrinsic one, which would be significantly influenced by the adsorbent surface area (Gang and Weixing 1998).

Surface morphology

The SEM micrographs for the EFBB and RHB before and after adsorption of Pb are shown in Fig. 6. The pore structures in both are shown in Fig. 6a and f, respectively. The surface morphology of the EFBB was smooth prior to adsorption of Pb (Fig. 6b) but became coarser after adsorption of Pb (Fig. 6d). The EDS spectra of the EFBB before and after Pb adsorption are shown in Fig. 6c and e, respectively, while the spectra for the RHB are shown in Fig. 6c and j. C, O, Mg, K, Ca, and P were present on the surface of the EFBB, but prior to adsorption, whereas Pb was not. After adsorption, Pb was present on the surface, confirming that adsorption had occurred. The surface of the RHB was smooth before adsorption of Pb (Fig. 6g), and there was no considerable change in the surface morphology after the adsorption of Pb (Fig. 6i). However, the adsorption of Pb is confirmed by the EDS spectra (Fig. 6j), confirming that adsorption of Pb by the RHB was low compared to that of the EFBB. The surface morphologies for EFBB and RHB before and after the adsorption of Cu and Zn (figures not shown) were similar to the patterns observed before and after adsorption of Pb.

Conclusion

Both biochars were able to adsorb Zn, Cu, and Pb from aqueous solutions. Although the EFBB had a much lower surface area than that of the RHB, it had a higher adsorption capacity for the heavy metals, suggesting that

surface area was less important than oxygen-containing functional groups, the zeta potential, the amount of functional groups and polarity indices in determining Zn, Cu, and Pb adsorption by these biochars. Finally, it is suggested here that the adsorption of Zn, Cu, and Pb by both biochars was complexation of heavy metals by surface functional groups and not intrinsic, which would instead be significantly influenced by adsorbent surface area.

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