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# Metal immobilization by sludge-derived biochar: roles of mineral oxides and carbonized organic compartment

Weihua Zhang · Xinchun Huang · Yanming Jia ·  
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**Abstract** Pyrolyzing sludge into biochar is a potentially promising recycling/disposal solution for municipal wastewater sludge, and the sludge-derived biochar (SDBC) presents an excellent sorbent for metal immobilization. As SDBC is composed of both mineral oxides and carbonized organic compartment, this study therefore compared the sorption behaviour of Pb and Zn on SDBC to those of individual and mixture of activated carbon (AC) and amorphous aluminium oxide ( $Al_2O_3$ ). Batch experiments were conducted at 25 and 45 °C, and the metal-loaded

sorbents were artificially aged in the atmosphere for 1–60 days followed by additional sorption experiments. The Pb sorption was generally higher than Zn sorption, and the co-presence of Pb reduced Zn sorption on each studied sorbent. Higher sorption capacities were observed at 45 °C than 25 °C for SDBC and AC, while the opposite was shown for  $Al_2O_3$ , indicating the significance of temperature-dependent diffusion processes in SDBC and AC. Nevertheless, metal sorption was more selective on  $Al_2O_3$  that showed a greater affinity towards Pb over Zn under competition, correlating with the reducible fraction of sequential extraction. Furthermore, significant amounts of Pb and Zn were additionally sorbed

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on SDBC following 30-day ageing. The X-ray diffraction revealed the formation of metal-phosphate precipitates, while the X-ray photoelectron spectroscopy showed a larger quantity of metal–oxygen bonding after 30-day ageing of metal-loaded SDBC. The results may imply favourable long-term transformation and additional sorption capacity of SDBC. In conclusion, SDBC resembles the sorption characteristics of both organic and mineral sorbents in different aspects, presenting an appropriate material for metal immobilization during soil amendment.

**Keywords** Metal sorption · Sludge-derived biochar · Mineral oxides · Activated carbons

## Introduction

Compared to direct application of dewatered sludge in farmland, pyrolyzing sewage sludge into biochar is considered as a potentially excellent strategy for sludge recycling/disposal and carbon subtraction (Liu et al. 2014; Song et al. 2014; Wesenbeeck et al. 2014; Kuppasamy et al. 2016). More importantly, the sludge-derived biochar (SDBC) have been found capable of immobilizing different kinds of heavy metal species such as cationic Pb/Zn and oxy-anionic Cr(VI)/As(III) (Lu et al. 2012; Zhang et al. 2013, 2015; Inyang et al. 2016). Contrary to the biochars produced from plant residues (e.g. raw straw and wood strips, Chen et al. 2012) and animal manure (e.g. cattle manure and poultry manure, Cao and Harris 2010), SDBC contains a lower content of organic carbon but a higher content of mineral oxides (Zhang et al. 2013).

The mineral oxides originate from colloids in municipal wastewater are entrapped in sewage sludge, especially when primary sedimentation tank is absent from wastewater treatment process due to the low chemical oxygen demand of the wastewater. These colloids are natural soil components and mainly present as amorphous mineral oxides, thus presenting the bulk of active sites of SDBC. A number of research studies have reported successful metal stabilization by these mineral oxides, such as aluminium oxides (Hovsepyan and Bonzongo 2009), ferric oxides (Komárek et al. 2013) and manganese oxides (Zaman et al. 2009). Besides, the carbonized organic

components of biochars accommodate a range of functional groups for metal species in the solution (Tong et al. 2011; Rees et al. 2014). Both carbonized organic components and inorganic mineral oxides should be considered for metal immobilization by SDBC (Qian and Chen 2013), where heterogeneous sorption mechanisms may occur depending on multiple surface properties and their association with pollutants.

The dual role of SDBC has been illustrated in recent studies (Qian and Chen 2013; Lu et al. 2012), and SDBC can serve as an effective dual sorbent for cationic metals ( $\text{Pb}^{2+}$ , Zhang et al. 2013), oxyanions ( $\text{CrO}_4^{2-}$ ,  $\text{AsO}_2^-$ , Zhang et al. 2015), as well as organic pesticides (Zhang et al. 2015; Tan et al. 2015). However, the individual roles of mineral oxides and carbonized organic compartments are not elucidated; in particular, their corresponding sorption kinetics and dependence on environmental conditions are yet to be figured out. Therefore, activated carbons (AC) and active aluminium oxides ( $\text{Al}_2\text{O}_3$ ) were selected as the representative carbonized organic compartment and mineral oxide, respectively, on which Pb and/or Zn sorption was compared to those on SDBC to identify the underlying mechanisms.

In addition, previous studies found that ageing processes may have a significant influence on the metal sorption behaviour (Eick et al. 1999; Ford et al. 1999). The ageing process after sorption can strengthen metal bonding via microporous diffusion, incorporation induced by re-crystallization, and formation and stabilization of surface precipitates (Rorff et al. 2006). As a result, when applying the SDBC for soil fixation, the ageing process may facilitate the metal immobilization. Therefore, the influence of ageing process on metal sorption on SDBC as well as AC and  $\text{Al}_2\text{O}_3$  was also investigated, with a focus on the sorption capacity and bonding strength.

## Materials and methods

Aluminium oxide, activated carbon, and sludge-derived biochar

Active aluminium oxide ( $\text{Al}_2\text{O}_3$ , HPLC grade) and activated carbon (AC) were bought from Sinopharm Chemical Reagent Ltd Co (Shanghai, China), and their properties are summarized in Table 1. The SDBC used

herein was prepared in an LTKC-6-12 pipe oven (Lantian Instrument limited Corp., Hangzhou, China), full of  $N_2$  at a rate of  $5 \text{ m}^3 \text{ h}^{-1}$  to ensure inert conditions. Sequentially, the temperature in the pipe oven rose up to  $400 \text{ }^\circ\text{C}$  at a rate of  $20 \text{ }^\circ\text{C min}^{-1}$  and then maintained for 2 h, which are the optimal conditions for pyrolyzing the dewatered sewage sludge into biochar based on our previous study (Zhang et al. 2013). The used sewage sludge was collected from Lijiao Sewage Treatment Plant in Guangzhou ( $23^\circ 20' \text{N}$ ,  $113^\circ 30' \text{E}$ ), where an oxidation ditch process with an average hydraulic retention time of 18 h was employed to remove  $\text{BOD}_5$ , nitrogen, and phosphorus nutrients without the primary sedimentation process. The details on the sludge pyrolysis and properties of SDBC were given in our previous studies (Zhang et al. 2013, 2015), and the major properties of SDBC are indicated in Table 1. Based on the contents of Al and TOC of SDBC, a mixture of  $\text{Al}_2\text{O}_3$  and AC (6:4 by mass) was also used to simulate the SDBC behaviour.

### Metal sorption experiments

Batch sorption experiments were conducted by mixing 0.1 g of (1) SDBC, (2) AC, (3)  $\text{Al}_2\text{O}_3$ , and (4) mixture of AC and  $\text{Al}_2\text{O}_3$ , respectively, with 25 mL of solutions containing various amounts of  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Zn}(\text{NO}_3)_2$  ( $0.01\text{--}0.5 \text{ mmol L}^{-1}$ ) on a 160 rpm shaker at  $25$  or  $45 \text{ }^\circ\text{C}$  for 24 h. The solution pH was recorded, and the suspension was filtered with  $0.45\text{-}\mu\text{m}$  poresize PES disposable filters (Jinteng, China). The filtrate was acidified to  $\text{pH} < 2$  and stored at  $4 \text{ }^\circ\text{C}$ . The concentrations of dissolved metals were determined

by Optima 3000 XL inductively coupled plasma-atomic emission spectrometer (PerkinElmer, USA), based on Method 6010C of USEPA SW-846.

The residual sorbents were subject to further characterization. X-ray photoelectron spectroscopic (XPS) spectra were obtained via scanning the SDBC with an ESCALAB 250 X-ray photoelectron spectroscopy (Thermo-VG Scientific, USA). The existence and crystalline form of chemical precipitates on the sorbent surfaces after sorption were identified using Empyrean X-ray powder diffractometer (XRD) (PANalytical B.V., Holland) equipped with a  $\text{Cu K}\alpha$  radiation source worked at 40 kV and 40 mA. The surface structure of the SDBC before and after sorption was analysed by scanning electron microscopy (SEM S-520, Hitachi, Japan) and electron dispersive X-ray analysis (EDX system, INCA 300, Oxford, UK). The EDX system was coupled with SEM using mixed BSE (back scatter electron) combined with LSE (lateral secondary electron) signal detector.

To probe the influence of ageing time on metal immobilization by SDBC, additional batch sorption experiments were conducted, where  $0.25 \text{ }\mu\text{mol L}^{-1}$  Pb and/or Zn solutions were used with the four sorbents for 24 h at  $25 \text{ }^\circ\text{C}$  with the above-mentioned sorption procedure. Solution was separated by centrifugation and filtration with  $0.45\text{-}\mu\text{m}$  filter paper, and the resulting Pb or Zn-loaded sorbents were exposed to ambient air at room temperature for 1–30 days. These artificially “aged” sorbents were then put again into contact with  $0.25 \text{ }\mu\text{mol L}^{-1}$  Pb and/or Zn solution following the above procedure. The sorption capacity of aged sorbents was calculated from the remaining metal concentration in solution and compared to those

**Table 1** Properties of different sorbents

Sorbents	Sludge-derived biochar (SDBC)	Activated carbon (AC)	Aluminium oxide ( $\text{Al}_2\text{O}_3$ )
pH (1:10 in DI water)	$7.39 \pm 0.08$	$6.85 \pm 0.05$	$7.31 \pm 0.03$
BET specific surface ( $\text{m}^2 \text{ g}^{-1}$ )	34.0	1263	147.1
Elemental content ( $\text{mg kg}^{-1}$ )			
Al	$74,252 \pm 532$	$5808 \pm 2134$	
Fe	$36,400 \pm 632$	$559 \pm 69$	
Organic functional groups ( $\text{mmol g}^{-1}$ )			
Phenolic/hydroxyl	0.175	0.201	Not applicable
Carboxyl	0.310	0.285	
Lactones	0.045	0.112	

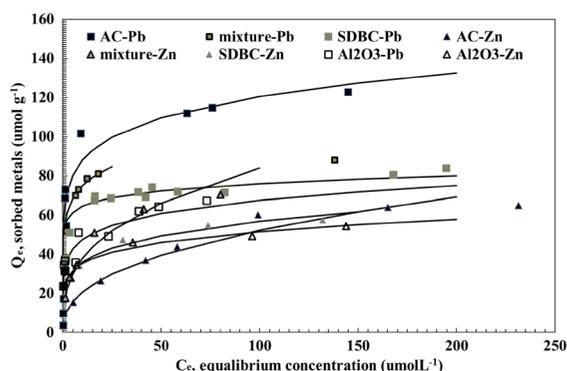
of fresh sorbents. All experiments were performed in triplicate.

The associations of Pb and Zn to both fresh and aged sorbents were characterized by traditional sequential extraction scheme (Tessier et al. 1979), categorizing into five fractions: (1) cation-exchangeable, (2) acid extractable, (3) reducible, (4) oxidizable, and (5) residual fractions. The details of the extraction procedures are given in our previous studies (Zhang et al. 2010).

## Results

### Pb and Zn sorption onto different sorbents

Sorption isotherms of single-metal solutions at 25 °C fitted with Freundlich equation are presented in Fig. 1. Table 2 lists the corresponding sorbed amounts on different sorbents for comparison when the initial [Pb] or [Zn] was fixed at 250  $\mu\text{mol L}^{-1}$ . The Pb sorption capacity was consistently higher than the corresponding Zn sorption capacity for each tested sorbent (SDBC, AC,  $\text{Al}_2\text{O}_3$ , and AC +  $\text{Al}_2\text{O}_3$ ), especially for AC. The Pb sorption followed the decreasing order of affinity: AC > AC +  $\text{Al}_2\text{O}_3$  > SDBC >  $\text{Al}_2\text{O}_3$ . Yet, the Zn sorption showed a different order of affinity: AC +  $\text{Al}_2\text{O}_3$  > SDBC >  $\text{Al}_2\text{O}_3$  > AC. The sorption capacity of SDBC for both metals was in between those of the mixture of AC +  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  alone.



**Fig. 1** Pb and Zn sorption isotherms at 25 °C in single-metal solutions on: (a) AC (0.05 g in 50 mL), (b) amorphous  $\text{Al}_2\text{O}_3$  (0.1 g in 50 mL), (c) mixture of AC and  $\text{Al}_2\text{O}_3$  (4:6 by mass, 0.1 g in 50 mL), and (d) SDBC (0.1 g in 50 mL) (better fitted by Freundlich equation as shown)

Our preliminary study did not find any detectable Al in the solution in contact with  $\text{Al}_2\text{O}_3$ -containing sorbents (data not shown), eliminating the possibility of  $\text{Al}_2\text{O}_3$  dissolution and resorption on AC surface. In contrast, SEM image indicated that some  $\text{Al}_2\text{O}_3$  colloids entered the micropores of AC (as illustrated in the supplementary materials, Fig. S1).

### Temperature and metal competition

The results of sorption kinetics at 25 and 45 °C in single-metal and binary-metal solutions of Pb and Zn are presented in Fig. 2. Higher sorption capacities of SDBC and AC were reached at 45 °C than 25 °C. However, for  $\text{Al}_2\text{O}_3$ , higher sorption capacities were observed at 25 °C instead of 45 °C in both single-metal and binary-metal solutions. For the mixture AC +  $\text{Al}_2\text{O}_3$ , there was no difference in sorption at 25 and 45 °C except for Zn sorption in single-metal solution which was higher at 45 °C than 25 °C.

In the sorption isotherms, Pb sorption was consistently higher than Zn sorption, but on SDBC, sorption capacity of Zn was comparable to that of Pb at 45 °C in single-metal solutions. There were higher sorption capacities in single-metal solutions compared to binary-metal solutions. In particular, Zn sorption was decreased by up to 10 times in the presence of Pb, while Pb sorption was only decreased by 10–30 % in the presence of Zn.

### Artificial ageing

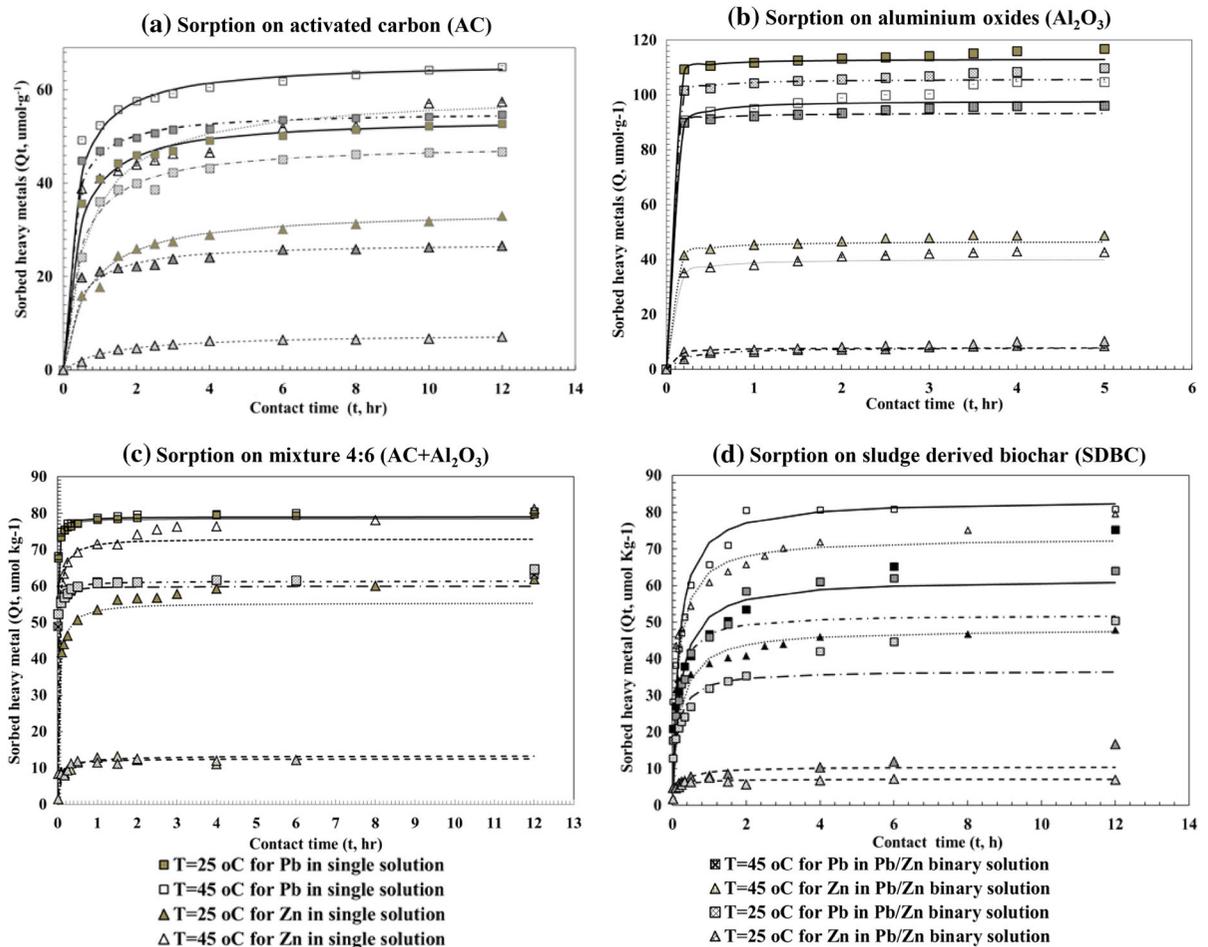
Additional amounts of Pb and Zn were immobilized on the different sorbents following the ageing process (Fig. 3), with the exception of Zn sorption in binary-metal solutions on AC. The longer the ageing time was, the larger additional amounts of Pb and Zn were sorbed on  $\text{Al}_2\text{O}_3$  and SDBC. However, there was no conclusive effect of ageing time on AC and AC +  $\text{Al}_2\text{O}_3$ . In particular, a higher amount of Zn was sorbed on AC +  $\text{Al}_2\text{O}_3$  compared to SDBC at a shorter ageing time, but sorption on SDBC became greater than AC +  $\text{Al}_2\text{O}_3$  after 30-day ageing.

Sequential extraction results of AC,  $\text{Al}_2\text{O}_3$ , and SDBC before and after 30-day ageing are shown in Fig. 4. For AC, Zn was largely present in the cation-exchangeable fraction and the reducible fraction, while Pb was mainly found in the oxidizable fraction. For  $\text{Al}_2\text{O}_3$ , more than 95 % of Zn sorption was

**Table 2** Sorbed amounts of Pb and Zn on different sorbents

System	Metal	Temp (°C)	Amount of sorbed metals ( $\mu\text{mol g}^{-1}$ )				
			SDBC	Al <sub>2</sub> O <sub>3</sub> (1)	AC (2)	AC + Al <sub>2</sub> O <sub>3</sub>	Combination <sup>a</sup>
Single-metal	Pb	25	75.08	54.00	117.11	79.94	91.86
		45	82.10	65.96	106.18	80.52	90.09
	Zn	25	48.17	34.26	49.58	61.96	43.45
		45	79.81	59.35	43.67	80.97	49.94
Binary-metal	Pb	25	50.58	48.52	109.87	64.23	85.33
		45	65.10	55.40	96.71	62.77	80.19
	Zn	25	7.15	7.83	10.71	12.28	9.56
		45	10.53	27.29	9.10	11.54	16.37

<sup>a</sup> Calculated by  $(1) \times 0.6 + (2) \times 0.4$ , where initial [Pb] or [Zn] was fixed at  $250 \mu\text{mol L}^{-1}$



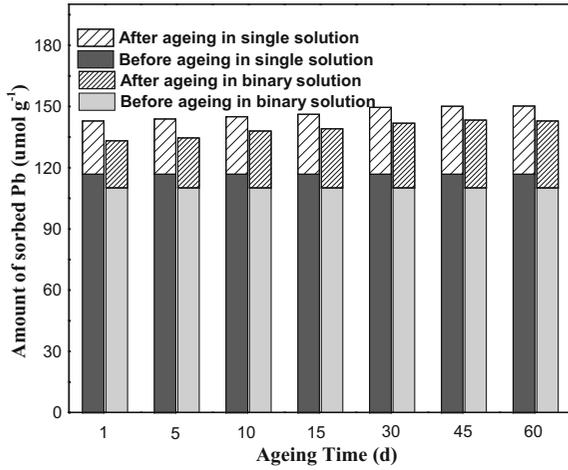
**Fig. 2** Pb and Zn sorption kinetics at 25 and 45 °C fitted with second-order kinetic model on: **a** AC (0.05 g in 50 mL), **b** amorphous Al<sub>2</sub>O<sub>3</sub> (0.1 g in 50 mL), **c** mixture of AC and

Al<sub>2</sub>O<sub>3</sub> (4:6 by mass, 0.1 g in 50 mL), and **d** SDBC (0.1 g in 50 mL) (initial [Pb(II)] and [Zn(II)] were 0.25 mM in both single- and binary-metal solutions)

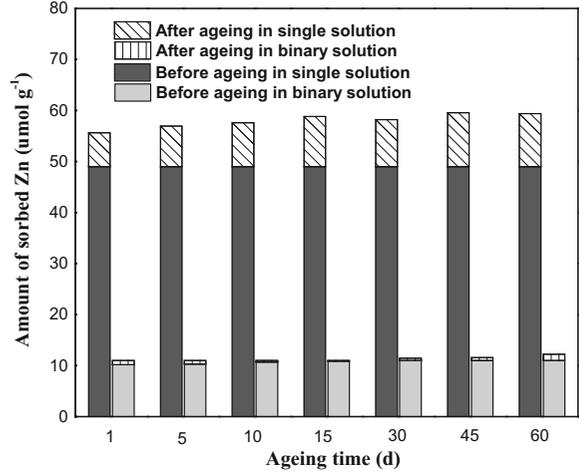
correlated with the reducible fraction, whereas Pb in the acid extractable fraction and the oxidizable fraction were equal or higher than the reducible

fraction. For SDBC, oxidizable and residual fractions represented more than 75 % of the Pb sorption while the cation-exchangeable, acid extractable, and

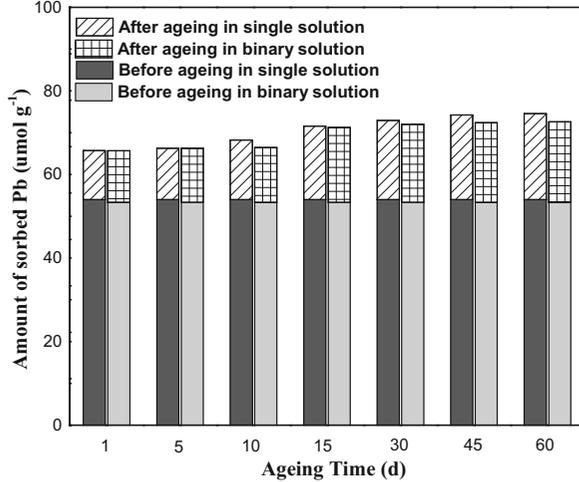
(a) Sorption of Pb on activated carbon (AC)



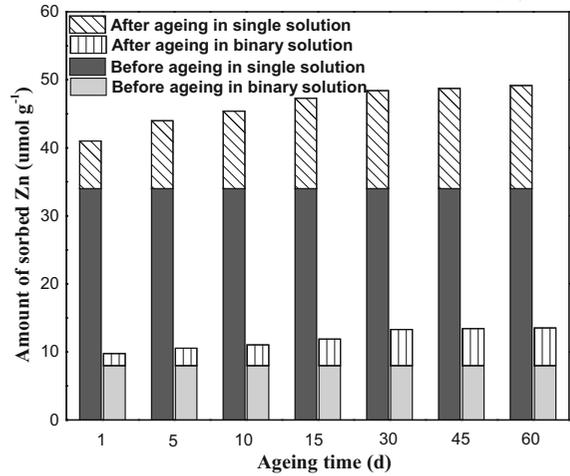
(b) Sorption of Zn on activated carbon (AC)



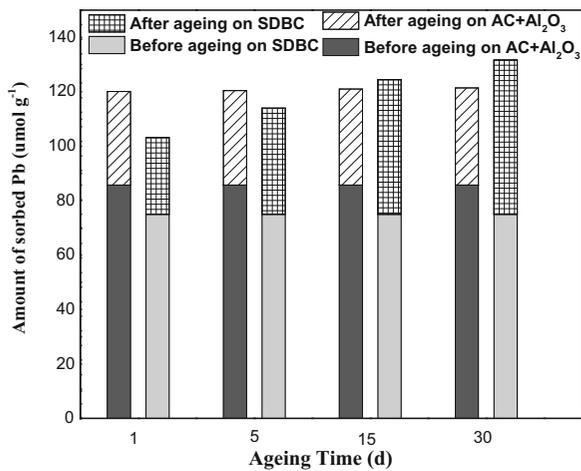
(c) Sorption of Pb on aluminium oxides (Al<sub>2</sub>O<sub>3</sub>)



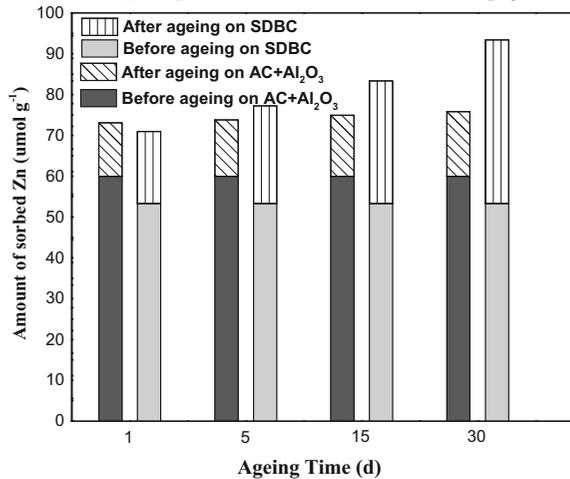
(d) Sorption of Zn on aluminium oxides (Al<sub>2</sub>O<sub>3</sub>)



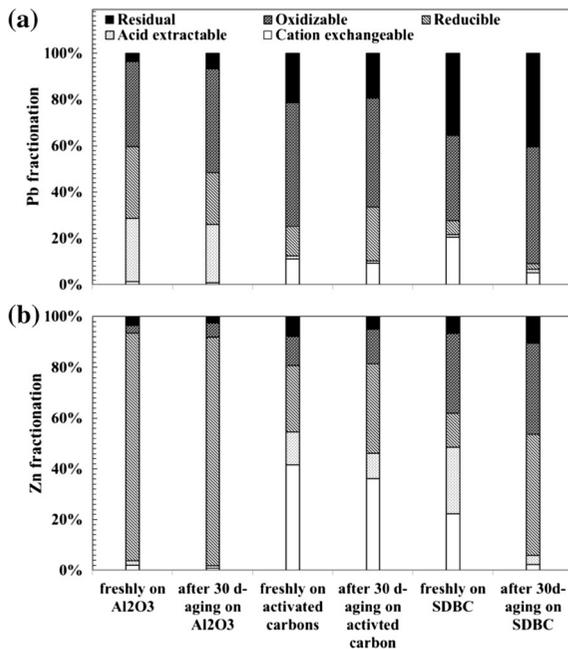
(e) Sorption of Pb on SDBC or on AC+Al<sub>2</sub>O<sub>3</sub>



(f) Sorption of Zn on SDBC or on AC+Al<sub>2</sub>O<sub>3</sub>



**Fig. 3** Metal sorption on different sorbents after varying artificial ageing time: **a** Pb sorption on AC (0.05 g in 50 mL), **b** Zn sorption on AC (0.05 g in 50 mL), **c** Pb sorption on amorphous  $\text{Al}_2\text{O}_3$  (0.1 g in 50 mL), **d** Pb sorption on amorphous  $\text{Al}_2\text{O}_3$  (0.1 g in 50 mL), **e** Pb sorption on mixture of AC and  $\text{Al}_2\text{O}_3$  (4:6 by mass) and SDBC (0.1 g in 50 mL), and **f** Pb sorption on mixture of AC and  $\text{Al}_2\text{O}_3$  (4:6 by mass) and SDBC (0.1 g in 50 mL) (Initial  $[\text{Pb}(\text{II})]$  or  $[\text{Zn}(\text{II})]$  was 0.25 mM in all solutions)



**Fig. 4** Sequential extraction of Pb (a) and Zn (b) sorbed on  $\text{Al}_2\text{O}_3$ , AC, or SDBC, before or after 30-day ageing, respectively

oxidizable fractions accounted for the majority of Zn sorption.

It was found that 30-day ageing had no influence on the distribution of sorbed Zn on  $\text{Al}_2\text{O}_3$ , but resulted in a higher oxidizable fraction and a lower reducible fraction for sorbed Pb. The opposite phenomenon was observed with 30-day ageing of AC, where sorbed Pb was present as a higher reducible fraction and a lower oxidizable fraction but both the reducible and oxidizable Zn increased with less cation-exchangeable fraction. For SDBC, 30-day ageing increased the oxidizable and residual fractions of Pb and decreased the cation-exchangeable and reducible fractions. On the contrary, the reducible fraction of Zn sorbed on SDBC was considerably increased by ageing, while the cation-exchangeable fraction was reduced.

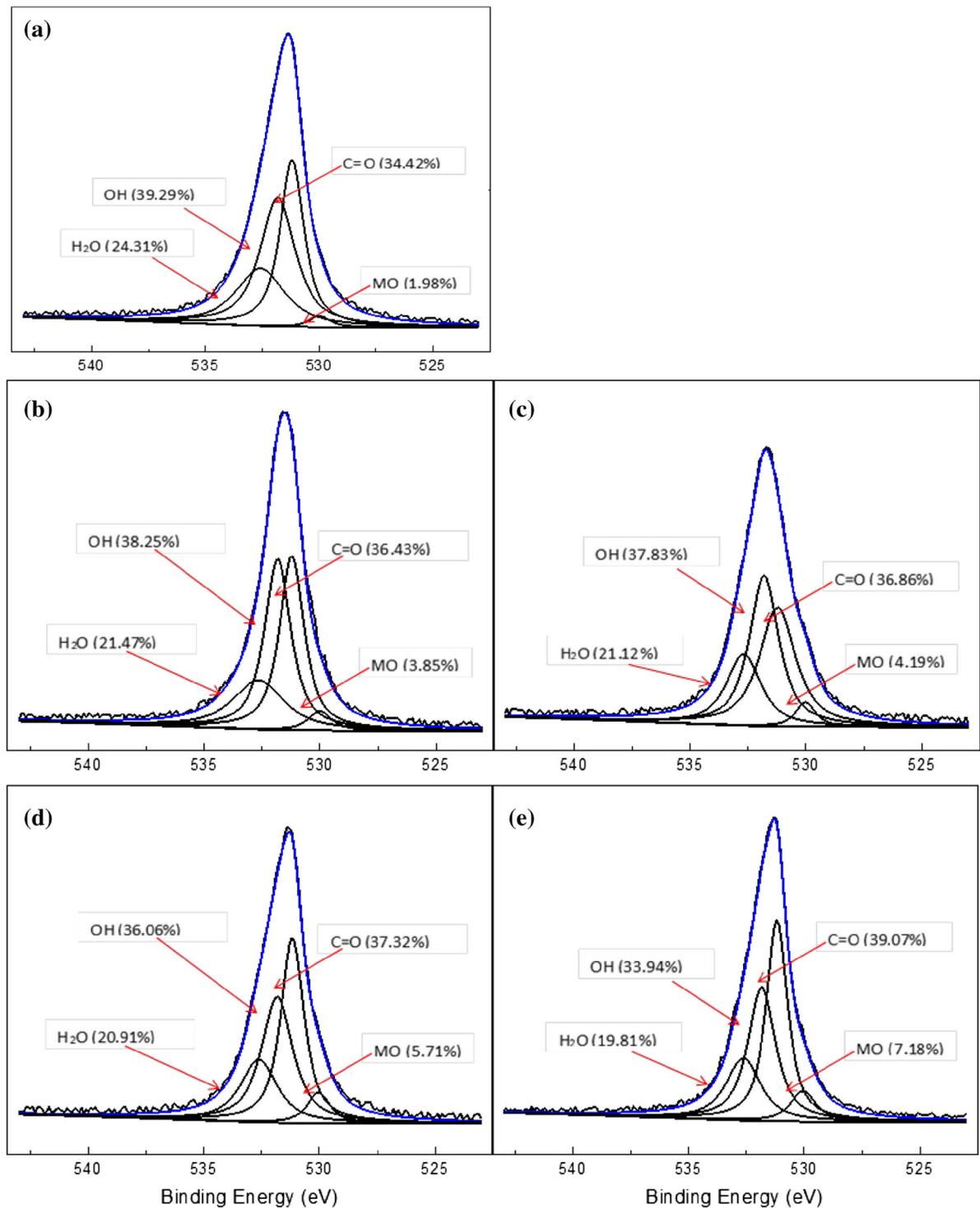
The XRD spectra (as illustrated in the supplementary materials, Fig. S2) proved the existence of crystalline  $\text{K}_2\text{Pb}(\text{PO}_3)_4$  on the surface of Pb-loaded SDBC, but they were observed only after 30-day ageing. The XPS  $\text{O}_{1s}$  spectra (Fig. 5) also showed that 30-day ageing resulted in a larger proportion of M–O (Pb: from 3.85 to 5.71 %; Zn: from 4.19 to 7.18 %), indicating the increased intensity or coverage of Pb/Zn coordination with the oxygen-containing functional groups on the surface of SDBC.

## Discussion

### Competitive sorption of Pb and Zn

The sorption capacities of each material were higher for Pb than Zn (Fig. 1), which was also commonly observed with organic sorbents (Rees et al. 2014) and inorganic sorbents (Abdus-Salam and Bello 2015). The favourable sorption of Pb compared to Zn (Figs. 1, 2) may be explained by the smaller hydrated ionic radius (4.0 vs. 4.3 Å) and the greater electronegativity of Pb (2.33 vs. 1.65). These would facilitate diffusion of Pb inside micropores and enhance its affinity for cation exchange and surface complexation (Lu and Xu 2009; Depci et al. 2012). In this study, the difference in sorbed amounts of Pb and Zn was greater for AC than SDBC and  $\text{Al}_2\text{O}_3$  (Fig. 2), possibly reflecting the presence of micropores and non-selective sorption sites. Furthermore, the smaller difference at 45 °C than 25 °C suggested a greater importance of transport processes in AC and SDBC. It was because a higher temperature could accelerate diffusion processes and therefore curtail the preferential sorption of Pb over Zn due to its smaller size.

The Zn sorption (and Pb sorption to a lower extent) was diminished in the binary-metal solutions (Fig. 3), and some sorbed Zn on the aged sorbents was even released due to Pb competition when put in contact with binary-metal solutions again. Similar competitive effects were observed for Pb and Zn in multi-metal solutions (Mohan and Singh 2002; Tsang and Lo 2006; Depci et al. 2012; Rees et al. 2014). This illustrates metal competition for some commonly available sorption sites and electrostatic repulsion of metals with the same charge. The metal fractionation by sequential extraction (Fig. 4) reinforced that Pb was more strongly bound to the sorbents than Zn,



**Fig. 5** XPS  $O_{1s}$  spectra of SDBC with varying ageing time: **a** original SDBC, **b** freshly Pb-loaded, **c** Pb-loaded after 30-day ageing, **d** freshly Zn-loaded, and **e** Zn-loaded after 30-day ageing

accounting for the greater suppression of Zn sorption by coexisting Pb, but there was only a slight effect vice versa.

### Comparison of SDBC with AC and Al<sub>2</sub>O<sub>3</sub>

The sorption characteristics of SDBC may resemble that of Al<sub>2</sub>O<sub>3</sub> (i.e. model mineral sorbent) or that of AC (i.e. model organic sorbent). Despite the contrasting affinity of Pb and Zn for different sorbents, the observed sorption capacities of SDBC were more comparable to those of Al<sub>2</sub>O<sub>3</sub> than AC (Figs. 2, 3). The competition of Zn by coexisting Pb was also much stronger for SDBC and Al<sub>2</sub>O<sub>3</sub> than AC, suggesting that the mineral components may present sorption sites (e.g. silanol and aluminol groups at the edge or corners) that are characterized by a higher affinity towards Pb than Zn due to difference in their ionic radii and charge densities. The results of sequential extraction (Fig. 4) showed that sorption of Pb and Zn on AC and SDBC took place in all fractions despite with different proportions, while sorption on Al<sub>2</sub>O<sub>3</sub> was predominantly on reducible fraction corresponding to mineral oxides.

However, the influence of temperature on metal sorption on SDBC was more similar to that of AC than Al<sub>2</sub>O<sub>3</sub> (Fig. 2). An increase in sorption with increasing temperature was seen for SDBC and AC, indicative of an endothermic sorption process (Hefne et al. 2008; Dandanmozd and Hosseinpur 2010). This may correspond to an increase in the kinetic energy or a better solvation of the metal ions (Naseem and Tahir 2001). Similar results of increased sorption capacity and enhanced sorption kinetics on AC at a higher temperature were also reported for Pb (Gueu et al. 2007) and Zn (Marzal et al. 1996). An increase in temperature could facilitate both chemical sorption reactions and physical diffusion processes in SDBC, in a way similar to those in AC. These results reveal that well-recognized diversity of the surface active sites of SDBC plays different roles under varying environmental conditions, i.e. mineral oxides display a more selective sorption under metal competition, whereas carbonized organic compartments are governed by temperature-dependent diffusion processes.

### Ageing of sorbed metals

With artificial ageing of metal-loaded SDBC in ambient air, a change was observed in the relative importance of sorption processes. The weaker interactions via cation exchange and coordination with phosphate on SDBC were transformed into crystalline metal precipitates such as K<sub>2</sub>Pb(PO<sub>3</sub>)<sub>4</sub> identified in the XRD spectra after 30-day ageing (as illustrated in the supplementary materials, Fig. S2), suggesting the formation of stronger bonding with mineral oxides and organic matter. This may also explain why ageing led to a higher sorption capacity for all sorbents of this study, particularly for SDBC (Fig. 3), as the transformation of sorbed metals into precipitates may empty previously occupied sorption sites and/or create new reactive surfaces for additional metal sorption from the solution.

In addition, ageing is often associated with the oxidation of biochar surfaces, resulting in a larger quantity of oxygen-containing functional groups that could also lead to a higher sorption capacity via surface complexation (Tsang et al. 2007; Guo et al. 2014). This was confirmed by the XPS spectra (Fig. 5) where the proportions of Pb–O and Zn–O increased with ageing. The sequential extraction (Fig. 4) also revealed a larger oxidizable fraction of Pb on SDBC. On the contrary, this was not observed on AC because the surfaces had already been fully oxidized by the activation process during production. Furthermore, the time-dependent diffusion of metals along the interior surfaces and/or within the small pores of SDBC over time may also contribute to a higher sorption capacity with ageing, although it could not be confirmed in this study.

These beneficial effects of ageing on metal sorption by SDBC implies that the metal immobilization observed in the short term in SDBC-amended soils would probably last longer and become more stable than its sorption capacity measured in batch experiments (Rees et al. 2014; Fang et al. 2016). The slowly releasing metals from contaminated soils may still be sorbed on SDBC over time, yet the resilience of long-term metal immobilization against continuous leaching and varying field conditions (e.g. pH, redox, biotic disturbance) should be further attested (Tsang et al. 2013; Fang et al. 2016).

## Conclusions

Pyrolyzing sludge into biochar is a potentially promising recycling/disposal option for the increasing production of municipal wastewater sludge, from which the sludge-derived biochar presents an excellent sorbent for soil amendment because of its abundant contents of carbonized organic and mineral components. This study reveals that sludge-derived biochar can be evaluated as a mixture of activated carbon and aluminium oxide for elucidating the roles of different compartments under different environmental conditions. In particular, sorption on organic compartment is more temperature-dependent due to diffusion processes, while sorption on mineral oxides is more selective under metal competition. Furthermore, ageing of metal-loaded biochar in ambient air results in metal-phosphate precipitation and provides additional sorption sites, implying a favourable long-term effect of SDBC for metal immobilization in soil amendment that requires future investigations.

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