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ORIGINAL ARTICLE

Adsorption of Cd^{2+} and Pb^{2+} onto coconut shell biochar and biochar-mixed soil

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Abstract Permeable reactive barrier (PRB) systems containing effective and low-cost adsorbents for heavy metals are expected to function as in situ treatment methods for leachate from waste landfills and contaminated groundwater surrounding the landfills in developing countries. This study was conducted to characterize the adsorption of Cd^{2+} and Pb^{2+} onto coconut shell biochar (fine granules), a local soil from Sri Lanka (Entisol), and a biochar-mixed soil (1:1 mixture of biochar and soil) as potential adsorbents for PRB systems. Batch experiments were carried out to investigate the effects of solution pH, contact time, initial ion concentration, and competitive ions on the Cd^{2+} and Pb^{2+} adsorption. Results showed that the adsorption kinetics of Cd^{2+} and Pb^{2+} onto all adsorbents were well described by the pseudo second order kinetics model and that adsorption isotherms followed the Langmuir model. In the range of pH ≥ 3, the initial solution pH had a minor effect on efficiency of metal removal and the removal of metals mostly exceeded 80 % for all adsorbents. Measured maximum adsorptions onto soil and biochar-mixed soil were 30.1 mmol/g for Cd^{2+} and 44.8–46.7 mmol/g for Pb^{2+}. These adsorption capacities are similar to or higher than the values of biosorbents tested for wastewater treatment in previous studies, suggesting our tested materials would be useful as adsorbents of Cd^{2+} and Pb^{2+} in PRB systems. Additional analysis by scanning electron microscopy linked with energy dispersive X-ray revealed that both Cd^{2+} and Pb^{2+} exhibited high adsorption affinity towards soil particles while adsorbing randomly to biochar granules.

Keywords Adsorption · Adsorbents · Batch experiments · Coconut shell biochar · Heavy metals · Permeable reactive barrier (PRB)

Introduction

Due to the rapid development and urbanization of the Asia–Pacific region, solid waste generation exceeded 1.3 million tons/day in 2012 (UNESCAP 2014). In particular, it has been reported that nearly 90 % of municipal solid waste (MSW) generated is disposed of in unengineered facilities in South and Southeast Asia (Tränkler et al. 2005). During the decomposition of buried waste in landfills, wastewater in the form of landfill leachate is generated by excess rainwater percolating through the waste layers in the landfill (Al-Yaqout and Hamoda 2003). Landfill leachate seeps into the soil and surrounding water bodies and contaminates the soil, surface water, and groundwater resources, causing serious environmental problems. Landfill leachate contains various types of organic and inorganic compounds including heavy metals and hazardous substances (Baun et al. 2004; Sewwandi et al. 2013; Wijesekara et al. 2014). For example, Sewwandi et al. (2013) investigated water qualities of landfill leachate from ten waste landfills under different

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climate conditions in Sri Lanka and reported that cadmium (Cd) concentrations ranged from 100 to 200 ppm (0.89–1.78 mmol/L) and lead (Pb) concentrations ranged from 100 to 500 ppm (0.48–2.41 mmol/L).

As practical and effective technologies for in situ treatment of contaminated groundwater, permeable reactive barrier (PRB) systems have been considered worldwide as simple and inexpensive solutions (Devare and Bahadir 1994; Park et al. 2002). The PRB is defined as "an emplacement of reactive media in the subsurface designed to intercept a contaminated plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier (Devare and Bahadir 1994)". The basic substance of a PRB is a reactive material, which is placed across the plume of contaminated groundwater. Depending on the target contaminants to be treated, several kinds of reactive materials have been used in PRB systems. Especially, apatite, activated carbon, and fly ash have been tested for the removal of heavy metals in groundwater and wastewater (Park et al. 2002; Di Natale et al. 2008; Brooks et al. 2010). The barriers are designed to be more permeable than the existing natural subsurface media so that the polluted water can pass through easily while transforming the contaminants into non-toxic or immobile substances (Henderson and Demond 2007).

To develop an effective PRB system as the in situ treatment method for landfill leachate from waste landfills and for contaminated groundwater surrounding the landfills in developing countries, low-cost and easily available local materials should be utilized as adsorbents in the PRB. A local material suitable for the PRB adsorbent is an effective geo-material with high chemical exchange and adsorption capacities which are involved in the removal process of heavy metals in soils (Appel et al. 2008; Vithanage et al. 2007; Altin et al. 1999). Other useful local materials for the PRB adsorbent are biomaterials such as waste and by-products of agricultural activities. Different types of biomaterials such as sawdust (Božić et al. 2009; Sewwandi et al. 2012), rice husk (Bansal et al. 2009), and coconut husk (Sewwandi et al. 2014) have been tested for heavy metal removal. Among different types of biomaterials, biochar has recently gained a significant research interest as a soil amendment as well as a long-term solution for global warming (Lehmann et al. 2006). Further, it is commonly used as a cost-effective adsorbent in wastewater treatment (Yao et al. 2011; Chen et al. 2011).

Several approaches have been made to enhance heavy metal adsorption of soils by mixing it with biochar. For example, Jiang et al. (2012) investigated adsorption of Pb^{2+} by tropical soils with low cation exchangeable capacity (CEC) incubated with rice straw biochar and showed that the incorporation of biochar significantly increased Pb^{2+} adsorption from the incubated soils with increasing negative surface charge. Further, Uchimiya et al. (2010) revealed that increasing the pH by addition of biochar immobilized heavy metals. Those studies suggest that mixing biochar with soil is effective to improve adsorption characteristics of heavy metals onto adsorbents. However, various factors such as solution pH, initial metal concentration, and competitive ions affect heavy metal adsorption onto biochar-amended/mixed soil. To have a better understanding of heavy metal adsorption onto soil and biochar-amended/mixed soil, further studies are needed to examine adsorption characteristics of heavy metals under various chemical conditions.

In this study, to develop a suitable PRB system equipped with low-cost and effective adsorbents in Sri Lanka, we selected a local soil from Sri Lanka (Entisol) based on previous studies (Mapa et al. 2010; Paranavithana et al. 2013) and fine granules of coconut shell biochar (<75 μm), which is inexpensive and abundantly available in tropical countries, including Sri Lanka (Child 1940; Babel and Kurniawan. 2004; Shenbagavalli and Mahimairaja. 2012) as testing materials. As target pollutants, the two heavy metals Cd^{2+} and Pb^{2+}, which are typically detected in landfill leachate, were used in this study. The objectives of this study were (1) to characterize adsorption properties of Cd^{2+} and Pb^{2+} onto coconut shell biochar, a local soil, and a biochar-mixed soil (1:1 mixture of biochar and soil) under various chemical conditions, and (2) to examine the effectiveness of tested materials as PRB adsorbents based on quantified adsorption capacities.

Materials and methods

Materials used

A local soil from Bangadeniya, North Western Province, Sri Lanka, was used in this study. The soil is a loamy alluvial soil and is categorized as an Entisol in the FAO classification system (FitzPatrick 1980; Mapa et al. 2010; Kang and Tripathi 2015). Properties of the soil are tabulated in Table 1. The soil texture was sandy clay loam. The soil is known as a naturally acidic soil and possesses a relatively high CEC (Mapa et al. 2010). Paranavithana et al. (2013) investigated detailed soil physical properties of eight typical soils in Sri Lanka. They found that the selected soil from Bangadeniya was rich in micropores in the range from 0.5 to 50 μm, which are effective for water retention (Pagliai et al. 2004). In addition, the surface charge of the Bangadeniya soil was predominantly permanent (less pH-dependent charge) based on the

Table 1 Material properties of selected soil from Bangadeniya, Sri Lanka

Description	Value
Location	Bangadeniya, Sri Lanka
Order of soil	Entisols
Soil name	Alluvial loamy soil
USDA textural classification	Sandy clay loam
Climate zone	Intermediate
Moisture content (%)	2.23
pH (H_2O)	4.7
Electrical conductivity (μS/cm)	59
Particle density (g/cm^3)	2.69
BET surface area (m^2/g)	28.5
Cation exchange capacity (cmol/g)[a]	5–50
Major constituents	Kaolin minerals
	Smectite group
Minor constituents	Quartz
	Goethite

[a] Mapa et al. (2010)

results from surface charge measurements of suspended clay solution (ζ-potentials). Thus, the loamy alluvial soil from Bangadeniya with a relatively high CEC (dominantly permanent charge) and rich micropores was expected to better adsorb heavy metals and was chosen as a suitable geo-material for the PRB adsorbent in Sri Lanka.

An easily locally available coconut shell biochar was used in this study. In order to mix soil and biochar easily, the coconut shell biochar was crushed and sieved in the laboratory, and fine granules of <75 μm were used in the study. Basic physical and chemical properties of the coconut shell biochar were measured by following standard International Biochar Initiative (IBI) and ASTM methods (IBI 2013). An elemental assay to determine the concentrations of carbon, hydrogen, nitrogen, and oxygen was performed by utilizing elemental analyzers (MT-5, Yanaco, Japan; FLASH 2000 CHNS/O Analyzers, Thermo Scientific, USA). To determine the moisture, volatile matter, and ash concentrations, a Muffle furnace (FO300, Yamato, Japan) was utilized according to ASTM D1762-84 instructions. The pH and EC were determined by mixing biochar with Millipore water in a 1:20 ratio with a reciprocating shaking time of 90 min as described by the standards. The Brunauer–Emmett–Teller (BET) method was utilized to determine the BET surface area using a BET analyzer [Tristar 3020 (II), Micrometrics, USA]. A Mercury Intrusion Porosimeter (AutoPore IV 71V9510, Micrometrics) was utilized to analyze the pore size distribution and porosity of the biochar as per ASTM D4404-10. In addition, Boehm and surface titrations were conducted in the presence of different concentrations of biochar to quantify the basic and acidic groups (Fidel 2012; Fidel et al. 2013; Tseschansky and Graber 2014).

Basic physical and chemical properties of the coconut shell biochar are summarized in Table 2. For reference, values reported in previous studies are also given in the table. The elemental analysis of the tested coconut shell biochar is similar to previously reported results by Shenbagavalli and Mahimairaja (2012). Further, the measured BET surface area of 212 m^2/g ranged in the reported values of 112–378 m^2/g (Wang et al. 2013). The total basic and acidic functional group values determined by the Boehm titration were similar to previously reported values (Al-Wabel et al. 2013).

Batch adsorption experiments

A standard batch method recommended by the Organization of Economic Cooperation and Development (OECD 2000) was used for all batch adsorption experiments in this study. Initially, clean 50 mL Violamo centrifuge tubes (AO1350002, Sigma-Aldrich, USA) were filled with 1 g of each adsorbent, and 10 mL of adsorbate of known concentrations was added. The tubes were then placed on a reciprocating shaker and shaken for 24 h at 100 rpm and 25 °C. After that, the tubes were centrifuged at 8000 rpm for 15 min, and supernatants were filtered through a membrane filter (Millipore 0.23 μm). Then, the supernatants were diluted to achieve measurable concentration ranges and measured by either atomic adsorption spectrophotometry (AA 6200, Shimadzu, Japan) or inductive cumulative plasma mass spectrophotometry (ICPM-8500, Shimadzu). For batch adsorption experiments, three test materials, a selected soil (Entisol), biochar, and biochar-mixed soil (1:1 mixture of biochar and soil), were used as adsorbent. To prepare heavy metal solutions, $PbCl_2$ and $CdCl_2$ (>99.5 %, Wako Pure Chemical Industries, Ltd., Japan) were used.

Kinetics experiments on Cd^{2+} and Pb^{2+} adsorption

To determine Pb^{2+} and Cd^{2+} adsorption kinetics onto the tested materials, a Cd^{2+} solution with a concentration of 2.67 mmol/L (~300 ppm) and a Pb^{2+} solution with a concentration of 1.69 mmol/L (~350 ppm) were used in this study. Triplicate samples were sequentially collected from the shaker after 0, 5, 10, 30, 60, 180, and 360 min at natural pH for the adsorbents. Kinetics models such as interparticle diffusion, pseudo first order kinetics, and pseudo second order kinetics models were used to characterize the adsorption kinetics (Javed et al. 2007;

Table 2 Material properties of biochar

Measured property	Measured value	References
Carbon (%)	86.6	91 (Shenbagavalli and Mahimairaja 2012) 63 (Tsai et al. 2006)
Hydrogen (%)	3.03	6.73 (Tsai et al. 2006)
Nitrogen (%)	0.08	0.09 (Shenbagavalli and Mahimairaja 2012) 0.43 (Tsai et al. 2006)
Oxygen (%)	10.3	28.3 (Tsai et al. 2006)
Ash content (%)	5.53	0.7 (Lehmann and Joseph 2006) 3.38 (Tsai et al. 2006)
pH	8.8	9.18 (Shenbagawalli and Mahimairaja 2012)
EC (µS/cm)	139	730 (Shenbagawalli and Mahimairaja 2012)
BET surface area (m^2/g)	212	112–378 (Wang et al. 2013)
Total pore volume (mL/g)	0.21	–
Total basic groups (µmol/g)	3048	3550 (Al-Wabel et al. 2013)
Total acidic groups (µmol/g)	272	220 (Al-Wabel et al. 2013)
Carboxylic groups (µmol/g)	156	–
Lactone groups (µmol/g)	72	–
Phenol groups (µmol/g)	44	–

Shenbagavalli and Mahimairaja. (2012): domestic coconut shell biochar; Tsai et al. (2006): coconut shell biochar at 500 °C; Lehmann (Lehmann et al. 2006): coconut shell biochar; Al-Wabel et al. (2013): conocarpus biochar at 800 °C; Wang et al. (2013): straw based biochar; this study: coconut shell biochar

Sewwandi et al. 2014). The intraparticle diffusion model can be simply described as:

$$Q_t = D\sqrt{t} \tag{1}$$

where Q_t = amount adsorbed per kg of adsorbent at time t (mmol/kg), D = intraparticle diffusion constant (mmol/kg/$\sqrt{}$min), and t = time (min).

The pseudo first order kinetics model can be defined as

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \tag{2}$$

where Q_e = amount adsorbed per kg of adsorbent at equilibrium (mmol/kg) and K_1 = pseudo first order constant (1/min). For the initial condition at $t = 0$ and $Q_t = 0$, Eq. (2) becomes:

$$\ln(Q_e - Q_t) = \ln(Q_e) - K_1 t \tag{3}$$

The pseudo second order kinetics model can be defined as

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \tag{4}$$

where K_2 = pseudo second order constant (kg/mmol/min). For the initial condition at $t = 0$ and $Q_t = 0$, Eq. (4) becomes:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{5}$$

Effect of initial metal ion concentration on Cd^{2+} and Pb^{2+} adsorption

Batch adsorption experiments were carried out to test materials at natural pH by changing initial Cd^{2+} concentrations from 0.889 to 17.8 mmol/L (100–2000 ppm) and Pb^{2+} concentrations from 0.483 to 9.65 mmol/L (100–2000 ppm). Suspensions of test materials and solutions were shaken for 360 and 60 min, which were decided by kinetics experiments for Cd^{2+} and Pb^{2+}, respectively. The Cd^{2+} and Pb^{2+} adsorption data were fitted to the Langmuir model (Eq. 6) and Freundlich model (Eq. 7) (Bulgariu and Bulgariu. 2012; Cheng et al. 2012):

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{6}$$

where C_e = equilibrium aqueous metal ion concentration (mmol/L), Q_e = amount adsorbed per kg of adsorbent at equilibrium (mmol/kg), b = Langmuir constant related to binding strength (L/mmol), and Q_m = maximum adsorption capacity

$$Q_e = K_f C_e^{\frac{1}{n}} \tag{7}$$

where K_f = Fruendlich adsorption capacity (mmol/kg) and n = adsorption intensity.

Effect of initial pH of metal ion solutions on Cd^{2+} and Pb^{2+} adsorption

To determine the effects of initial pH of metal ion solutions on Pb^{2+} and Cd^{2+} adsorption onto testing materials, adsorption experiments were performed using a Cd^{2+} solution with a concentration of 2.96 mmol/L (333 ppm) and a Pb^{2+} solution with a concentration of 1.57 mmol/L (325 ppm) in the pH range from 2 to 8. The pH values for metal ion solutions were adjusted by adding either sodium hydroxide (NaOH) or hydrochloric acid (HCl). For every pH, triplicate samples were used.

Effect of competitive metal ion on Cd^{2+} and Pb^{2+} adsorption

To examine the effects of competitive metal ions on adsorption onto testing materials, batch adsorption experiments were carried out by using binary metal solutions of Cd^{2+} and Pb^{2+}. For the binary metal solutions, Cd^{2+} to Pb^{2+}, mixed at ratios of 1:1, 1:2, 1:3, 1:4, and 1:5 were used to investigate the effect of Pb^{2+} concentrations on Cd^{2+} adsorption (corresponding initial Cd^{2+} concentration was 0.89 mmol/L). Similarly, the same mixing ratios of Pb^{2+} to Cd^{2+} were used to investigate the effect of Cd^{2+} on Pb^{2+} adsorption (corresponding initial Pb^{2+} concentration was 0.48 mmol/L).

Scanning electron microscopy and X-ray energy dispersion analysis

Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analyses were carried out to study the elemental mapping on metal-adsorbed surfaces of the biochar-mixed soil samples before and after metal adsorption tests. An SEM (SU1510, Hitachi, Japan) and EDX analyzer (Quantax Axis Nova, Bruker AXS K.K., Japan) were used in this study.

Results and discussion

Adsorption kinetics of Cd^{2+} and Pb^{2+}

Amounts of Cd^{2+} and Pb^{2+} adsorbed onto tested adsorbents [Q_t = amount adsorbed per kg of adsorbent (mmol/kg)] were plotted against shaking time [t (min)], as shown in Fig. 1. For all adsorbents, Q_t values for Cd^{2+} and Pb^{2+} became almost constant after 360 min, indicating that adsorption has ceased. Except for the Cd^{2+} adsorption on biochar, rapid adsorption processes for both Cd^{2+} and Pb^{2+} were observed for all adsorbents, and the adsorption of Pb^{2+} reached the maximum after 60 min of shaking.

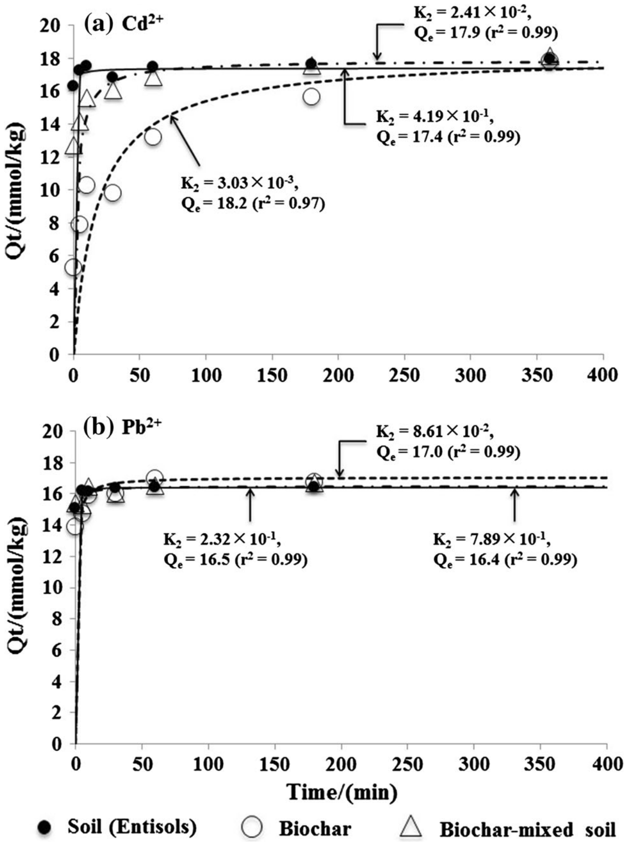

Fig. 1 Fitted curves of Pseudo second order kinetics model for, **a** Cd^{2+} adsorption and **b** Pb^{2+} adsorption

Three kinetics models, intraparticle diffusion (Eq. 1), pseudo first order (Eq. 2), and pseudo second order (Eq. 4), were fitted to measured kinetics data. Out of the three models, the pseudo second order kinetics model performed the best with coefficients of determination (r^2) >0.97 for both Cd^{2+} and Pb^{2+} adsorption onto all adsorbents. Fitted curves and parameters from the pseudo second order kinetics model are also shown in Fig. 1. This result is in accordance with a previous study by Liu and Zhang (2009) that also found a pseudo second order kinetics model best described time dependency of heavy metal adsorption onto biochar.

Effect of initial metal ion concentration on Cd^{2+} and Pb^{2+} adsorption

Measured adsorptions of isotherms of Cd^{2+} and Pb^{2+} onto tested adsorbents are shown in Fig. 2. Two adsorption isotherm models, Langmuir (Eq. 6) and Fruendlich Eq. 7), were tested by fitting the two models to the measured sorption equilibrium data. The Langmuir isotherm model performed with $r^2 > 0.99$ for both Cd^{2+} and Pb^{2+}, better than the Fruendlich adsorption model. Fitted curves and parameters from the Langmuir isotherm model are also

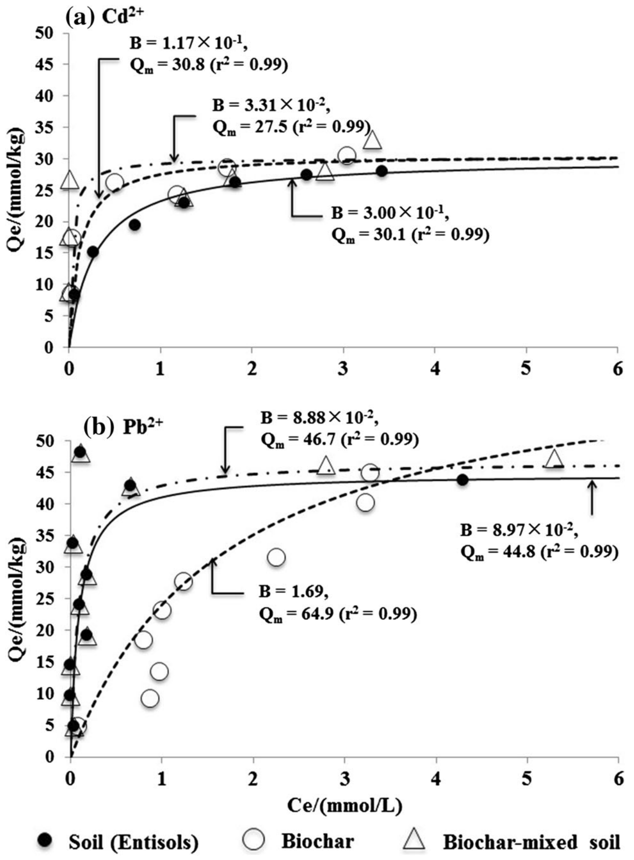

Fig. 2 Fitted curves of Langmuir isotherm model for **a** Cd^{2+} adsorption and **b** Pb^{2+} adsorption

shown in Fig. 2. For all adsorbents, Pb^{2+} adsorption (Fig. 2b) was higher than Cd^{2+} adsorption (Fig. 2a), and Q_m values for Pb^{2+} adsorption ranged from 44.8 to 64.9 and Q_m values for Cd^{2+} adsorption ranged from 30.1 to 30.8 mmol/kg (see Table 3). It is noted that measured Q_m values of Pb^{2+} adsorption onto all tested adsorbents were higher than those for Cd^{2+} adsorption, which is consistent with previous studies (Cheng et al. 2012; Sewwandi et al. 2014). This is probably due to low free energy of hydration and higher reactivity of Pb^{2+} than Cd^{2+} (Cheng et al. 2012).

Figure 3 shows the relationships between metals adsorbed onto adsorbents [Q_e = amount adsorbed per kg of adsorbent at equilibrium (mmol/kg)] from measured adsorption isotherms (Fig. 2) and the difference between initial solution pH and pH after shaking, ΔpH. As seen in Fig. 3, there are good linear relationships between Q_e and ΔpH for both Cd^{2+} and Pb^{2+} adsorption onto all adsorbents. For the tested soil (Entisol of Sri Lanka), ΔpH became mostly negative with increased Q_e, indicating that the pH value decreased after shaking due to the heavy metal adsorption. This may be because the hydroxyl group (R–OH) on the soil surface is the dominant reactive site for the heavy metal adsorption and that H^+ released due to the deprotonation after the heavy metal adsorption caused a decrease in pH (Abd-Elfattah and Wada 1981; Costa et al. 2010). For the biochar and biochar-mixed soil samples, ΔpH decreased when the Q_e values increased for all the adsorbents for both Cd^{2+} and Pb^{2+}. The results of Boehm titration (see Table 2) show that the coconut shell biochar consists predominantly of basic functional groups. These are mainly hydroxyl functional groups as reported by previous studies on biochar (Liu and Zhang 2009). The positive ΔpH values for the adsorption by biochar and biochar-mixed soil indicate that the final pH is higher than the initial pH. However, the increase in the final pH value is decreased while Q_e increased, which resulted in a decrease in ΔpH with the increase of Q_e. This is due to higher H^+ release caused by high deprotonation which is a result of the high adsorption of Cd^{2+} and Pb^{2+} (Jiang et al. 2012; Inyang et al. 2012).

The Langmuir model suggests that the adsorption is caused by monolayer chemical adsorption onto adsorbents (Igwe and Abia 2007). The maximum limits for Cd^{2+} and Pb^{2+} detected in Sri Lankan landfill leachate were 1.78 and 2.41 mmol/L, respectively (Sewwandi et al. 2013). The percentage removals of Cd^{2+} and Pb^{2+} by all three

Table 3 Comparison of maximum adsorption capacities with previous studies

Adsorbent	Cd^{2+}		Pb^{2+}		References
	Q_m/(mmol/kg)	% Removal[a]	Q_m/(mmol/kg)	% Removal[a]	
Soil (Entisols)	30.1	84.7	44.8	92.5	This study
Biochar	30.8	97.6	64.9	63.6	This study
Biochar-mixed soil (1:1 mixture of biochar and soil)	30.1	99.9	46.7	92.5	This study
5 % Peanut straw biochar-amended soil (oxisols)	38.2	–	68	–	Xu and Zhao (2013)
5 % Canola straw biochar-amended soil (oxisols)	28.5	–	49	–	Xu and Zhao (2013)
Coconut coir husk	215.3	75[b]	102.3	80[b]	Sewwandi et al. (2014)
Humic acid-treated coconut coir husk	420.7	75[b]	319	75[b]	Sewwandi et al. (2014)

[a] Values at equilibrium concentrations similar to the maximum detected limits in Sri Lankan leachate in waste landfills (Sewwandi et al. 2014)

[b] Values were calculated based on reported values in reference

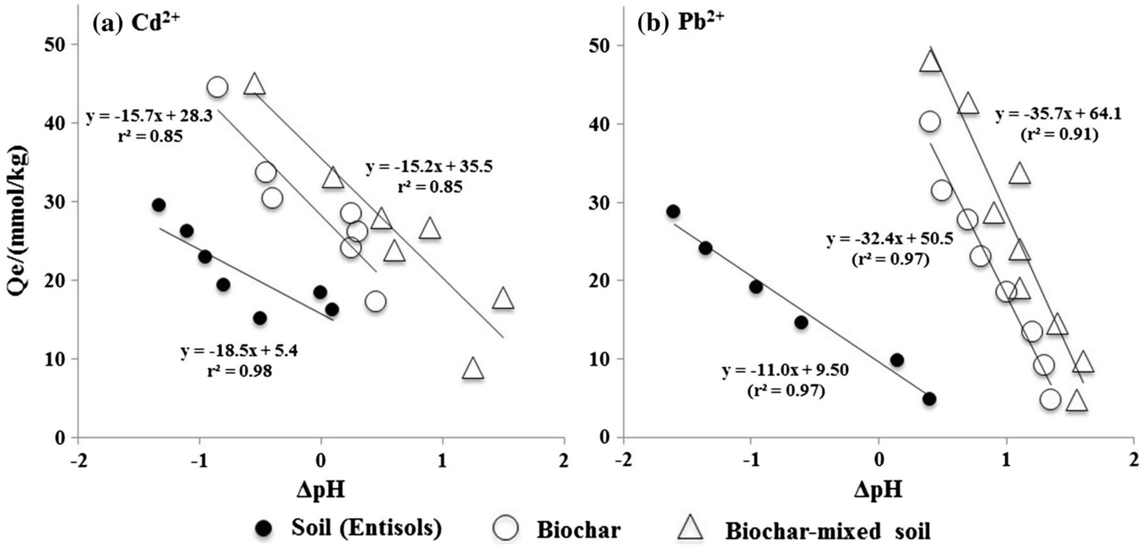

Fig. 3 Relationship between equilibrium concentration Q_e and ΔpH for **a** Cd^{2+} adsorption and **b** Pb^{2+} adsorption

adsorbents corresponding to these recorded concentrations were calculated by Eq. (8) and are shown in Table 3:

$$\text{Percent removal } (\%) = [(C_i - C_e)/C_i] \times 100 \quad (8)$$

where C_i = initial aqueous metal ion concentration (mmol/L), and C_e = equilibrium aqueous metal ion concentration (mmol/L). For both Cd^{2+} and Pb^{2+} removal by the biochar-mixed soil, the removals exceeded 90 %. Consequently, the mixing of 50 % of biochar into the selected loamy alluvial soil (Entisol) was effective to develop a useful PRB adsorbent for the removal of both Cd^{2+} and Pb^{2+} from landfill leachate.

Effect of initial pH of metal ion solutions on Cd^{2+} and Pb^{2+} adsorption

To examine the effects of initial pH of Cd^{2+} and Pb^{2+} solutions on the adsorption onto testing materials, batch adsorption experiments were performed using Cd^{2+} and Pb^{2+} solutions with different initial pH values, pH_i, from 2 to 8. Removal Percentages of Cd^{2+} and Pb^{2+} calculated by Eq. (8), ΔpH (difference in pH after shaking and initial solution pH), and final pH values after shaking were plotted against pH_i (Fig. 4).

The removals for Cd^{2+} and Pb^{2+} were relatively constant in the >70 % range for the tested soil and in the >80 % range for the tested biochar and biochar-mixed soil, except for the markedly lower removal percentages at a pH_i of 2 (Fig. 4a, b). Previous studies show that surface functional groups linked with H^+ in solution are inaccessible to heavy metals at low pH, reducing the removal efficiency (Annadural et al. 2003; Liu and Zhang. 2009). On the other hand, at higher pH (typically $3 \leq pH_i \leq 5$), the occurrence of deprotonation and subsequent increase in negative charges provide an opportunity for heavy metals to coordinate with surface functional groups, increasing the removal efficiency.

Several phenomena have occurred simultaneously during the process of heavy metal adsorption onto the adsorbents that reduce the pH of the solution. When soil is the adsorbent, this is predominantly due to release of H^+ from Hydroxyl groups. When biochar is the adsorbent it is caused by the release of basic groups and carboxylic groups. Mainly, the release of CO_3^{2-} from carbonate groups in the biochar and hydrolysis of metals, occurred in heavy metal adsorption onto the adsorbents. For adsorbents tested in this study, ΔpH decreased with increasing pH_i as per Fig. 4c, d. Feather, a clear pH buffering occurred as shown in Fig. 4e, f after the natural pH of test soils (pH 4.7) in this study. In parallel, the percentage removals were constant at the conditions of $pH_i \geq 5$. One of the important phenomena that hamper the heavy metal adsorption at higher pH is assumed to be the hydrolysis of metals, i.e., increased OH^- in aqueous solution competed to react with Cd^{2+} and Pb^{2+} and form either Cd(OH−) or Pb(OH−) soluble hydroxyl complexes, which reduced heavy metal adsorption onto adsorbents (Blázquez et al. 2005; Kula et al. 2008). Based on the results, we note that the hydrolysis of metals became more effective with increased pH for conditions of at the conditions of $pH_i \geq 5$ for tested adsorbents.

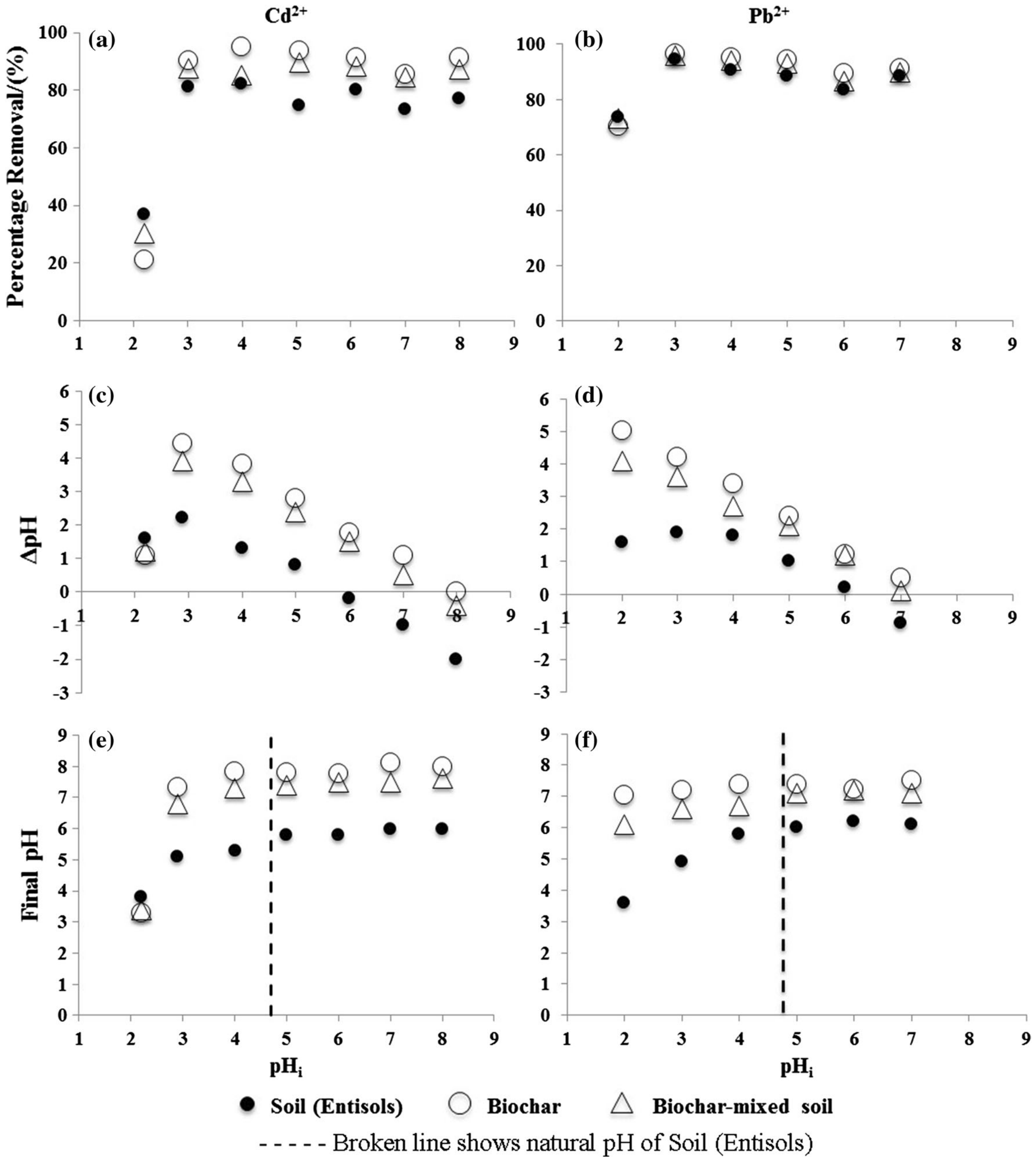

Fig. 4 pH$_i$ effect on **a** percentage removal of Cd^{2+}, **b** percentage removal of Pb^{2+}, **c** ΔpH of Cd^{2+} removal, **d** ΔpH of Pb^{2+} removal, **e** Final pH of Cd^{2+} removal, **f** Final pH of Pb^{2+} removal

Effect of competitive metal ions on Cd^{2+} and Pb^{2+} adsorption

Figure 5 shows that the results of competitive adsorptions of Cd^{2+} and Pb^{2+} onto all adsorbents. In the figures, measured percent removals for either Cd^{2+} or Pb^{2+} in binary metal solutions were plotted against the Cd:Pb ratio. The Cd^{2+} adsorption slightly decreased when the Pb^{2+} concentration increased, as shown in Fig. 5a, while the Pb^{2+} adsorption was not affected by the increase in Pb^{2+} concentration, as shown in Fig. 5b. Similar results on the competitive adsorptions of Cd^{2+} and Pb^{2+} have been reported by Qin et al. (2006) and Sewwandi et al. (2014). They found that selective adsorptions of heavy metals were observed in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$ onto peat, coconut coir husks, and humic acid-treated coconut coir husks.

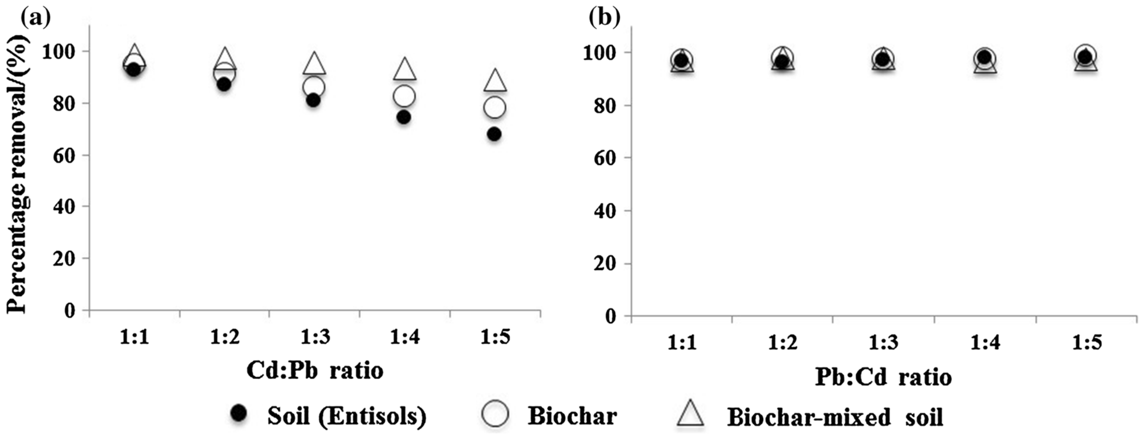

Fig. 5 Adsorption variations in **a** Cd^{2+} and **b** Pb^{2+} binary metal solutions

In general, the composition of landfill leachate is complicated and not only Cd^{2+} and Pb^{2+} but also various kinds of heavy metals are detected in landfill leachate (Sewwandi et al. 2013; Wijesekara et al. 2014). In some cases, therefore, Cd^{2+} and Pb^{2+} might not be major components of heavy metals in landfill leachate. To have better understanding of the effect of the competitive metal ions on Cd^{2+} and Pb^{2+} adsorption onto adsorbents for PRB systems, representative components of heavy metals in target landfill leachate should be identified first and their influence on heavy metal adsorption should be then evaluated.

Comparison of adsorption capacities with other biochar-mixed soils

Table 3 summarizes maximum adsorption capacities, Q_m, and removal percentages of Cd^{2+} and Pb^{2+} for adsorbents tested in this study and for previously reported biochar-mixed soils and biosorbents. For Cd^{2+} adsorption, the Q_m values for our tested adsorbents were lower than biosorbents such as coconut coir husk and humic acid-treated coir husk (Sewwandi et al. 2014), but were similar to other tested biochar-mixed soils for wastewater treatment (Xu and Zhao 2013). Similarly, the Q_m values for Pb^{2+} adsorption of our tested adsorbents were similar to those of other tested biochar-mixed soils (Xu and Zhao 2013). In addition, it should be noted that the percentage removals (%) corresponding to the maximum Cd^{2+} and Pb^{2+} concentrations in Sri Lankan landfill leachate for the biochar-mixed soil tested in this study exceeded 90 % for both Cd^{2+} and Pb^{2+} adsorption, and the percent removals were higher than those of biosorbents such as coconut coir husk and humic acid-treated coir husk. This suggests that our tested biochar-mixed soil material would be a useful adsorbent in PRB systems for the actual ranges of Cd^{2+} and Pb^{2+} concentrations observed in Sri Lanka landfill leachate.

SEM and EDX

SEM and EDX analyses were performed on biochar-mixed soil samples after Cd^{2+} and Pb^{2+} adsorption. The original SEM images in Figs. 6a and 7a show the heterogeneous nature of tested grains in this study. Grains which possess Si (Figs. 6d, 7d) and Al (Figs. 6f, 7f) correspond to soil particles while grains which show mainly carbon (C) correspond to biochar particles. Figures 6b and 7b show Cd^{2+} and Pb^{2+} distributions onto soil and biochar particles. For both Cd^{2+} and Pb^{2+}, adsorption occurred onto both soil and biochar particles with high affinity towards soil, while adsorption occurred randomly onto carbon particles.

Conclusions

This study was conducted to characterize the adsorption of Cd^{2+} and Pb^{2+} onto coconut shell biochar, a local soil from Sri Lanka, and a biochar-mixed soil (1:1 mixture of biochar and soil) as potential adsorbents for treating landfill leachate in PRB systems. Results of batch experiments indicated that adsorption kinetics of Cd^{2+} and Pb^{2+} onto all adsorbents were fitted by the pseudo second order kinetics model and that adsorption isotherms were well described by the Langmuir model. In the normal pH range ≥ 3, percent removals of both Cd^{2+} and Pb^{2+} by the tested biochar-mixed soil exceeded 90 %. Further studies to ensure a robust, long-term heavy metal removal at larger (semi-field and field) scale conditions during transient inlet concentration and water flow conditions while at the same time maintaining a sufficiently high and constant permeability

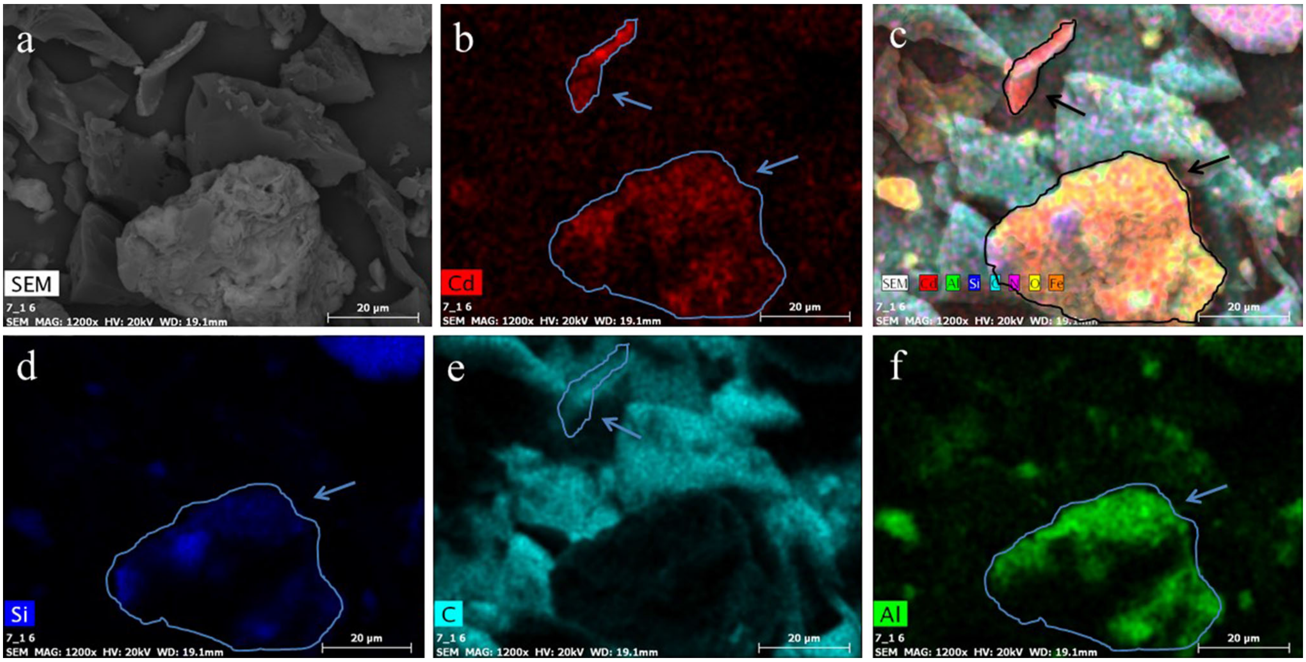

Fig. 6 SEM and EDX images of Cd^{2+} adsorption onto Biochar-mixed soil. **a** SEM image, and EDX images for, **b** Cd, **c** multiple elements, **d** Si, **e** C, and **f** Al. For the eye guide, target mineral particle and biochar are surrounded by *solid lines*

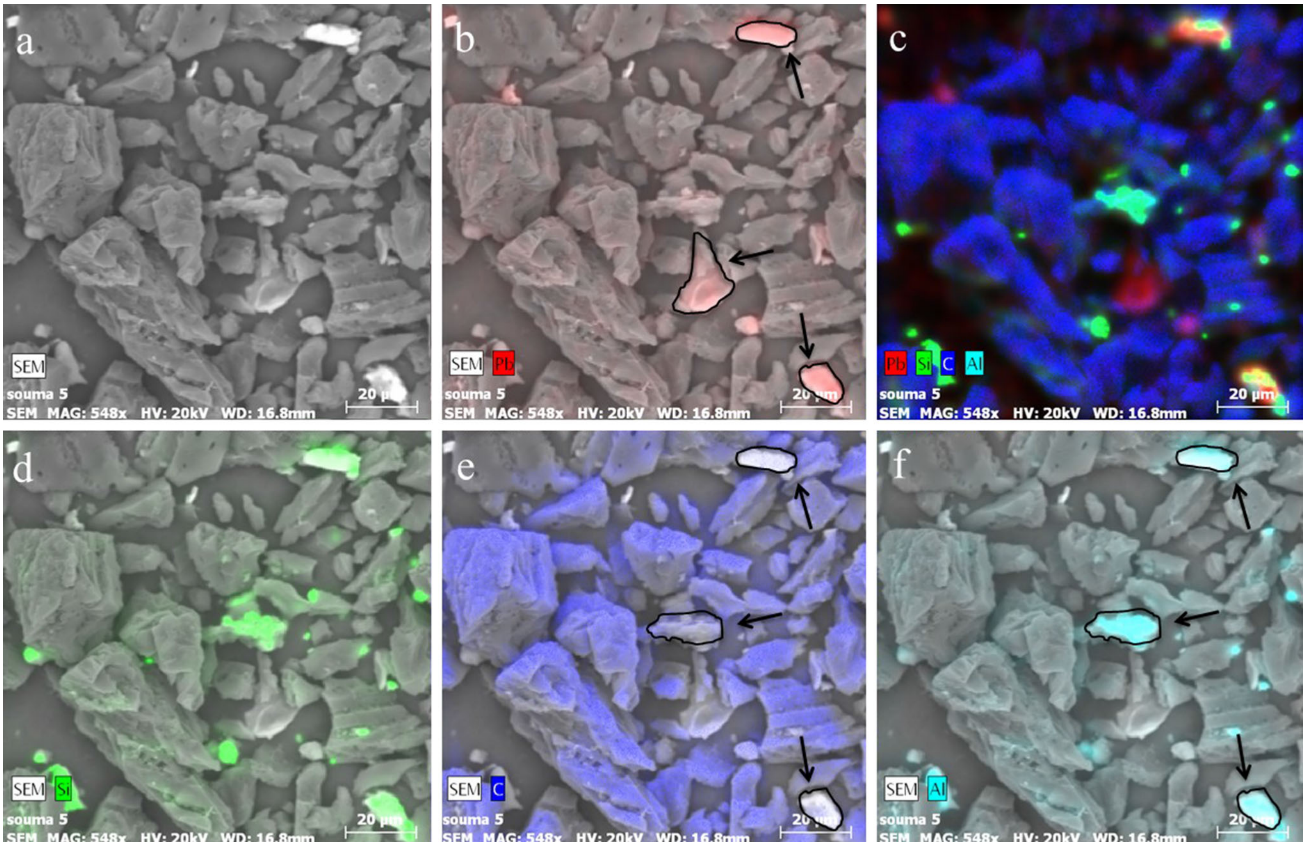

Fig. 7 SEM and EDX images of Pb^{2+} adsorption onto biochar-mixed soil. **a** SEM image, and EDX images for, **b** Pb, **c** multiple elements, **d** Si, **e** C, and **f** Al. For the eye guide, target mineral particle and biochar are surrounded by *solid lines*

of the PRB materials are needed to develop an applicable PRB system. However, our tested biochar-mixed soil has good potential as a low-cost and locally available adsorbent in the PRB system for treating landfill leachate rich in Cd^{2+} and Pb^{2+}.

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