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Towards Understanding the Mechanism of Heavy Metals Immobilization in Biochar Derived from Co-pyrolysis of Sawdust and Sewage Sludge

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Abstract
Biochar was prepared by mixing sewage sludge with sawdust via a co-pyrolysis with different mixture ratios and temperatures. The results showed that the sawdust addition resulted in a lower yield of biochar with higher C content. The total concentrations of Pb and Cd in biochar were reduced. Besides, pyrolysis can transform the potentially toxic Pb and Cd to stable fractions. However the sawdust addition had slight influence on the chemical forms of Pb and Cd in the biochar. The biochar with 50% sawdust at 600°C exhibited a remarkable reduction of the leachable metal concentrations. The possible transformation mechanisms of Pb and Cd were inferred as the formation of aluminum and silicon-containing minerals. These results provide insights into the influence of sawdust addition on the characteristics of biochar and the possible Pb and Cd immobilization mechanisms during co-pyrolysis process.

Keywords Co-pyrolysis · Lead · Cadmium · Immobilization · Biochar

Pyrolysis is considered as a promising strategic approach to the management of organic waste and has been extensively investigated in the recent years. Pyrolysis is able to reduce the volume of wastes, kill the intrinsic pathogens and parasites, immobilize metals, produce value-added bio-energy and carbon-rich biochar. Sewage sludge is a preferable feedstock because of the compositions of hydrocarbons and inorganic materials (Pedroza et al. 2014). Previous researchers focused on the characteristics of sludge-based biochar (Ruiz-Gomez et al. 2017) and applied sludge-based biochar as adsorbent (Tan et al. 2014) and soil remediation material (Yue et al. 2017). However, the presence of heavy metals in sewage sludge causes many challenges in its application. Thus, the attempts to decrease the concentrations of heavy metals in the biochar attract continuously attention (Liu et al. 2016).

Recently, a few of researchers had examined the behavior of heavy metals during pyrolysis process, focusing on their distribution and mobility in the biochar using empirically defined sequential chemical extraction methods (Zhao et al. 2017). The previous researchers found that co-pyrolysis of animal manures and biomass with lower heavy metals contents may lead to a decrease of the heavy metal contents in the obtained biochar compared to the single manure pyrolysis (Huang et al. 2017; Meng et al. 2018a). Meanwhile, co-pyrolysis process can possibly show inconsistent effects on the chemical speciation and the availability of different metals in biochar. It had been reported that mixing sewage sludge with rice straw or sawdust at 50% mixture ratio and co-pyrolysis had a minimal effect of on the mobility of different heavy metals in biochar (Huang et al. 2017). Some researchers found that the addition of bamboo sawdust during sludge pyrolysis can transform the unstable metals into more stable fractions at the same 50% mixture ratio (Jin

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et al. 2017). These inconsistent results may be attributed to the feedstock types and operating conditions (Xu et al. 2019). More work is urgently required to identify the feasibility of this metal-alleviating method for biochar and further focus on the transformation mechanism of heavy metals during the co-pyrolysis process.

Therefore, the purposes of this study were: (1) to explore the effects of pyrolysis temperature and sawdust mixture ratios on the properties of biochar; (2) to evaluate the total concentrations, the speciation distribution and leachable metal concentrations in biochar; (3) to propose the possible transformation mechanism of Pb and Cd during co-pyrolysis process. The results of this study will be helpful to further explore the biomass addition on the characteristics of biochar and the heavy metals distribution during the co- pyrolysis process.

Materials and Methods

The sewage sludge (water content = 82.4%) was collected from a municipal wastewater treatment plant, Zhengzhou, China. Extra Pb (II) and Cd (II) (in the form of nitrate in 0.1 M HNO_3 solution) were spiked into the sludge to increase the corresponding concentrations of 2000 mg kg^{-1} and 45 mg kg^{-1} (dry basis) based on the previous researches (Chen et al. 2015; Shi et al. 2013). Then the sludge feedstock (spiked with Pb and Cd) was aged for 3 weeks. The sawdust feedstock (water content = 20.2%) was purchased from a furniture factory, Yuanyang, China. Pb and Cd contents in sawdust (dry basis) were 0.30 ± 0.04 and 0.03 ± 0.02 mg kg^{-1}, respectively. Both sawdust and sewage sludge were further dried in an oven at 105°C for 24 h and the water in the feedstocks was volatilized. Then the two feedstocks were grinded and filtrated by a 10-mesh sieve to remove large particles. The pH and organic matter of the sewage sludge (dry basis) were 6.90 ± 0.21 and $50.0\% \pm 2.3\%$, respectively, and 7.01 ± 0.11 and $96.9 \pm 0.1\%$ for the sawdust (dry basis). The results of element analysis and ash contents were listed in Table 1.

The mixture ratios of sawdust and sludge were 0:10, 1:9, 3:7 and 5:5, respectively (sawdust / sludge, w/w) and the four mixture ratios were marked as b0, b10, b30 and b50, respectively. The pyrolysis experiments were performed in a tube furnace. In detail, 50 g of mixed feedstock were introduced into the tube furnace and then the tube furnace was heated to 300, 400, 500, and 600°C, respectively, for 2 h. The 99.99% N_2 was continuously inputted throughout the pyrolysis process. The biochar produced at different temperature, were labeled as $b0_x$, $b10_x$, $b30_x$, and $b50_x$, respectively. Here the x was referred to as pyrolysis temperature.

The yields were calculated by percentages the weight of the produced biochar versus the feedstocks. The pH of the sewage sludge, sawdust and biochar were determined by a pH meter (solid/water = 1:20). The ash contents of different samples were measured by percentages of the residual weight after heating the received product at 750°C for 6 h in the muffle furnace. The organic matter in sewage sludge, sawdust and biochar can be calculated by difference between total amount and ash. The total organic carbon (C), hydrogen (H) and nitrogen (N) contents in the two feedstocks and the resultant products were determined by an elemental analyzer (Vario III, Elementar, Germany). The main mineral compositions were analyzed by X-ray fluorescence method (XRF) (S4 Pioneer, Bruker, Germany). Fourier transform infrared (FTIR) spectra were used to analyze the main chemical groups (Nicolet iS50, Thermo Scientific, USA).

Atomic absorption spectrometry (AAS) equipped with graphite furnace (ZEEnit 700P, Jena, German) was used to measure the metal concentrations. The percentages of the four different chemical forms of Pb and Cd were conducted by the modified three-step sequential extraction procedure according to the Commission of the European Communities Bureau of Reference (BCR) (Sungur et al. 2014), which were named as the acid soluble (F1), the reducible (F2), the oxidizable (F3), and the residual fractions (F4), respectively. The detailed extraction procedures are presented in Table S1. The bioavailability and mobilization of heavy metal speciation were decreased according to the following sequence: F1 > F2 > F3 > F4. The concentrations of F1, F2 and F3 in the samples were also analyzed by AAS. For F4 fraction, the samples were digested firstly and then determined by AAS. The leaching characteristics of Pb and Cd in the sludge and biochar were conducted to assess further the metal leachability and bioavailability according to the standard Toxicity Characteristic Leaching Procedure (TCLP) (US EPA 1994). The percentages

Table 1 The general properties of the feedstocks and the received biochar

Items	Elements composition[a] (%)				Ash[a] (%)	pH
	C	H	N	O[b]		
Sludge	25.0 ± 1.0	7.75 ± 0.38	4.55 ± 0.23	12.70 ± 0.04	50.0 ± 2.3	6.90 ± 0.21
Sawdust	45.6 ± 2.1	4.58 ± 0.23	0.60 ± 0.02	46.12 ± 0.21	3.1 ± 0.10	7.01 ± 0.11

[a]Dry basis

[b]By difference

of leachable metal concentration were calculated by the percent ratio of leachable metal mass to the total metal mass in the sample.

The effects of sawdust mixture ratios on the characteristics of biochar were determined by One-way analysis of variance (ANOVA) through the SPSS (SPSS19.0, SPSS Inc., America). The least significant difference (LSD) tests were performed to explore the significant differences at the 0.05 level of probability. Pearson correlation analysis were conducted to investigate the intrinsic correlation between the leachable heavy metal percentages and the properties of biochar.

Table 2 The yields of biochar (%) obtained at the different temperatures and mixture ratios

Items	300°C	400°C	500°C	600°C
b0	76.2 ± 3.5a	68.2 ± 3.2ab	62.5 ± 3.0bc	60.0 ± 3.1c
b10	73.5 ± 3.2a	64.0 ± 2.6a	60.1 ± 2.4b	60.1 ± 2.6c
b30	68.2 ± 3.6a	57.2 ± 2.9a	50.7 ± 2.7b	49.6 ± 2.6c
b50	63.7 ± 3.4a	47.4 ± 3.0a	44.1 ± 3.1b	41.9 ± 3.0c

Results and Discussion

The biochar yields produced at different pyrolysis temperatures and mixture ratios are listed in Table 1. Sawdust mixture ratios and pyrolysis temperatures can both affect biochar yields, in which higher temperature and sawdust mixture ratio reduced the biochar yields. The highest biochar yield of 76.2% ± 3.5% was obtained at 300°C without sawdust addition and decreased to 63.7% ± 3.4% with sawdust mixture ratio at 50% at the same temperature. It can be attributed to the high organic matter content in sawdust (96.9% ± 0.8%) compared to sewage sludge (50.0% ± 2.64%) which led to a higher fraction of volatile compounds. The yields also decreased with the increasing of pyrolysis temperature (Table 2) because more organic substances could be decomposed at the higher pyrolysis temperatures.

Different lowercase letters after the values indicate significant difference between the treatments at the same pyrolysis temperature ($p < 0.05$). b0, b10, b30, b50—0%, 10%, 30%, 50% sawdust mixture ratio. Data are presented as mean value ± standard deviation (triplicate).

Properties the received biochar are presented in Table 3. The pH value of sludge was slightly acidic (6.90 ± 0.21), and increased from 7.32 ± 0.15 to 11.3 ± 0.35 with pyrolysis

Table 3 The general properties of the feedstocks and the received biochar

Items	Elements composition[a] (%)				Ash[a] (%)	pH
	C	H	N	O[b]		
300°C						
$b0_{300}$	20.9 ± 1.1	7.43 ± 0.33	3.53 ± 0.18	7.44 ± 0.03	60.7 ± 3.1	7.32 ± 0.15
$b10_{300}$	22.0 ± 1.2	7. 9 ± 0.44	3.34 ± 0.16	11.56 ± 0.03	55.2 ± 2.3	7.31 ± 0.14
$b30_{300}$	24.3 ± 1.4	6.50 ± 0.51	3.87 ± 0.18	19.23 ± 0.06	46.1 ± 2.3	7.22 ± 0.13
$b50_{300}$	26.7 ± 1.2	8.01 ± 0.48	3.02 ± 0.14	21.27 ± 0.10	41.0 ± 2.1	7.13 ± 0.11
400°C						
$b0_{400}$	17.7 ± 1.1	6.07 ± 0.35	2.46 ± 0.14	8.17 ± 0.03	65.6 ± 3.3	7.96 ± 0.17
$b10_{400}$	23.8 ± 1.2	7. 0 ± 0.37	2.53 ± 0.12	9.77 ± 0.05	56.9 ± 2.3	7.90 ± 0.16
$b30_{400}$	34.8 ± 1.3	4.30 ± 0.22	2.59 ± 0.13	10.71 ± 0.04	47.6 ± 2.3	7.70 ± 0.20
$b50_{400}$	43.4 ± 2.2	7.57 ± 0.32	2.21 ± 0.11	3.12 ± 0.06	43.7 ± 1.8	7.32 ± 0.22
500°C						
$b0_{500}$	17.0 ± 1.4	6.04 ± 0.32	1.95 ± 0.08	6.51 ± 0.04	68.5 ± 3.3	9.42 ± 0.23
$b10_{500}$	23.9 ± 1.2	4.91 ± 0.26	2.25 ± 0.11	7.04 ± 0.03	61.9 ± 3.2	9.31 ± 0.23
$b30_{500}$	40.6 ± 1.2	3.72 ± 0.14	2.38 ± 0.14	3.70 ± 0.06	50.6 ± 2.0	9.20 ± 0.30
$b50_{500}$	50.8 ± 1.2	3.91 ± 0.26	2.05 ± 0.09	1.36 ± 004	44.6 ± 1.4	9.12 ± 0.39
600°C						
$b0_{600}$	16.3 ± 1.2	5.97 ± 0.30	1.69 ± 0.07	5.64 ± 0.03	70.4 ± 3.3	11.30 ± 0.35
$b10_{600}$	21.1 ± 1.1	3.81 ± 0.13	1.90 ± 0.08	6.19 ± 0.05	67.2 ± 3.1	11.21 ± 0.38
$b30_{600}$	31.7 ± 1.2	2.73 ± 0.16	1.73 ± 0.09	5.96 ± 0.08	59.8 ± 2.7	11.21 ± 0.40
$b50_{600}$	42.6 ± 1.3	2.98 ± 0.18	1.68 ± 0.06	0.36 ± 0.01	45.1 ± 1.5	11.03 ± 0.42

[a]Dry basis

[b]By difference. b0, b10, b30, b50 present 0%, 10%, 30%, 50% sawdust mixture ratio, respectively. The subscripts (300, 400,500 and 600) refer to the different pyrolysis temperature, respectively

temperature elevated from 300 to 600°C. The pH values of biochar were increased after pyrolysis compared to the two feedstocks, and the increasing temperature produced biochar with higher alkalinity. This phenomenon was mainly attributed to the decomposition of organic matters and the accumulation of alkali salts in the received products with the increasing pyrolysis temperature (Table 3) (Yuan et al. 2011). The pyrolysis temperature (at 300–600°C) was the predominant factor which affect the pH of biochar. While the ash contents in biochar were influenced by temperature and the sawdust mixture ratios, which was consistent with the pH fluctuation.

The C contents in the sludge biochar decreased with the increasing temperature at 300–600°C (Table 2). The addition of sawdust to the sewage increased the C contents of biochar, and the highest C content was occurred in b50 at pyrolysis temperature of 500°C. Meanwhile, the pyrolysis temperature at 600°C led to a C content decline in b10, b30 and b50. It has been reported that hemicellulose in sawdust decomposed in the range of 200–315°C, cellulose degraded from 315 to 400°C and lignin degraded in the range of temperature from 180 to 600°C (Gupta and Mondal 2019). Therefore, the C content was decreased slightly at 600°C due to the decomposition of lignin in the sawdust. The sawdust was mainly composed of organic constituents (96.9% ± 0.1%), while the sludge contains considerable inorganic compositions (ash, 50.0% ± 2.3%) (Table 3). It can be concluded that this different composition in the feedstocks led to a higher C contents in biochar after the sawdust addition.

Figure 1 illustrates the concentrations of Pb and Cd in biochar. After the single pyrolysis of sludge, most of Pb and Cd remained in biochar. The contents of Pb in biochar ($b0_{300,}$ $b0_{400,}$ $b0_{500}$ and $b0_{600,}$) increased from about 2000 mg kg^{-1} to 2650 ± 130, 2871 ± 140, 3088 ± 160 and 3459 ± 178 mg kg^{-1} at 300–600°C, while the corresponding concentrations of Cd were 61.18 ± 3.23, 66.67 ± 3.90, 70.22 ± 4.12 and 73.16 ± 3.45 mg kg^{-1}, respectively from initial 45 mg kg^{-1}. Compared to the single pyrolysis sludge biochar at the same temperature, the total concentrations of Pb and Cd in the co-pyrolysis biochar were lower (Huang et al. 2017). The Pb concentrations in the biochar received at 300°C were 2652 ± 128, 2209 ± 110, 2101 ± 108 and 1600 ± 58 mg kg^{-1} at the four different mixture ratios, respectively. The corresponding Cd contents were 61.18 ± 3.23, 56.62 ± 2.93, 50.23 ± 2.83 and 38.42 ± 2.28 mg kg^{-1}, respectively. There was a significantly decrease especially when the mixture ratio of sawdust was higher than 30% (Fig. 1). Therefore, at the same pyrolysis temperature, the total Pb and Cd concentrations was decreased gradually with the increasing mixture ratio of sawdust with the addition of sawdust. Obviously, different initial heavy metals concentrations in sawdust and sludge led to the varying Pb and Cd contents in biochar at different sawdust mixture ratios. Meanwhile, the total Pb and Cd concentrations increased with pyrolysis temperature increasing at the same sawdust mixture ratio, due to the lower biochar yield and most of Pb and Cd in the feedstocks remained in biochar. The recovery rates of metals were 90%–112% and presented in Table S2.

The availability of heavy metals could be related partly to the total concentration. Besides, the fraction distribution of heavy metals could directly affect their ecotoxicity. As shown in Fig. 2, the F1 fractions of Pb in the raw sludge were 29.4%. The F2 and F3 fraction were 56.7 and 9.0 respectively. And the F4 fraction, which was more stable than the other three fractions, was below 5%. Pyrolysis significantly increased the F4 fraction (> 97%) at all temperatures. The F1+F2+F3 fraction of Pb, which can be generally considered as directly and potentially toxic or bioavailable fractions, was below 3%. Most of unstable Pb in the sludge feedstock was immobilized and the potential toxicity of Pb was reduced. While the F1, F2, F3 and F4 fractions of Cd in the sludge feedstock were 28.1%, 47.8%, 14.1% and 9.9%, respectively. A steady increase of the F4 fraction of Cd was observed in the biochar received from sludge single pyrolysis at 300–600 °C. The F4 fraction of Cd in $b0_{600}$ (92.2%) increased sharply compared to $b0_{300}$ (75.0%). As mentioned above, both Pb and Cd can be immobilized through pyrolysis. However, it is worth noting that the addition of sawdust

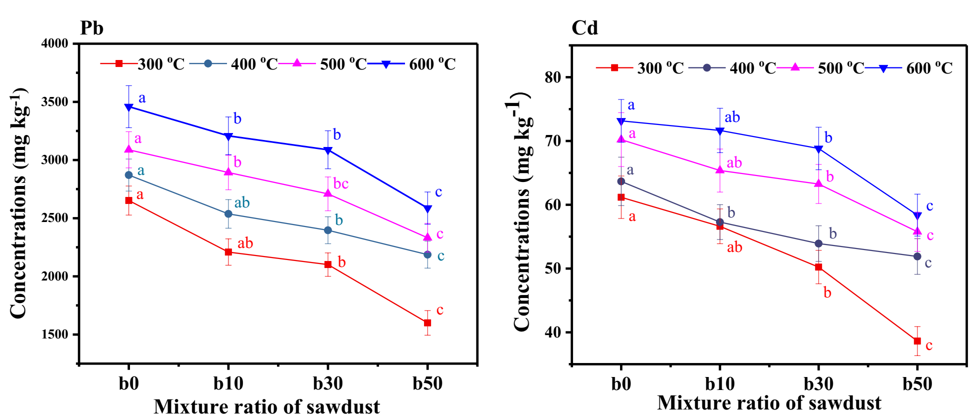


Fig. 1 The total Pb and Cd concentrations in biochar. Different lowercase letters indicate significant difference between the treatments at the same pyrolysis temperature ($p < 0.05$). b0, b10, b30, b50 refer to the 0%, 10%, 30% and 50% sawdust mixture ratio, respectively

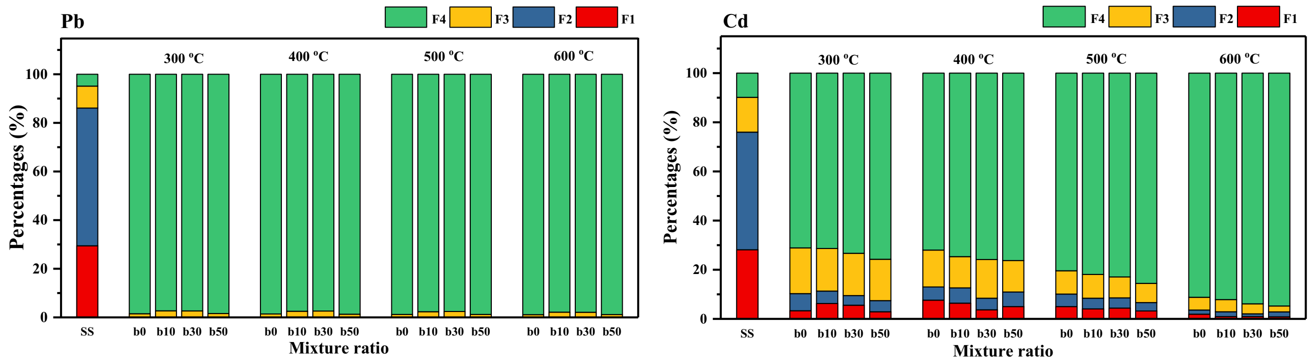


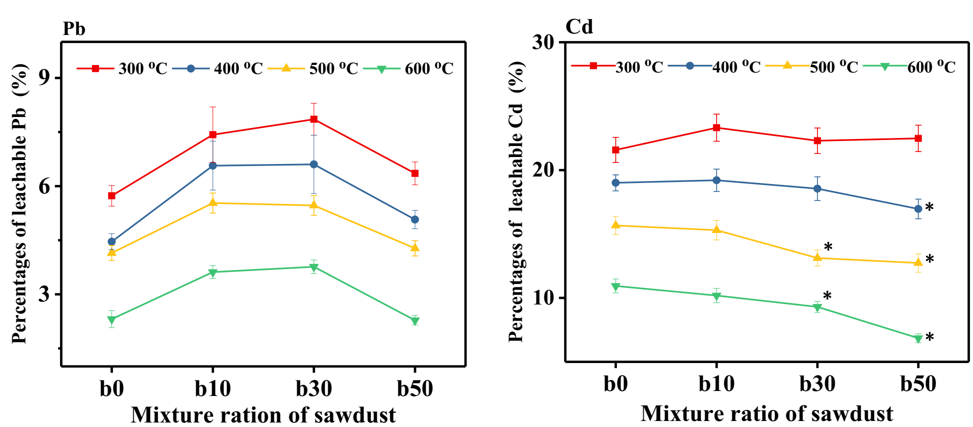
Fig. 2 Fraction distribution of Pb and Cd in samples. SS-sludge pretreated with Pb and Cd. F1, F2, F3, F4—Acid-soluble, reducible, oxidizable and residual metal fraction. b0, b10, b30, b50 refer to the 0%, 10%, 30% and 50% sawdust mixture ratio, respectively

exhibited little influences on the speciation distribution of Pb and Cd during the co-pyrolysis process. The speciation distribution of Pb was not significantly affected by pyrolysis temperature and raw material composition. While the pyrolysis temperature can significantly influence the speciation distribution of Cd.

The leachable Pb and Cd concentrations in the feedstock and biochar were evaluated through the TLCP method, as described in the TCLP of USEPA (Nair et al. 2008). The leachable Pb and Cd percentage in biochar were used to illustrate the proportion of Pb and Cd in the leachable state and their leachability (Fig. 3). The leachable Pb and Cd percentages in the sludge before pyrolysis were 68.4% ± 3.1% and 58.7% ± 1.2%, respectively (showed in Table S3). While after sawdust addition, the percentages of leachable Pb (below 8.18% ± 0.43%) and Cd (below 26.6 ± 2.1%) in biochar were low, indicating pyrolysis significantly reduced the percentages of leachable heavy metals, and the leachability of heavy metals was also decreased. The higher pyrolysis temperature led to the lower percentages of leachable metal in most treatments. When the pyrolysis temperature increased from 300 to 600°C, the percentages of leachable Pb in the biochar derived from single pyrolysis of sludge were 5.73 ± 0.24, 4.46 ± 0.20, 4.15 ± 0.22, 2.31 ± 0.23% and the percentages of leachable Cd concentrations were 21.6 ± 1.0, 19.0 ± 0.6, 15.7 ± 0.7, 10.9% ± 0.5%, respectively. These results confirmed that the heavy metals were immobilized in the biochar through pyrolysis which was consistent with the speciation distribution of Pb and Cd.

The Fig. 3 results showed that the leachable Pb percentages increased from 2.31% to 3.76% with 30% sawdust addition at 600°C possibly because there was more organic Pb in the biochars compared to the sludge single pyrolysis. Yet at the 50% sawdust mixture ratio, more fraction of Pb can be immobilized compared to b10 and b30 due to the higher sawdust amount and heat value (Zhang et al. 2009). Similar trend occurred at the other three pyrolysis temperatures. In contrast, the leachable Cd percentages in the biochar were depressed with the addition of sawdust, especially at the 50% mixture ratio at 600°C. Pb can be immobilized efficiently than Cd through pyrolysis because Pb can mainly existed as primary minerals in sludge and biochar (Chen et al. 2019). Co-pyrolysis of sawdust and sludge could have different influence on the leachable Pb and Cd because of specific

Fig. 3 Heavy metal leaching of biochar expressed as percentages of Pb and Cd concentrations based on the TCLP method. b0, b10, b30, b50 referr to the 0%, 10%, 30% and 50% sawdust mixture ratio, respectively. Symbol *Indicates that the leachable metal percentages in the corresponding treatment were significantly decreased compared with b0 ($p < 0.05$)



speciation and different intrinsic characteristic (Huang et al. 2018). It had been reported that the rice husk addition exhibited a reduction effect on the leaching toxicity of Cd possibly because the heavy metals were restricted by the enlarged structure of biochar (Shi et al. 2013). Debela et al. (2012) also reported the leachable Cd was decreased during co-pyrolysis of the metal contaminated soil and woody biomass. Yet it failed to alleviate the Pb obviously during co-pyrolysis of sewage sludge and rice straw (Huang et al. 2017). Based on the references and the current study, we concluded that co-pyrolysis of sawdust and sludge could have different influence on the leachable Pb and Cd because of their different characteristic.

In order to investigate the intrinsic correlation between the leachable heavy metal percentages and the properties of biochar, Pearson correlation analysis were conducted to explain the possible metal transformation mechanism and the results were listed in Table 4. The percentages of leachable Pb during pyrolysis were significantly affected by the pH values, N contents and the chemical forms of Pb ($p < 0.05$). While the percentages of leachable Cd had a significantly correlation with the pH values, H and N contents, the H/C and the N/C molar ratio and the chemical forms of Cd ($p < 0.01$). These results were consistent with the Fig. 3 results and indicated that the fluctuations of heavy metals availability were mainly affected by the alkalinity, the formation of aromatic structures and the chemical forms of Pb and Cd in biochar.

Based on the above results, the 50% sawdust addition was beneficial to obtain the biochar with lower total and leachable concentration of Pb and Cd. In order to explore the mechanism of how biomass influence the leaching of heavy metals in biochar after co-pyrolysis, the biochar samples ($b50_{300}$, $b50_{400}$, $b50_{500}$, $b50_{600}$ and $b0_{600}$, $b10_{600}$, $b30_{600}$, $b50_{600}$) were analyzed by FTIR and XRF, respectively. As shown in Fig. 4a and b, the peaks at 3430 cm^{-1} were attributed to -OH (Chen et al. 2019). The peaks at 2925 cm^{-1} and 1430 cm^{-1} were corresponded to the aliphatic C–H vibration (Tang et al. 2019). The strong peaks at 1035 cm^{-1} and 794 cm^{-1}demonstrated the aromatic C = O bonds (Wang et al., 2019). Both the -OH and aliphatic C-H vibration were gradually disappeared with the higher temperature and mixture ratios (Fig. 4a, b). While the aromatic rings (1600 cm^{-1}) and aromatic C = O (794 cm^{-1}) was quite stable. These results suggested that large amounts of hydroxyl groups and aliphatic compounds were decomposed after pyrolysis. Moreover, the higher temperature and sawdust addition both make the pyrolysis process more thoroughly and promote the further carbonization. It is worth noting that, at the same pyrolysis temperature, the percentages of aromatic carbon in biochar can be increased through the co-pyrolysis (Table 3, Fig. 4a, b). The aromatic compounds can supply π-electron and have a strong ability to bond heavy metal cations, and thus reduce the release of metals (Harvey et al. 2011). Meanwhile, the higher pyrolysis temperature and the increasing sawdust mixture ratio can also reduce

Table 4 Pearson correlation coefficient (n = 16) between leachable metal concentrations and the biochar properties

Item	C	H	N	O	H/C	N/C	O/C	pH	Ash
Leachable Pb (%)	− 0.119	0.453	0.785**	0.204	0.421	0.451	− 0.179	− 0.817**	0.062
Leachable Cd (%)	− 0.381	0.807**	0.890**	0.127	0.792**	0.766**	0.131	− 0.933**	0.141

*Significant level of $p < 0.05$, ** Significant level of $p < 0.01$

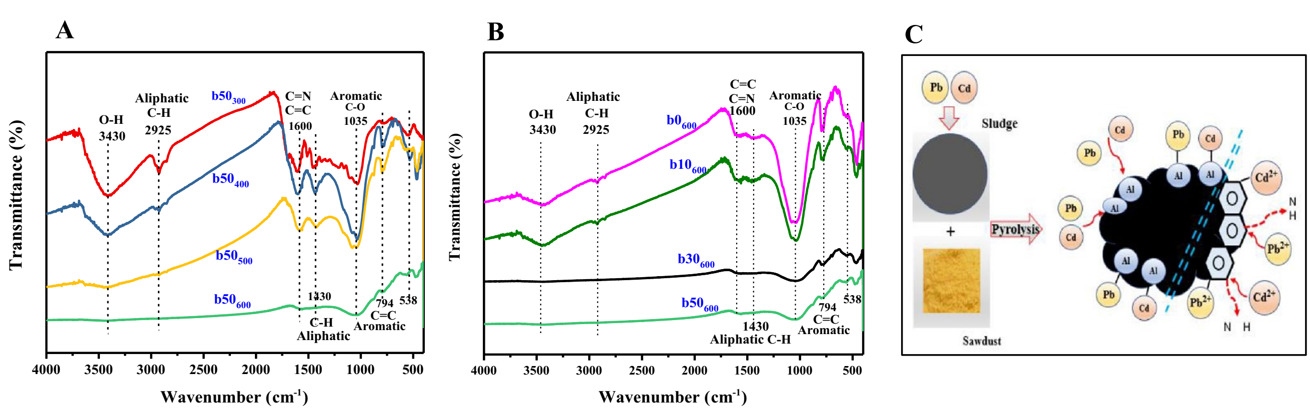


Fig. 4 FTIR patterns of different biochar. **a** Samples obtained with 50% sawdust mixture ratio at 300–600°C. **b** Samples received at 600°C with different mixture ration. **c** The possible transformation mechanism of Pb and Cd during the co-pyrolysis process. $b50_{300}$, $b50_{400}$, $b50_{500}$ and $b50_{600}$ -biochar received under 50% sawdust mixture ratio at 300–600°C, respectively. $b0_{600}$, $b10_{600}$, $b30_{600}$ and $b50_{600}$—biochar received at 600°C with 0%, 10%, 30%, 50% sawdust mixture ratio, respectively

H and N polar sites in the biochar. The less polar sites in biochar had a lower hydrophilicity (Rajapaksha et al. 2015). Thus, the percentages of leachable heavy metal, especially Cd, may be reduced with the elevated temperature and sawdust mixture ratio.

The peaks at 538 cm^{-1} were assigned to the symmetric stretching of Al–O–Si and the 453 cm^{-1} peaks in biochar referred to the bending vibration of Si–O–Si (or O–Si–O) (El-Eswed et al., 2017). The peaks around 1035 cm^{-1} can also be assigned to the Si–O–T (T = tetrahedral Si or Al unit) asymmetric stretching (Wang et al. 2018). It can be concluded that the inorganic structure in biochar was mainly composed of [SiO_4] and [AlO_4] tetrahedrons structure. The Al (III) in the oxides of Si and Al bonded four oxygen atoms, led to a negative charge in the biochar (Meng et al. 2018b). Therefore, Pb or Cd may participate directly to balance the charge and $PbAl_2O_4$ or $CdAl_2O_4$ may be generated during co-pyrolysis. This may be the main reason for the Pb and Cd immobilization. Meanwhile, the XRF results further showed that major inorganic compounds (> 5%) in the biochar were SiO_2, Al_2O_3, P_2O_5 and CaO (Table S4). The Si-Al compounds were the predominant inorganic substances in the received biochar. The XRF results were consistent with the FTIR patterns. Figure 4C plotted the main transformation mechanisms of Pb and Cd during the co-pyrolysis of sawdust and sludge (Adapted from Shen et al., 2018).

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