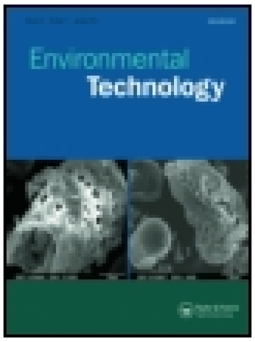

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Effects of co-pyrolysis of rice husk and sewage sludge on the bioavailability and environmental risks of Pb and Cd

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ABSTRACT
In this study, biochars were produced by co-pyrolysis of rice husk and sewage sludge, the environmental risk of heavy metal (Pd and Cd) in the biochars was assessed. Co-pyrolysis resulted in a lower yield but a higher C content compared with sewage sludge pyrolysis alone, the relative contents of Pb and Cd in biochars were declined. Co-pyrolysis process transformed the bioavailable heavy metals into stable speciation. The environmental risk assessment codes of Pb and Cd were reduced by 1–2 grades. The co-pyrolysis technology provides a feasible method for the safe disposal of heavy metal-contaminated sewage sludge.

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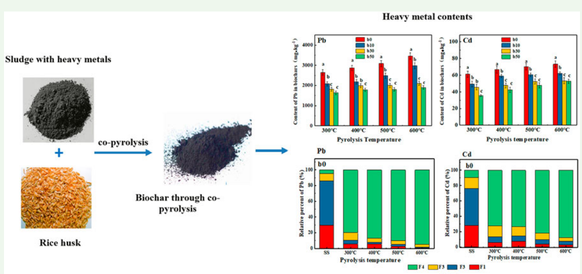

1. Introduction

According to the statistics, more than 30 million tons of sewage sludge (moisture content of 80%) were produced in China each year [1]. Numerous technologies have been developed for sludge disposal, e.g. incineration, landfill, land application. Yet these methods may cause secondary pollution due to the inadequate treatment of heavy metals [2]. Landfill and direct agricultural applications may generate undesired heavy metal leaching to soil and groundwater [3]. On the other hand, sludge incineration has also a high potential risk to the environment due to the dioxin production [4]. Compared to these methods, pyrolysis is an alternative technology and can efficiently minimize the volume of sludge, kill the pathogens and transform organic substances to bio-energy (e.g. bio-oil and pyrolytic gas) and biochars [5]. Previous studies have reported that sludge derived biochar can be used in the following options: agronomic application [6], activated carbon [7] and catalyst [8].

The heavy metals in the sludge can be kept and concentrated in the resultant biochars through pyrolysis because organic compounds were volatilized and transformed to bio-oil and pyrolytic gas [9]. The presence of heavy metals in sewage sludge may increase the environmental problems and secondary pollution to the environment [3]. Meanwhile, the bioavailability and the leaching toxicity of heavy metal are not only related to the total amount but also depend on the distribution of heavy metal speciation. Hossain et al. reported the accumulation of heavy metal in biochars, yet an obvious decline in available heavy metal contents [10]. The biochars showed lower heavy metals leaching characteristics because of the fixation by the pyrolysis [11,12]. Therefore, determining the bioavailability and leaching toxicity of heavy metals in biochars offer valuable references for its risk assessment on environment and organisms.

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Co-pyrolysis of sludge with various biomasses, such as cotton stalks [13], hazelnut shell [14] and bamboo sawdust, etc. [15], has been explored recently. Co-pyrolysis of sewage sludge with other biomasses may be a potential method to further resolve the problem of heavy metal pollution in sewage sludge-based biochar products. Some efforts have been made to explore the kinetics and products of co-pyrolysis of sewage sludge and other biomasses [16,17]. There are only a few studies concerning the leaching toxicity and bioavailability of heavy metals in the biochars during the co-pyrolysis process. For instance, Liu et al had found that the leaching concentrations of Cu, Ni, Cd, Cr and Zn were greatly reduced and lower than the standards in China during co-pyrolysis process of municipal sewage sludge and walnut shell (municipal sewage sludge/walnut shell, 4:1, w/w) at 500°C [18]. Yet the knowledge about this field is still scattered, more attention should be paid on the evaluation of bioavailability and leaching toxicity of heavy metals of sludge-based biochars through various co-pyrolysis conditions.

In this work, rice husk was selected as the representative agricultural waste biomass to conduct co-pyrolysis with sewage sludge at different temperatures (300–600°C) and mixture ratios (0%, 10%, 30%, 50%, rice husk/sludge, w/w). The higher Pb contents of children's blood can lead to neurological diseases [19]. And the Cd-induced chronic kidney disease had also been reported [20]. Thus Pb and Cd were considered as the representative heavy metals in sludge because of the high ecological risk. The objectives of this research are (1) to explore the effect of rice husk addition on the properties of the biochar; (2) to investigate the chemical speciation distribution and the leachable contents of Pb and Cd in the biochars; (3) to explore the influence of co-pyrolysis on the environmental risk of Pb and Cd in the biochars.

2. Materials and methods

2.1. Pyrolysis feedstocks

Raw sludge was sampled from the sludge dewatering unit in Wulongkou Municipal Wastewater Treatment Plant in Zhengzhou city, China, in which biological treatment (anaerobic tank, pre-denitrification tank and oxidation ditch) was used. In the oxidation ditch, Sludge retention Time, hydraulic retention time, mixed liquor suspended solids were 13.1 d, 20.5 h and 3500 mg·L^{-1}, respectively. Considering the low concentration of heavy metals in the sludge, extra Pb (II) and Cd (II) (in form of nitrate in 0.1 M HNO_3) were adding to increase the corresponding concentrations to 2000 mg·kg^{-1} and 45 mg·kg^{-1} [9,21]. Then the mixed sample was aged for three weeks. The heavy metals spiked sludge was dried in an oven (DH101-1B, Yanfei, China) at 60°C. The rice husk (Pb: 0.45 ± 0.05 mg·kg^{-1}, Cd: 0.08 ± 0.01 mg·kg^{-1}) was collected from a rice processing factory in Yuanyang city, China. Both sewage sludge and rice husk were further dried in the oven at 105 °C for 24 h, then grinded with an agate mortar and filtrated by a 10-mesh sieve. The undersize materials were collected in a plastic bag and stored in a desiccator. In this research, all the chemicals were analytical grade and purchased from Aladdin Chemical Reagent Co.

2.2. Experimental design

The sewage sludge and rice husk were thoroughly mixed as the ratios of 0%, 10%, 30%, 50%, respectively (rice husk /sludge, w/w), signed as b0, b10, b30 and b50.

The pyrolysis experiment was conducted in a temperature-controlled tube furnace (SLG1100-100, Shanghai Shengli, China). In detail, the mixed feedstocks (50.00 g) were placed in the ceramic crucible, each covered with a fitting lid, and then pyrolysed in the temperature-controlled tube furnace. Considering the possible volatilization of cadmium, we controlled the pyrolysis temperature in the range of 300–600°C The pyrolysis temperatures were raised to 300°C, 400°C, 500°C, or 600 °C at a heating rate of 10 °C·min^{-1} and held constant for 2 h [22]. A constant N_2 flow of 0.5 L·min^{-1} was maintained throughout the pyrolysis and cooling stages to ensure O_2-free conditions in the internal reaction zone of the furnace. Biochars from various temperatures were signed as BSRb_x, where b represents the mixture ratio (%) of rice husk and x represents temperature (°C). The biochars were then cooled to room temperature and stored in plastic bags for pH, yield and heavy metal analysis. All the treatments were performed in triple replicates.

2.3. Analysis methods

In this study, the yields were determined as the weight ratio of the produced biochar versus the feedstocks. The pH values of the feedstocks and the obtained biochars were measured (sample/water, 1:20, w/v) with a pH meter (PHS-3E, Leici, China). The organic carbon (C), hydrogen (H) and nitrogen (N) contents in the samples were determined by combustion at 950 °C using an automatic elemental analyser (Vario III, Elementar, Germany) [23].

The ash content was measured by the residual weight after heating the samples at 750 °C for 6 h in a muffle furnace. The content of organic matter (OM), including volatile fraction and fixed carbon, was calculated by the difference between the total amount and ash content. The content of volatile organic matter (VOM) was determined as the mass-loss rate after burning at 500°C for 1 h in a muffle. The fixed carbon (FC) was estimated as the difference between OM and VOM [24].

The total concentrations of Pb and Cd were determined using atomic absorption spectrometry (AAS) (ZEEnit 700P, Jena, German). In detail, the samples (about 0.2 g) were firstly digested in the 10 mL mixture acid of HNO_3: HCl: HF = 6:2:1 (v/v/v) with the assist of a microwave instrument (Mars 6.0, CEM, USA). The contents were evaporated till nearly dry. After cooling down, the obtained residues were dissolved with 5% HNO_3, transferred into a volumetric flask through a 0.45 μm membrane filter and then diluted to 50 mL [25].

The concentration of the chemical speciation of Pb and Cd in the sewage sludge and the obtained biochars were sequentially extracted using the three-step sequential extraction procedure which was proposed by the Commission of the European Communities Bureau of Reference (BCR) [26]. Using BCR sequential extraction the heavy metals can be divided into four fractions, namely the exchangeable and acid-soluble (F1), the reducible (F2), the oxidizable (F3), and the residual (F4) fractions. The bioavailability and mobilization of heavy metal are decreased according to the following sequence: F1 > F2 > F3 > F4. The contents of F1, F2 and F3 in the samples were also analysed by AAS. For the fraction F4, the samples were digested firstly and then the concentrations of Pb and Cd were determined by AAS. About 1.00 g sample was used for each extraction experiment. The detailed extraction scheme was shown in Table S1.

The toxicity characteristic leaching procedure (TCLP) was applied to assess the leaching characteristics of heavy metals in biochars [27]. The TCLP method of biochar was carried out in the glacial acetic acid solution (pH = 2.8) (liquid-to-solid ratio, 20:1, w/w). The biochar samples along with leaching fluid were placed in a shaker and shaken at 120 rpm for 20 h. After the extraction, the mixed samples were centrifugated at 4000 rpm for 20 min and the liquid phase was filtered through a 0.45 μm membrane filter [28]. The concentrations of heavy metals in the leaching solution were determined by the same method mentioned in the above section.

The risk assessment code (RAC) of different samples, which can be referred to the availability of the heavy metals in the sludge and biochars, were applied to evaluate the environment potential risk of Pb and Cd. It has been widely used in the environmental science field to assess the heavy metal toxicity of environment [28,29]. The degree evaluated by RAC of risk of heavy metals was based on the proportion unstable fraction accounted for of the total content, and RAC was calculated by the following formula:

$$\mathrm{RAC} = \text{the amount of F1/Total amount of heavy metals} \times 100\%$$

Risk classification in terms of RAC is: 'no risk' indicates F1 fraction of the total heavy metal is lower than 1%, 'low risk' indicates F1 fraction is in range from 1% to 10%, 'medium risk' indicates F1 fraction is in range from 10% to 30%, 'high risk' indicates F1 fraction is in range from 30% to 50% and 'very high risk' indicates F1 fraction is higher than 50%. The detailed risk classification of RAC was presented in Table S2.

2.4. Data analysis

All data were processed using the Origin software (OriginPro 2017, Origin Lab Corp., United States of America). Statistical analysis was performed using the SPSS statistical package (SPSS19.0, SPSS Inc., United States of America). One-way analysis of variance (ANOVA) was used to determine the effects of rice husk mixture ratio or pyrolysis temperature on heavy metal contents and leachable Pb and Cd concentrations. Significant differences among treatments were analysed by least significant difference (LSD) tests at the 0.05 level of probability.

3. Results and discussion

3.1. The properties of biochars

The yields of biochars produced at different pyrolysis temperatures are presented in Figure 1. Both the

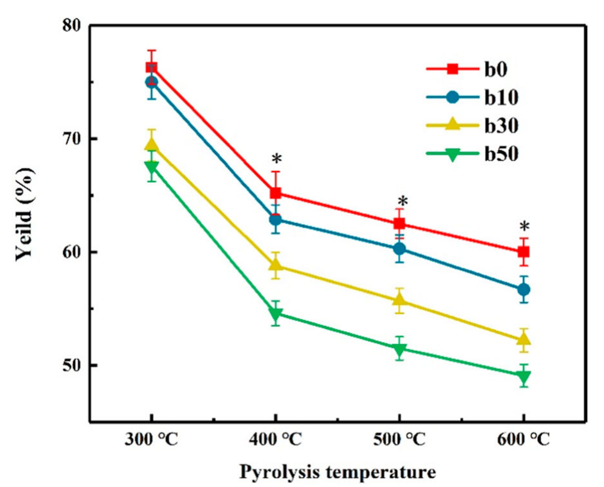

Figure 1. The yields of biochars at different pyrolysis temperatures. * indicates a significant difference between the according treatment and b0 ($P < 0.05$).

mixture ratios and pyrolysis temperatures affected biochar yields, and higher temperature and mixture ratios reduced the biochar yields. The yield of sewage sludge biochars (b0) declined from 76.3 ± 1.5% to 60.0 ± 1.5% at 300–600 °C. It was attributed to the more organic materials decomposition at the higher temperatures [24,30]. Meanwhile, the addition of rice husk reduced the yields owing to the lower ash content in rice husk (15.1 ± 0.6%) (Table 1). When the mixture ratio increased to 50%, the yields sharply decreased to 49.1 ± 1.0% at 600 °C. Huang et al. confirmed that the addition of rice straw obviously reduced the yield of biochar due to the low ash contents of biomass at the 50% mixture ratio [31].

The elemental compositions of the feedstocks and the biochars are shown in Table 1. Pyrolysis temperature and the mixture ratios of rice husk both affected the C contents in the biochars. When the temperature increased from 300 to 600 °C, the C contents decreased from 22.9 ± 0.1% to 16.3 ± 0.2% in the sewage sludge biochars. The higher pyrolysis temperature caused a lower C content in the biochars. Meanwhile, the addition of rice husk during the pyrolysis process led to an increasing C content in the biochars. The C content in the sewage sludge biochars (b0) at 300–600 °C were 22.9 ± 0.1%, 17.7 ± 0.2%, 17.0 ± 0.1% and 16.3 ± 0.2%, respectively. The corresponding C contents in the biochars (b50) were 38.8 ± 0.6%, 38.0 ± 0.7%, 32.6 ± 0.6% and 30.5 ± 0.5%, respectively. The C contents were increased by 69–115% with 50% mixture ration at 300–600 °C. The previous research had reported that co-pyrolysis of sewage sludge and cotton stalks increase the C contents with the increasing mixture ratio (10–90%) at 650 °C. Similar results were reported for biochars produced via co-pyrolysis of sewage sludge with sawdust [31] and hazelnut shell [32].

The ash contents were influenced by the pyrolysis temperature and the rice husk mixture ratios (Table 1). As the pyrolysis temperature rose from 300 to 600°C, the ash contents in the biochars (b0) were continuously increased from 55.7 ± 1.2% to 73.4 ± 0.6%, respectively (Table 1). It is noteworthy that the rice husk addition decreased the ash contents in the biochars at the same temperature. Meanwhile, the ash contents were declined significantly with the increasing rice husk mixture ratio at the same pyrolysis temperature (Table 1, $P < 0.05$). At 300 °C, The highest ash content of 55.7 ± 1.2% was obtained at b0 and decreased to 35.2 ± 1.7% at b50. The ash content in the rice husk (15.1 ± 0.6%) was lower than that in the sludge (50.0 ± 2.1%) and thus the higher content of organic matter was added into the feedstock [31].

The pH values of the sewage sludge and the rice husk were close to neutral as present in Table 1, yet the pH values of the sewage sludge biochars (b0) increased to 11.31 ± 0.40 with pyrolysis temperature elevated from 300°C to 600°C. Tan et al. reported that the pH values of biochars derived from sludge gradually increased to 12 at 300–700°C [5]. The pH values of biochars were significantly influenced by pyrolysis temperature (Table 1, $P < 0.05$). Almost all metal oxides and minerals as ash content maintained in the biochars, these alkaline substances induce the alkaline pH of the biochars [33].

Table 1. The pH, element contents and proximate analysis of the feedstocks and the derived biochars.

Sample	pH	Elements (d.b.[a], wt.%)			Proximate analysis (d. b., wt. %)			
		C	H	N	Ash	OM[b]	VOM	FC[b]
Sludge	6.68 ± 0.21	25.0 ± 0.4[c]	7.75 ± 0.03	4.55 ± 0.21	50.0 ± 2.1	50.0 ± 2.1	46.3 ± 0.02	3.7 ± 0.02
Rice husk	7.04 ± 0.13	39.0 ± 0.1	8.62 ± 0.04	0.74 ± 0.01	15.1 ± 0.6	84.9 ± 0.6	83.1 ± 0.3	1.8 ± 0.3
$BSR0_{300}$	7.32 ± 0.31 c	22.9 ± 0.1 a	7.23 ± 0.02 a	3.53 ± 0.01 a	55.7 ± 1.2 d	44.3 ± 1.2 a	42.2 ± 0.2 a	2.1 ± 0.2 c
$BSR0_{400}$	7.86 ± 0.26 c	17.7 ± 0.2 b	5.32 ± 0.02 b	2.45 ± 0.02 b	68.6 ± 1.0 c	31.4 ± 1.0 b	29.2 ± 0.3 b	2.2 ± 0.3 b
$BSR0_{500}$	9.42 ± 0.25 b	17.0 ± 0.1 c	4.99 ± 0.01 c	1.95 ± 0.02 c	72.4 ± 1.1b	27.6 ± 1.1 c	25.3 ± 0.2 b	2.3 ± 0.2 ab
$BSR0_{600}$	11.31 ± 0.40 a	16.3 ± 0.2 d	4.77 ± 0.02 d	1.59 ± 0.01 d	73.4 ± 0.6 a	26.6 ± 1.6 d	23.9 ± 0.3 d	2.7 ± 0.3 a
$BSR10_{300}$	7.56 ± 0.19 c	23.5 ± 0.1a	8.47 ± 0.03 a	3.55 ± 0.02 a	48.3 ± 1.8 c	51.7 ± 1.8 a	49.2 ± 0.2 a	2.5 ± 0.2 bc
$BSR10_{400}$	8.10 ± 0.27 c	21.4 ± 0.2b	8.10 ± 0.04 b	2.39 ± 0.01 b	59.3 ± 1.0 b	40.7 ± 1.0 b	38.1 ± 0.3 b	2.6 ± 0.3 b
$BSR10_{500}$	9.45 ± 0.34 b	21.2 ± 0.2bc	7.68 ± 0.03 c	2.22 ± 0.01 c	65.2 ± 1.2 a	34.8 ± 1.2 c	32.0 ± 0.4 c	2.8 ± 0.4 ab
$BSR10_{600}$	11.65 ± 0.42 a	20.7 ± 0.1c	5.30 ± 0.02 d	1.35 ± 0.02 d	67.8 ± 1.5 a	32.2 ± 1.5 c	29.2 ± 0.3 d	3.0 ± 0.3a
$BSR30_{300}$	7.47 ± 0.22 c	33.5 ± 0.3 a	4.86 ± 0.02 a	2.56 ± 0.02 a	40.1 ± 1.9 c	59.9 ± 1.9 a	55.6 ± 0.3 a	4.3 ± 0.3 b
$BSR30_{400}$	7.84 ± 0.19 c	32.2 ± 0.5 b	4.14 ± 0.01 b	2.38 ± 0.01 b	50.2 ± 1.9 b	49.8 ± 1.9 b	45.1 ± 0.2 b	4.7 ± 0.2 ab
$BSR30_{500}$	9.30 ± 0.32 b	30.4 ± 0.2 c	4.05 ± 0.01 c	1.59 ± 0.02 c	56.1 ± 1.6 a	43.9 ± 1.6 c	39.0 ± 0.4 c	4.9 ± 0.4 a
$BSR30_{600}$	11.58 ± 0.45 a	29.7 ± 0.1 d	4.00 ± 0.02 d	1.84 ± 0.02 d	58.8 ± 1.7 a	41.2 ± 1.7 c	36.1 ± 0.2 d	5.1 ± 0.2 a
$BSR50_{300}$	7.13 ± 0.34 c	38.8 ± 0.6 a	4.58 ± 0.03 a	2.47 ± 0.01 a	35.2 ± 1.7 c	64.8 ± 1.6 a	59.8 ± 0.1 a	5.0 ± 0.1 a
$BSR50_{400}$	7.28 ± 0.32 c	38.0 ± 0.7 a	4.34 ± 0.04 b	1.88 ± 0.02 b	48.6 ± 2.1 b	51.4 ± 2.1 b	46.2 ± 0.2 b	5.2 ± 0.2 a
$BSR50_{500}$	9.22 ± 0.39 b	32.6 ± 0.6 b	3.14 ± 0.04 c	1.59 ± 0.03 c	52.8 ± 2.7 a	47.2 ± 2.7 c	41.4 ± 0.4 c	5.8 ± 0.4 a
$BSR50_{600}$	11.42 ± 0.50 a	30.5 ± 0.5 c	3.06 ± 0.02 d	1.52 ± 0.01 d	55.8 ± 2.5 a	44.2 ± 2.5 c	37.9 ± 0.2 d	6.3 ± 0.2 b

Notes: BSR*bx*, biochar derived from sewage sludge pyrolysis and co-pyrolysis of the sewage and the rice husk at X (°C) temperature, the addition radio of rice husk was b (%). Different lowercase letters behind the values denotes significant differences ($P < 0.05$) among different pyrolysis temperature.
[a]On a dry basis.
[b]By difference.
[c]Average values ± standard deviation.

However, the mixture ratio seems no obvious influence on the pH change of biochars.

3.2. The total contents and chemical speciation of Pb and Cd in the biochars

Figure 2 depicts the total contents of Pb and Cd in biochars. The different initial metal concentrations in rice husk and sludge (Table S3) resulted in the varying Pb and Cd concentrations in biochars derived from different mixture ratios. The recovery efficiencies of Pb and Cd after the co-pyrolysis process were 90–110% (Table S4), indicating most metals were stored in the biochars. The contents of Pb and Cd in the biochars were found to be higher compared to that in the sewage sludge. The contents of Pb in the sludge biochars (b0) were increased to 2652 ± 142, 2871 ± 133, 3088 ± 144 and 3459 ± 162 mg·kg^{-1} at 300–600°C and the corresponding contents of Cd were 61.2 ± 3.6, 66.7 ± 4.3, 70.2 ± 3.9 and 73.2 ± 3.9 mg·kg^{-1}, respectively. Increasing pyrolysis temperature improved the heavy metals concentrations in the biochars. This accumulation might be attributed to the higher metal thermal stability than other organic matters in the sewage sludge [30]. Meanwhile, the total contents of Pb and Cd in biochars were decreased significantly at the same pyrolysis temperature (Figure 2, $P < 0.05$). When the rice husk mixture ratio was 50%, the contents of Pb and Cd in BSR50$_{600}$ were 1901 ± 92 and 52.6 ± 2.6 mg·kg^{-1}, and slightly decreased to 1785 ± 85.25 and 42.40 ± 2.97 mg·kg^{-1} in BSR50$_{400}$. While the higher pyrolysis temperature increased the Pb and Cd concentration of 3459 ± 163 and 73.2 ± 4.0 mg·kg^{-1} in BSR0$_{600}$. The decrease of heavy metals in the biochars can be attributed to the low heavy metals concentrations in the rice husk (Cd: 0.08 ± 0.0031 mg·kg^{-1} and Pb: 0.45 ± 0.021 mg·kg^{-1}) (Table 1) [34].

The BCR sequential extraction procedure was used to analyse the chemical speciation of Pb and Cd in the sludge and biochars [25]: F1, acid soluble; F2, reducible fraction; F3, oxidizable fraction and F4, residual fraction. As illustrated in Figure 3, the F1, F2, F3 and F4 fraction of Pb in raw sludge were 29.4%, 56.7%, 9.0% and 4.9%, respectively. The chemical speciation of Pb was obviously changed with the increase of pyrolysis temperature. The F4 fractions were 80.0%, 90.0%, 93.4% and 97.1% in the biochars with the different mixture ratios at 300 °C. While the corresponding contents were 94.7%, 94.7%, 97.7% and 98.3%, respectively, at 600 °C. Pyrolysis significantly increased the F4 fraction (>80%) in all temperatures, which were much higher than that in the raw sewage sludge (4.9%). The contents of F1 fraction of Pb were all below 10%, indicating that the mobile fractions (F1) were lower and Pb was more stable in the biochars than that in the sewage sludge.

The chemical speciation distribution of Cd was also affected by the pyrolysis temperature. The factions of F1 + F2 + F3, which was belonged to the directly and potentially toxic and bioavailable category, were 27.7%, 26.1%, 18.0%, and 12.4% respectively in the sludge biochars (b0) at 300–600°C. The results indicated that the F1 + F2 + F3 contents in the biochars were obviously declined through the co-pyrolysis process. Meanwhile, a steady increase in the non-toxic and fraction (F4) in biochar was observed (Figure 3). The F4 fraction of Cd were 72.3%, 76.6%, 79.1% and 76.2% in the biochars with different mixture ratios at 300 °C. In contrast, the corresponding content of F4 increased to 87.6%, 93.5%, 94.7% and 94.4%, respectively. Therefore, a large portion of unstable heavy metals in sludge was immobilized and the bioavailable toxic forms of heavy metals

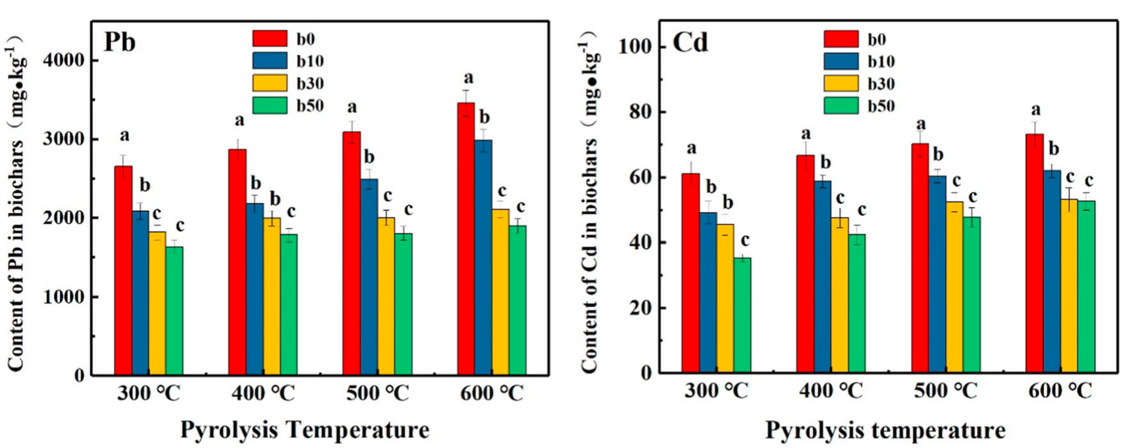

Figure 2. Pb and Cd contents in biochars. Different lowercase letters on top of the bar denote significant differences ($P < 0.05$) among the treatments.

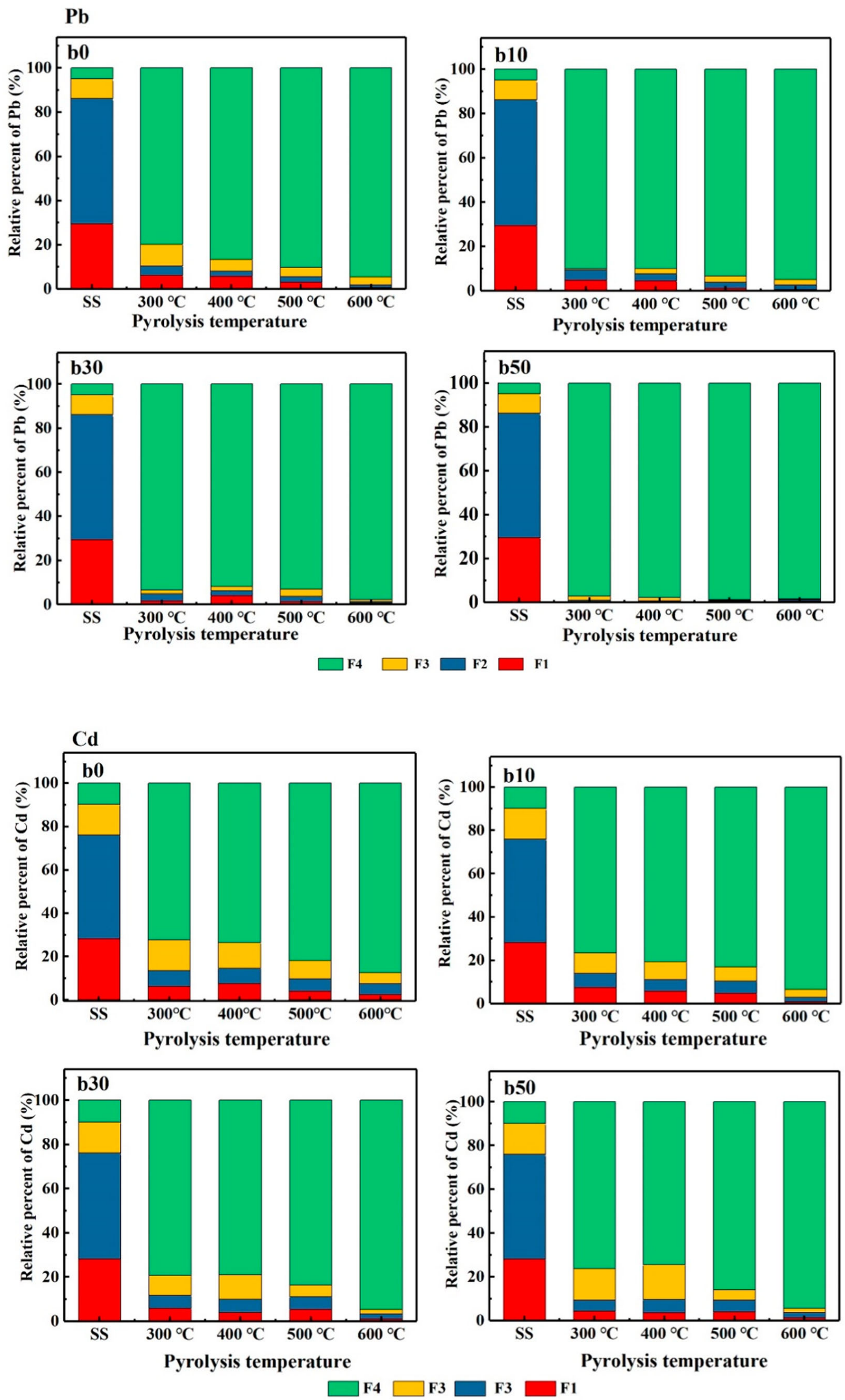

Figure 3. Chemical speciation of Pb and Cd in the samples.

decreased via pyrolysis. However, the mixture ratio of rice husk had indistinctive influence on the chemical speciation of Pb and Cd.

3.3. The leaching toxicity of Pb and Cd variation during co-pyrolysis

The leachable contents of Pb and Cd in the sludge and biochars were assessed using the TLCP method and assess the leaching toxicity, the results were compared with the threshold values described in the TCLP of USEPA [27]. In this study, the leaching toxicity of Pb and Cd were evaluated by the concentrations in the leachate. Figure 4 presents the concentrations of leachable Pb and Cd in the biochars. The highest leachable contents of Pb and Cd were 0.38 ± 0.02 and 0.090 ± 0.004 mg·L^{-1}, respectively, in BSR0$_{300}$ and BSR10$_{300}$, which were lower than the threshold values (Pb:5.0 mg·L^{-1} and Cd:1.0 mg·L^{-1}).

Pyrolysis significantly suppressed the leachable contents of Pb and Cd in the biochars. The mobility of heavy metals were restricted in the inorganic minerals or in the enlarged structure of biomass during the thermal process [21,35]. Nevertheless, the mechanisms, especially for the contribution of organic ingredients (such as lignin and cellulose contained in rice husk), inorganic substances (mainly including phosphate, silicate, carbonate, aluminium, and calcium in the sludge) and the functions of groups formed during pyrolysis, need to be further investigated. The leachable content of Pb from biochars with 50% rice husk addition was significantly lower than that derived from sludge alone (Figure 4, $P < 0.05$). But the leaching toxicity of Pb and Cd in the biochars were not significantly affected by the other two treatments (b10 and b30) (Figure 4, $P >$ 0.05). The leaching of heavy metals at different conditions may be relevant to the pyrolysis conditions and the competition between the metals. There is a report indicated that the leachability of Pb and Zn had a contrary trend in the sintered product at 600°C [36].

3.4. The risk assessment of Pb and Cd

In this study, the risk assessment code (RAC) was applied to evaluate the environment potential risk of Pb and Cd in the biochars. The RAC assesses the availability of the heavy metals in the sludge and biochar using the proportion of heavy metals present in the F1 fraction (calculated according to BCR) [37]. The F1 fraction of heavy metals represents the weakly bounded fraction and can easily release into the environment, thus reflecting the highest environmental risk.

As shown in Table 2, the RAC assessment indicated that the risk levels of Pb and Cd in raw sludge were middle environmental risk (Pb:29.4, Cd:28.1), showing

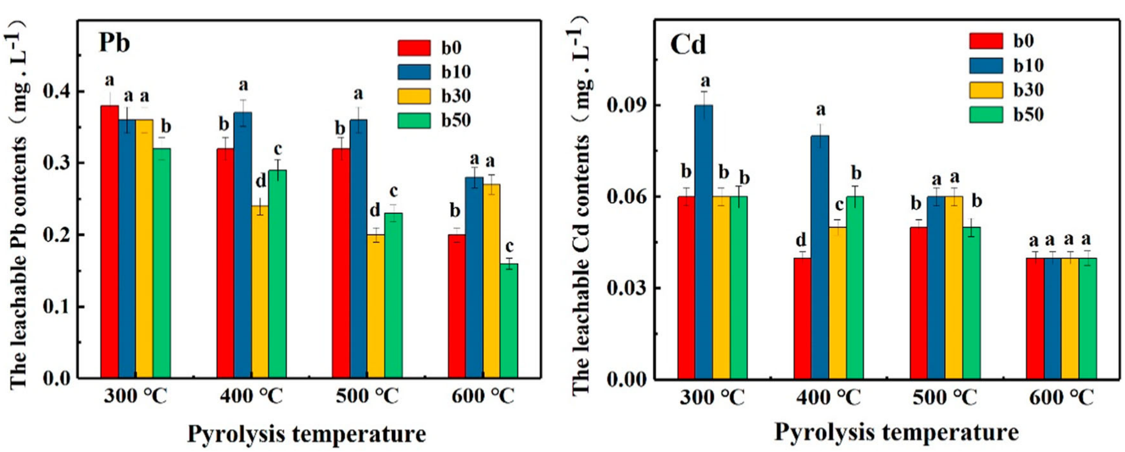

Figure 4. The leachable Pb and Cd contents. Different lowercase letters on top of the bar denote significant differences ($P < 0.05$) among the treatments.

Table 2. Risk assessment code (RAC) of Pb and Cd in biochars.

Sample	Pb (%)				Cd (%)			
	300°C	400°C	500°C	600°C	300°C	400°C	500°C	600°C
SS	29.4 (M)				28.1 (M)			
BSR0	6.1/LR	5.71/LR	3.0/LR	0.7/NR	6.1/LR	7.5/LR	4.0/LR	2.5/LR
BSR10	4.7/LR	4.4/LR	1.1/LR	0.5/NR	7.4/LR	5.8/LR	4.6/LR	0.9/NR
BSR30	1.6/LR	3.9/LR	1.2/LR	0.1 /NR	5.8/LR	4.0/LR	5.3/LR	1.0/NR
BSR50	0.5/NR	0.3/NR	0.5/NR	0.5/NR	4.3/LR	3.6/LR	4.1/LR	1.0/NR

potential toxicity to the environment. Almost all risk levels of Pb and Cd in the biochars were assessed to be low environmental risk after pyrolysis. The RACs of Pb and Cd were reduced by 1–2 grades after pyrolysis, indicating lower toxicity to the environment. It can be seen that the risk levels of Pb and Cd remained at no risk in the co-pyrolysis biochars when the pyrolysis temperature was higher than 600°C. It was evidenced that rice husk addition can give a further decrease in the potential risk of Pb and Cd during co-pyrolysis and be beneficial to reduce the environmental risk.

The cost of pyrolysis depends on feedstock, product yields, the value of the pyrolysis products, and production scale, etc. The economic benefits of pyrolysis maybe not the optimum compared to electrolysis, precipitation, surface adsorption and ion exchange, due to the considerable energy consumption. However, pyrolysis possessed greater environmental benefits because of the secondary application of by-products [38]. The received biochars can be used as adsorbent [39], catalyst [8], and the bio-oil have the potential of diversifying energy resources [40]. Therefore, pyrolysis is an effective technology for sludge disposal. In this study, the pyrolysis experiment was conducted at a small-scale. The performance verification in a pilot-scale experiment and the optimization of operation conditions are still required.

4. Conclusion

This paper revealed the effects of co-pyrolysis of rice husk and sludge on the properties and the bioavailability of Pb and Cd. Co-pyrolysis resulted in a lower biochars yield. The C content can be increased by 69–110% after husk rice addition. The relative Pb and Cd contents in the co-pyrolysis biochars were reduced through co-pyrolysis. Meanwhile, co-pyrolysis can transform the bioavailable heavy metals into stable fractions, led to a considerable decrease of direct toxicity in the co-pyrolysis biochars. The environmental risk level of Pb and Cd were also decreased by 1–2 grades. Therefore, co-pyrolysis of sludge and rice husk could be a feasible management alternative for the safe disposal of metal-contaminated sewage sludge.

Disclosure statement

No potential conflict of interest was reported by the authors.

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