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Chemical forms and risk assessment of heavy metals in sludge-biochar produced by microwave-induced low temperature pyrolysis

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Biochar, a stable, carbon-rich solid produced during biomass pyrolysis, has been widely used in soil conditioning. A promising option to alleviate the problem of sludge management. In this study, Cr, Ni, Zn, Cd, As, Pb and Cu were studied owing to their relatively high content in the sludge and their potential to cause environmental damage. Sludge-biochars were produced at different temperatures (300 °C, 350 °C, 400 °C and 450 °C) by microwave pyrolysis. BCR (European Community Bureau of Reference: a sequential extraction) analysis reveals that speciation distribution varied largely with the different heavy metals. Three risk analysis models were adopted to evaluate the risk of heavy metals: the risk assessment code (RAC), geo-accumulation index (I_{geo}) and potential ecological risk index (E_r). The heavy metals risk in the biochar were lower compared with the sludge except for Pb (sludge: 4.3, biochar: 9.4–15.6) as assessed by RAC analysis. The E_r result shows that risk from heavy metals decreased except for Cd (sludge: 63.53, biochar: 153.53–189.38). The I_{geo} model indicated that all seven heavy metals were present at higher levels in biochar than in the sludge. Although the total metal concentration in biochar increased after pyrolysis, this result indicates that heavy metal risk of microwave pyrolysis sludge-biochar should be considered alongside local soil backgrounds and speciation distributions.

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1. Introduction

Sludge, the by-product of sewage treatment, is composed of nutrients, organic compounds, organic micro-pollutants, microorganisms and heavy metals. In recent years, the larger amount of sewage water generated and higher wastewater treatment ratios have resulted in significant sewage sludge production, which has already caused serious environmental problems.^{1,2} Stricter laws and regulations have also prompted a drive for the disposal and utilization of sewage sludge.^{3–5} Currently, the most commonly used methods for sludge disposal include incineration, placement in landfills and land application.⁶ However, these methods are usually hampered by negative environmental effects and poor public image. Thus, there exists increasingly high demand for developing other environmentally friendly disposal methods.

Pyrolysis is a promising technique and various forms of energy and resources, including non-condensable gases, bio-oil and biochar, can be recovered from sludge under high temperature and low oxygen concentrations.⁷ Biochar, as the main product of pyrolysis, is a recalcitrant and stabilized organic carbon.⁸ The specific properties of biochar include: a porous structure, large surface area, a variety of mineral components and enriched functional groups, all of which enable it to remove various inorganic or organic contaminants from solutions by absorption, such as heavy metals, mineral salts, phenolic compounds, organic pesticides and PAHs (polycyclic aromatic hydrocarbons).^{9,10} Compared with traditional heating, microwave heating possesses the superiority of a rapid heating rate and energy conservation.¹¹ In addition, biochar produced by microwave irradiation has a larger surface area and more plentiful pore structures than that obtained from traditional heating.⁷ Furthermore, lower microwave heating temperature is more conducive to the improvement of biochar output than traditional irradiation.¹² Therefore, microwave pyrolysis is a promising technology for sewage sludge treatment and biochar preparation.

In recent years, biochar has also received increasing attention as a soil conditioner or absorbent. Many studies have indicated that biochar is rich in nutrients and carbon, and free of pathogens. Therefore, biochar can increase nutrient

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retention, improve fertilizer efficiency and raise crop production.⁶ However, heavy metals in the biochar may pose a risk to public health and ecological systems during its application because of their toxic and non-biodegradable nature.^{13,14} One study on sludge liquefaction manifested that 70–80% of Zn and Ni, and more than 80% of Cd, Cr, Pb and Cu from the sludge remained in the biochar.¹⁵ The research into the transformation of Cr, Ni, Cu, Cd and Pb in sludge during the pyrolysis process showed that the heavy metals were more immobile in biochar than that in sludge, mainly because of the alkaline properties of the biochar.¹⁶ Furthermore, some previous studies have drawn the conclusion that increasing pyrolysis temperature can reduce the risk of heavy metals in the biochar. He *et al.*¹⁷ found that the leaching concentrations of Cu, Cd, Zn and Pb in biochar produced in a horizontal ceramic tube dropped sharply with increasing pyrolysis temperature in the range of 350–550 °C.

The total metal content is always used as a pollution indicator. It is generally found that the behavior or mobilization capacity of heavy metals is determined by their chemical forms.^{15,18–21} Therefore, the Community Bureau of Reference proposed the sequential extraction procedure (BCR) to divide the heavy metals into different forms^{14,15,22,23} that can also provide information about heavy metal potential reactivity, leaching potential and bioavailability in sludge or biochar. Different risk assessment models can be used to further analyze the risk of heavy metals: the risk assessment code (RAC)^{22,24} was applied to quantify heavy metal bioavailability in sediments, ashes, soils, and so on. Geo-accumulation index (GAI)^{24,25} is another method that can be used to measure the pollution levels of heavy metals. The potential ecological risk^{24,26} index (RI) can evaluate the ecological risk based on the intensity, sensitivity and toxicity of the heavy metals.

Publications have mainly focused on conventional conductive heating pyrolysis and only a few studies have paid attention to the heavy metal stability after microwave irradiation. Tian *et al.*²⁷ found that microwave irradiation was more effective at immobilizing heavy metals in the sediment sludge than the traditional drying process and blast heating. It is reported that microwave-assisted hydrogen peroxide oxidation can make the metals in the sediment more stable with a lower risk to the environment.²⁸ For land application, heavy metals are some of the top priority concerns. However, the characteristics of heavy metals in microwave pyrolysis sludge biochar are not yet clear. The risks posed by heavy metals in sludge-biochar produced by microwave irradiation at low temperatures should be further analyzed.

The objectives of this article are: (1) to study whether microwave heating at low temperature can stabilize the heavy metals, and the relationship between the pyrolysis temperature and heavy metal stability. (2) To analyze the chemical speciation of heavy metals in biochars produced at low temperature using microwave heating through sequential BCR analysis. (3) To investigate the pollution intensity of heavy metals from biochar during practical application by three risk assessment methods.

2. Experimental

2.1. Materials

Dewatered sludge was obtained from the Qinghe municipal wastewater treatment plant (A²/O) process in Beijing, China (a treatment capacity of 400 000 m³ per day). The initial moisture content was 83.6%. The sludge was dried naturally until its water content was 12.3% and then ground into a powder that could pass through an 18 mesh sieve. The physicochemical properties of the sludge are presented in Table 1. Prior to pyrolysis, the sieved sludge powder was mixed with a ZnCl₂ solution at a ratio of 2 : 1 (ZnCl₂ : dry sludge wt%). This ratio was chosen to maximize the specific surface area, porous structure and adsorption performance of the sludge biochar based on our preliminary experiment. ZnCl₂'s properties as a heat carrier positively influenced the initialization of pyrolysis and its addition also promotes the development of porosity in the biochar.²⁹ The solid–liquid mixture was shaken for 24 h and then filtered and finally dried in a drying oven at 105 °C.

Microwave pyrolysis equipment (Sineo MAS-II, Shanghai Sineo Microwave Chemistry Technology Co., Ltd., China) was used in this study. The maximum power was 1000 W (the power is adjustable). This microwave oven was designed with real-time temperature monitoring. The heating rate and heating up time of this oven were set up before pyrolysis while the input power varied as the temperature changed during the pyrolysis process. An infrared thermometer was used to detect the actual temperature during the process. The input power would be adjusted (increase or decrease) according to the rate of temperature rising, automatically, to ensure that the temperature rising rate was consistent with the preset value of approximately 20 °C min^{−1} during the pyrolysis process. The reaction vessel was a quartz glass tube with a capacity of 1000 mL.

2.2. Preparation and characteristics of the biochar

N₂ was injected into the vessel at a rate of 0.5 L min^{−1} before pyrolysis to make sure the environment was oxygen-poor.⁷ During pyrolysis, the N₂ flow rate was controlled at 0.1 L min^{−1} to ensure uniform heating conditions. Sludge is not good at absorbing microwave, while biochar can strongly absorb microwave effectively. In this study, 400 g dry sludge was mixed with 40 g biochar that was used as the microwave absorber, which was produced from the same sewage sludge in the preparative experiment. The pyrolysis temperature was raised to 300 °C, 350 °C, 400 °C and 450 °C at a rate of 20 °C min^{−1}, and then maintained for 1 h.³⁰ The biochar was cooled to room temperature in a nitrogen environment. The pyrolysis product was soaked in 0.5 M HCl solution for 24 h and then washed with deionized water until the pH reached 6–7. It was then dried in oven at a temperature of 105 °C.

Fourier transform infrared spectroscopy (FTIR) (Nicolet 8700) was used to analyze the functional groups of the biochar. Total C, N and S content in biochar were analyzed by an elemental analyzer (Vario EL III). The Brunauer–Emmett–Teller (BET) surface area, average pore size and total pore volume were measured using an automatic specific surface area and

Table 1 The physicochemical properties and surface characteristics^a

Sample	Yield	Proximate analysis (wt%)		Element analysis (wt%)				Surface characteristics		
		Organic matter	Ash	C	S	N	C/N	BET (m ² g ⁻¹)	APS (nm)	TPV (10 ⁻² m ³ g ⁻¹)
SS	—	74.3	27.2	35.33	1.53	6.39	5.53	—	—	—
SC300	70	59.12	41.09	36.87	0.87	5.81	6.35	180.57	5.31	20.17
SC350	64	57.14	44.87	39.38	0.74	5.59	7.04	201.42	4.63	25.32
SC400	60	54.34	46.48	44.68	0.62	5.43	8.23	261.03	4.09	29.01
SC450	54	50.89	48.06	45.72	0.74	4.88	9.37	250.01	4.26	28.51

^a SS: sewage sludge; SC: sludge biochar (pyrolysis temperature); BET: Brunauer–Emmett–Teller surface area; APS: average pore size; TPV: total pore volume.

micropore physical adsorption instrument (ASAP2020HD88). The heavy metal concentration was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (OPTIMA 8300). Duplicate sampling was performed and concentrations of metals in the sludge and biochar were determined in triplicate.

2.3. Heavy metal analysis methods (BCR)

The sequential extraction was performed using BCR (the European Community Bureau of Reference)^{15,23}, which has been used for several studies. The analysis procedure was divided into four steps as follows:

Step one: F_1 , exchangeable fractions and those bound with carbonate. 40 mL 0.11 M CH_3COOH solution was added to 0.5 g biochar in 50 mL polyethylene centrifuge tubes, then shaken for 16 h at 22 °C. The residues were separated by centrifuging at 4000 rpm for 20 min and then washed with 10 mL deionized water.

Step two: F_2 , fractions bound to Fe and Mn oxides (reducible fraction). 20 mL of 0.1 M hydroxyl ammonium chloride solution was adjusted to pH = 2 with HNO_3 . This liquid was then added to the residues from step one. The mixture was shaken for 16 h at 22 °C. The separation and rinse of the residues employed the same methods as in step one.

Step three: F_3 , fractions associated with organic matter (oxidizable fraction). 5 mL H_2O_2 (8.8 M, pH = 2.0–3.0) was added to the residues from step two, drop by drop. Next were the processes of digestion (1 h at 22 °C), heating (1 h at 85 °C) and evaporation (to make the content nearly completely dry). 25 mL (1 M ammonium acetate solution, pH = 2) was added to the cooled contents. The extraction and rinse procedures were the same as in step one.

Step four: F_4 , residual fractions. 5 mL HNO_3 , 3 mL H_2O_2 and 5 mL HClO_4 were added to the residues from step three, then heated and evaporated until dry. After cooling, the residues were dissolved in HNO_3 (5%).

Heavy metals can be divided into three categories on the basis of bioavailability: bioavailable fraction, potentially bioavailable fraction, and non-bioavailable fraction.¹⁸ The bioavailability is inclusive of the exchangeable and carbonate bounded forms (F_1), the potential bioavailability includes the fractions bounded to Fe and Mn oxides and the fraction associated with organic matter (F_2 and F_3), and the non-bioavailable category contained the F_4 residual fractions.

2.4. Evaluation methods of heavy metal risk

Three widely used methods were adopted for comparative analysis and comprehensive evaluation of the ecological risk of heavy metals in biochar.^{18,31} (1) The risk assessment code (RAC) can be used to indicate the heavy metal contamination intensity in the sludge and biochar. The RAC, determined as the percentage of carbonate and exchangeable-state heavy metal in the substance, can also be used to measure the biological accumulation of heavy metals. (2) The geo-accumulation index (I_{geo}) quantifies the bioaccumulation of heavy metals considering the local background values of heavy metals. The background heavy metals content in Beijing were 29.8 mg kg⁻¹ (Cr), 26.8 mg kg⁻¹ (Ni), 57.5 mg kg⁻¹ (Zn), 0.119 mg kg⁻¹ (Cd), 7.09 mg kg⁻¹ (As), 24.6 mg kg⁻¹ (Pb) and 18.7 mg kg⁻¹ (Cu).³² (3) The potential ecological risk index (RI) was used to analyze the harm caused by different heavy metals: it is a comprehensive evaluation of the ecological risk of heavy metals in biochar.

2.4.1 Risk assessment code (RAC). The RAC was used for the environmental risk assessment of heavy metals in sludge and biochar. This method is widely used in the evaluation of heavy metals in soil, sediment, ash content and liquid/gas composition. It is defined as the fraction of F_1 based on the BCR.

$$\text{RAC} = \frac{F_1}{C_n} \times 100\%$$

where F_1 is the fraction of exchangeable and carbonate fractions and C_n is the content of the corresponding heavy metal.

The RAC can be divided into five levels of risk (Table 2): no risk (NR), low risk (LR), medium risk (MR), high risk (HR) and very high risk (VHR).²²

2.4.2 Geo-accumulation index (I_{geo}). The I_{geo} ²⁵ was another index that can be employed to indicate the pollution intensity of heavy metals in sludge and biochar. The detailed calculation was as follows:

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5 \times B_n}$$

where C_n is the content of heavy metals in sludge or biochar and B_n is the local heavy metal content in soil. A factor of 1.5 is used to minimize the influence of possible variations in the local soil this method is used to analyze the impact of heavy metals on nature and mankind. The data of I_{geo} was divided into seven intervals (Table 2): uncontaminated (UC), uncontaminated to moderate contamination (UC-MC), moderate contamination

Table 2 Risk simulation results of heavy metals in biochar

		Heavy metal						
	Sample	As	Cd	Cr	Cu	Ni	Pb	Zn
RAC ^a	SS	21.1	15.9	2.3	9.1	8.8	4.3	10.7
	SC300	3.0	14.5	2.1	0.9	0.7	12.6	1.1
	SC350	3.3	17.6	2.1	0.8	0.5	9.4	1.2
	SC400	3.4	19.0	2.3	1.0	0.7	15.6	1.3
	SC450	5.8	18.7	2.2	0.9	0.5	12.2	1.6
<i>I</i> _{geo} ^b	SS	0.2	2.6	−0.3	1.6	−0.6	−0.6	2.0
	SC300	2.2	2.7	1.0	2.9	−0.1	−0.6	3.5
	SC350	1.8	2.7	1.1	2.8	0.2	−0.5	3.5
	SC400	1.8	2.6	0.9	2.7	0.1	−0.6	3.5
	SC450	1.7	2.8	1.0	2.8	0.3	−0.5	3.5
<i>C</i> _f ^c	SS	0.22	2.12	0.06	3.43	1.93	1.28	5.32
<i>E</i> _r ^d		2.23	63.53	0.13	17.16	9.63	6.40	5.23
RI ^e		104.29 ^f , 40.86 ^g						
<i>C</i> _f	SC300	0.26	5.12	0.22	0.26	2.85	1.61	1.13
<i>E</i> _r		2.63	153.53	0.44	1.30	14.24	8.07	1.13
RI		181.33 ^f , 27.80 ^g						
<i>C</i> _f	SC350	0.33	6.31	0.24	0.27	2.90	1.53	1.20
<i>E</i> _r		3.27	189.38	0.48	1.34	14.49	7.66	1.20
RI		271.82 ^f , 28.44 ^g						
<i>C</i> _f	SC400	0.30	5.75	0.23	0.18	2.06	1.90	1.17
<i>E</i> _r		2.97	172.50	0.46	0.88	10.28	9.51	1.17
RI		197.77 ^f , 25.27 ^g						
<i>C</i> _f	SC450	0.33	5.16	0.25	0.1	2.22	2.08	0.95
<i>E</i> _r		3.27	154.74	0.49	0.90	11.08	10.41	0.95
RI		181.84 ^f , 27.10 ^g						

^a RAC: <1 denotes no risk (NR); 1–10 denotes low risk (LR); 11–30 denotes medium risk (MR); 31–50 denotes high risk (HR); >50 denotes very high risk (VHR). ^b *I*_{geo}: <0 denotes uncontaminated (UC); 0–1 denotes uncontaminated to moderate contamination (UC-MC); 1–2 denotes moderate contamination (MC); 2–3 moderate contamination to heavy contamination (MC-HC); 3–4 denotes heavy contamination (HC); 4–5 denotes heavy to extreme contamination (HE-EC); >5 denotes extreme contamination (EC). ^c *C*_f = *C*_D/*C*_R. ^d *E*_r: ≤5 low risk (LE); 5–10 moderate risk (ME); 10–20 considerable risk (CE); 20–40 high risk (HE); >40 very high risk (VHE). ^e RI: <30 denotes low risk (LR); 30–60 denotes moderate risk (MR); 60–120 denotes considerable risk (CR); >120 denotes very high risk (VHR). ^f The RI based on seven heavy metals in total. ^g The RI based on six heavy metals (Cd not included).

(MC), moderate contamination to heavy contamination (MC-HC), heavy contamination (HC), heavy to extreme contamination (HC-EC) and extreme contamination (EC).

2.4.3 Potential ecological risk index (RI). The RI^{24,26} can be used to evaluate the ecological risk of heavy metals in sludge and biochar. This method is based on the intensity, concentration, sensitivity and toxicity of heavy metals and is widely used in environmental chemistry and biological toxicology. The detailed calculation of RI was follows:

$$C_f = \frac{C_D}{C_R}$$

$$E_r = T_r \times C_f$$

$$RI = \sum_{i=1}^n E_r$$

where *C*_D is the concentration of measured metal, *C*_R is the background concentration and *T*_r is the toxic response coefficient of each single heavy metal. The *T*_r of Zn, Cr, Cu, Ni, Pb, As and Cd are 1, 2, 5, 5, 5, 10 and 30, respectively. *E*_r is the potential ecological risk of a single heavy metal and can be divided into five parts (Table 2): low risk (LE), moderate risk (ME), considerable risk (CE), high risk (HE) and very high risk (VHE). RI is the potential ecological risk of all the measured heavy metals and can be divided into: low risk (LR), moderate risk (MR), considerable risk (CR) and very high risk (VHR).

3. Results and discussion

3.1. The characteristics of sludge and biochar

The results of the proximate analysis, element analysis and surface characteristics are shown in Table 1. The organic matter content decreased from 59.12% to 50.89%, which may be caused by the increased production of bio-oil and bio-gas. In addition, the ash content increased from 41.09% to 48.06% with increasing temperature. The high ash was caused by the high content of mineral constituents in sludge and biochar.¹² Ash contains minerals, so higher ash content could lead to an increase in the total heavy metal content in biochar. In the FTIR spectroscopy of sludge (Fig. 1), the peak at around 3430 cm^{−1} was always recorded as a result of the stretching vibrations of −OH in metal hydroxide or water molecules, and also could be caused by the presence of −NH or −NH₂. The peak became weaker after pyrolysis, which indicated the decomposition of metal hydroxides, the removal of water or protein decomposition. And the exchangeable heavy metals may react during pyrolysis as follows: metal ion → metal hydroxide → metal oxide, which could cause the peak to become weaker and stabilize the heavy metals. What is more, protein decomposition could give rise to an increase in C/N.^{33,34} From the surface characteristics of biochar, it could be concluded that high temperatures had a positive influence on improving the BET surface area. Compared with the heavy metal content in sludge, the contents in biochar became higher. Pyrolysis is a thermochemical decomposition that mainly generates bio-gas, biochar and bio-oil.³⁵ Most of the heavy metals (70–80%) remain in the biochar, except for some heavy metal release into bio-oil.²⁴ In this study, the As, Zn, Pb, Ni, Cd, Cr and Cu contents of biochar were more than 0.64, 1.60, 1.06, 0.25, 1.20, 0.33, and 0.97 times those in sludge, respectively, and most of the Zn, Pb, Ni and Cr remained within the biochar. Similar results have been reported in other studies.^{6,15,18,24,36}

3.2. The speciation distribution of heavy metals

The BCR^{15,23} for the heavy metal chemical analysis indicates the occurrence, mobilization and bioavailability of heavy metals. The heavy metals, which are exchangeable and bound with carbonate (*F*₁), have the highest bioavailability and the greatest potential to cause secondary environmental pollution.¹⁵ The heavy metal contents of *F*₁ (mg kg^{−1}) are shown in Fig. 2(a). For some heavy metals, there was a higher content in biochar compared with the sludge. The Cr and Pb contents of biochar

Fig. 1 The FTIR of sludge and biochar produced at different temperatures.

were as twice as that in sludge. There was no obvious change in the Cd content after pyrolysis. However, a decline was observed for the other four heavy metals. More than 59.9%, 74.9% and 87.8% reductions were seen in the biochar compared with the initial sludge for Zn, Cu and Ni, respectively, which meant that the pyrolysis had a positive influence on reducing the risk of Zn, Cu and Ni.

The heavy metal percentage was another indicator that helps determine the speciation distribution of heavy metals. The percentages of heavy metals in the F_1 category are presented in Fig. 2(b). Some variations appeared after pyrolysis: the percentage of fraction F_1 exhibited an obvious downward trend after pyrolysis for almost all heavy metals, most notably Cu, Ni and Zn. According to the calculations, the percentage of Cu (F_1), Ni (F_1) and Zn (F_1) in biochar was less than 4%, 7% and 13%, respectively. Arsenic also showed a downward trend after pyrolysis to a slight degree. All of this means that the process of pyrolysis could reduce the unstable fraction of Cu, Ni, Zn and As. However, the same trend did not appear in the Cr, Pb and Cd data. In fact, the percentages of Cr, Pb and Cd increased slightly after pyrolysis: more specifically, the percentage of Cr (F_1) in biochar was higher than that in the sludge. The percentages of Cd (F_1) and Pb (F_1) both showed a slight downward trend only in lower temperature pyrolysis (Cd: 300 °C, Pb: 350 °C).

A previous pyrolysis study²⁴ of pulp/paper indicated that increasing temperature reduces the risk from heavy metals. However, in our study of microwave heating, higher temperature did not have a positive influence on the enhancement of heavy metal stabilization. Looking at the heavy metal contents and percentages in the exchangeable fraction (F_1), it can be concluded that high temperature even increased the contents or percentages of the exchangeable forms, which meant that the risk of biochar would be increased during application.

Although the fractions bound to Fe and Mn oxides (F_2) and the fraction associated with organic matter (F_3) were actually

more stable than the F_1 , they were also still bioavailable and potentially labile when they went into the biosphere or the complex internal environment of living organisms.²² The F_2 fraction is thermodynamically unstable, which meant it could become available in an oxygen-deficient environment, and the F_3 fraction is easily transformed into F_2 and F_1 fractions in oxidizing conditions. Therefore, the potential risks of F_2 and F_3 fractions should not be overlooked. In Fig. 2(c), it could be seen that the content of heavy metals (F_2 and F_3) in biochars were higher than in the sludge, and a similar tendency appeared in the percentage of heavy metals, apart from Cu. Examining the content and percentage of Cu in fraction F_4 , it could be found that most of the Cu fractions were transferred from F_1 , F_2 and F_3 into F_4 through the process of pyrolysis.

The residual fraction was the most stable fraction and heavy metals could be held in the crystal structure.¹⁵ From Fig. 2(e) and (f), the content (fraction F_4) all heavy metals increased after pyrolysis. The percentages (fraction F_4) of Cd, Cr, Ni and Pb in biochar became lower than those in sludge, which indicated that the stable fraction of the four heavy metals were transferred into the unstable fraction after pyrolysis; but for As, Cu and Zn, the percentage of fraction F_4 decreased after the pyrolysis. This meant that these heavy metals were released during the pyrolysis procedure. This may be caused by the damage of the crystal structure in the sludge at high temperature.

Fig. 2 showed that the total content ($F_1 + F_2 + F_3 + F_4$) of zinc was higher than that of other heavy metals: this phenomenon was caused by the addition of zinc chloride, which acted as a chemical additive in the pyrolysis process. However, the most harmful fraction (F_1 , exchangeable or bound with carbonates) accounts for less than 3% of the total heavy metals in the biochar. More than 97% of the zinc was present in the fraction bound with Fe and Mn oxides (F_2), organic matter or sulfides (F_3) or non-silicate minerals (F_4). In our previous leaching experiment, the concentration of zinc was also higher than other heavy metals, which meant there was a higher risk associated with this heavy metal. To reduce the risk caused by heavy metals, especially zinc chloride, the biochar should be washed with acid and deionized water many times prior to use. Reducing the dosage of zinc chloride or using alternative chemical additives with low risk will be studied in our future research.

A similar phenomenon occurred in the form changes of Cu, As and Cr. The F_4 fractions of Cu, Ar and Cr with less potential bioavailability and mobility were the major fractions in the biochar. Based on this, most of the three heavy metals were probably contained in minerals like feldspars, quartz, etc. Some research¹⁷ has indicated that Cu was mainly bound to sulfides in nature, meaning the solubility will increase under oxidizing conditions. Therefore, the oxygen-deficient environment in the pyrolysis procedure is helpful for the stabilization of Cu (Fig. 2).

Cd, Ni and Pb were mainly found in the F_2 and F_3 fractions. Previous research has also found that the dominant fractions of Cd and Pb were oxidizable fractions (F_3).¹⁷ This was because less bio-gas and bio-oil were produced at low temperature, which resulted in a relatively high organic matter content that then produced more fractions associated with organic matter in the

Fig. 2 Chemical speciation of heavy metals in sludge or biochars. The content of fraction $F_i = F_i$ (mg)/sludge or biochar (kg); the percentage of fraction $F_i = F_i / (F_1 + F_2 + F_3 + F_4) \times 100\%$.

biochar. The chemical speciation analysis indicated that not all the heavy metals were transferred from unstable into stable fractions.

Leaching characteristics is another indicator for heavy metals risk, namely the heavy metal's bio-availability and mobility to natural lixiviation. In our previous study, the leaching concentration of zinc (about 20 mg kg^{-1}) was the highest among all the heavy metals. The addition of ZnCl_2 is the main reason for the highest leaching concentration of Zn. The second highest concentration was As and for the Pb, Ni, Cd and Cu, the concentrations are less than 0.4 mg kg^{-1} . It is also found that increasing temperature can reduce the leaching ability of heavy metals. In a word, there was some risk associated with the practical application of biochar based on the results of the leaching experiments and chemical forms.

3.3. Risk analysis of heavy metals

3.3.1 Risk assessment code (RAC). The risk assessment code was used to get more detailed insight on the environmental risk of heavy metals in sludge and biochar. The results are presented in Table 2. Cr, Cu, Ni and Pb in sludge presented low risk with an RAC of less than 9.1%; and the other three heavy metals, As, Cd and Zn, were associated with medium risk with an RAC level between 10.7% and 21.1%. After pyrolysis, the risk levels of As and Zn were changed markedly from MR to LR. Similarly, the risk level of Ni and Cu changed from LR to NR. In other words, the process of pyrolysis can reduce the risk of these four heavy metals. However, no prominent changes appeared in the RAC of Cd and Cr. Separately, the environmental risk of Pb was higher in biochar with the RAC moving from 4.3% (sludge)

to 9.4–15.6% (biochar). To avoid this phenomenon, some fixing agent should be added into the sludge. As a whole, the environmental risk of heavy metals in sludge and biochar calculated with the RAC method was mostly low (mainly in LR and MR). Only the risk of Pb increased during the pyrolysis. The process of pyrolysis could reduce the risk of most heavy metals in sludge and provided a positive influence on the production of sludge.

3.3.2 Risk assessment based on the I_{geo} . The calculated results of the I_{geo} are presented in Table 2. The I_{geo} of sludge was calculated to be between -0.6 and 2.6 . The I_{geo} of As in sludge was 0.2 , which meant it was in the category of UC to MC; but for the biochar, the I_{geo} values were between 1.7 and 2.2 , which were in the MC to HC bracket. For Cd, there was almost no change in the I_{geo} after pyrolysis. The I_{geo} of Cr in the sludge was -0.3 (UC); but in the biochar, the value was between 0.9 and 1.1 (UC-MC and MC). For Cu, the I_{geo} of the sludge was 1.6 (MC), and the index of the biochars were between 2.7 and 2.9 (MC-MHC). The same tendency of Ni and Zn was exhibited as with the above-mentioned heavy metals. For Pb, no changes were observed after pyrolysis: the I_{geo} in sludge and biochar were both in the interval of UC. According to the I_{geo} data, a huge rise in contamination occurred after pyrolysis. Other research has also indicated that the pyrolysis process can enable heavy metals in sludge to become concentrated, mostly in biochar,²⁴ which gave rise to the increase in the I_{geo} .

3.3.3 Potential ecological risk (RI and E_r). The potential risks of single heavy metals (E_r) and total heavy metals (RI) are presented in Table 2. According to the Cd data, the E_r was high in both the sludge and the biochar. This may be due to the low background value. A huge increase in the E_r could be found after pyrolysis as well, indicating that the risk from Cd in biochar was more severe than that in the sludge, although some changes in the E_r of the other six heavy metals were observed during the pyrolysis process, the risk level posed by them was all LR or MR. From the RI, the total risk of the seven heavy metals was all in the CR level; but the risk of six heavy metals (Cd not included) was in the LR level, the potential risk was mainly caused by the presence of Cd.

According to the GB/T23486-2009 standards in China, when soil pH was less than 6.5 , the Cd content should be lower than 5 mg kg^{-1} ; and when the pH of soil was higher than 6.5 , the Cd content should be lower than 20 mg kg^{-1} . Although the E_r of Cd in biochar was mainly in the ME or HE category, the concentration was still within the standard. This study suggests that prior to sewage sludge biochar application, a risk analysis should be carried out on the background levels of local soil heavy metal contamination.

3.4. Comparison of microwave heating and traditional heating

It has been proven that biochar produced by microwave pyrolysis had a larger surface area and more porous structure; but few research has reported the differences between microwave heating and traditional heating on heavy metal stabilization. Chen *et al.*¹⁴ have already done some research about the chemical forms of heavy metals in sludge-biochar produced by

traditional heating (CH-biochar). The result showed that the percentage of oxidizable Cu (F_3) in the sludge-biochar was about 70%, which meant that the oxidizable Cu was the major component. In our microwave sludge biochar (MW-biochar), the major component of Cu was the residual fraction (F_4) with the percentage of 81.36–85.94%. The Zn and Pb in CH-biochar mainly existed as the fraction of F_2 and F_3 , while in MW-biochar, the Zn and Pb were mainly distributed in the F_4 fraction with a percentage of about 50%. The Cr and Ni in CH-biochar were mainly concentrated in the F_4 fraction with a percentage of 53.20% and 50.35%, respectively. Similarly, the main fraction of Cr (about 80%) and Ni (about 40%) in MW-biochar were in the residual fraction (F_4). By contrasting CH and MW heating, it can be concluded that microwave heating has more advantages towards stabilizing the heavy metals Cu, Zn, Pb and Cr.

3.5. Future work

It is well known that pyrolysis conditions (*i.e.* pyrolysis temperature, retention time and heating rate) critically influence the surface characteristics of biochar and even affect the distribution of pyrolysis products between biochar, bio-oil and bio-gas. But for heavy metal stabilization, researchers have mainly focus on the influence of temperature in traditional pyrolysis and overlook the potential impact of the retention time and heating rate. In this study, we only focused on the temperature variation in microwave heating. The influence of retention time and heating rate on the heavy metals contents and chemical forms should be studied in future experiments.

In this study, due to the reason that heavy metals were mainly concentrated in the biochar when the heating temperature is below 505°C ,¹⁶ our primary research only examined the concentration and chemical forms of heavy metals in biochar. But in high temperature pyrolysis, more heavy metals are likely to emerge in the bio-oil or bio-gas and the heavy metal distribution will become more complicated. In this case, researchers should not only focus on the heavy metals in biochar, but also think about the mass balance of heavy metals in the biochar, bio-oil and bio-gas to facilitate a more comprehensive evaluation on heavy metal stabilization during the pyrolysis process.

4. Conclusions

(1) By means of heavy metals fraction analysis (including exchangeable, reducible, oxidizable and residual fraction), stabilization of As, Ni, Cu and Zn were strengthened after pyrolysis. Meanwhile the stabilization was reduced for Cd, Pb and Cr.

(2) Total heavy metals are enriched in the pyrolysis process according to the risk assessment of I_{geo} . Pb and Cd were in relatively high levels in biochar after pyrolysis through risk assessment of the RAC and E_r . More attention to these two metals should be paid during biochar application.

(3) In the range of 300 – 450°C , increasing microwave pyrolysis temperature does not have a definite or positive influence

on the heavy metal stabilization based on the chemical speciation and risk assessment from this research.

(4) Compared with traditional heating, microwave heating has more advantages on stabilizing the heavy metals Cu, Zn, Pb and Cr.

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