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Chemical speciation and risk assessment of heavy metals in biochars derived from sewage sludge and anaerobically digested sludge

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ABSTRACT

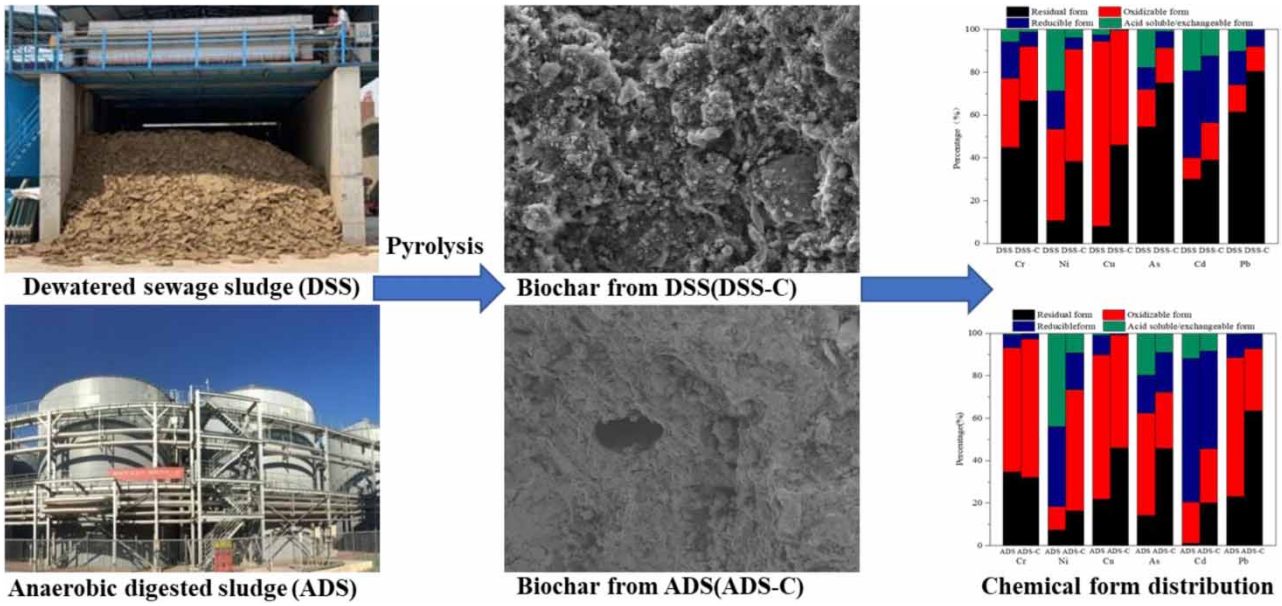
Dewatered sewage sludge (DSS) and anaerobically digested sludge (ADS) were pyrolyzed at 550 °C to investigate the characteristics of derived biochar and evaluate the risk of heavy metals (Cr, Ni, Cu, As, Cd, and Pb). The results showed that the pH value of the biochar derived from DSS (DSS-C) was slightly lower than that of the biochar derived from ADS (ADS-C), while DSS-C presented relatively higher specific surface area and total pore volume. DSS-C also showed higher H/C and lower O/C ratios than ADS-C, indicating a higher aromatic condensation and a lower polarity. Total concentrations of Cr, Ni, Cu, As, Cd, and Pb in DSS and ADS increased significantly after pyrolysis owing to the thermal decomposition of organic matter in the sludge, with corresponding rise of the Nemerow pollution index (NPI) of the biochars compared with the raw sludge. In addition, the sequential extraction procedure (BCR) analysis revealed that the pyrolysis process promoted the transformation of heavy metals from bio-available fractions to stable fractions. The potential environmental risk of heavy metals decreased from moderate and extremely high levels in the DSS and ADS to low risk and moderate levels in DSS-C and ADS-C after pyrolysis, respectively.

Key words: anaerobic digestion, biochar, chemical speciation, heavy metals, pyrolysis, sewage sludge

HIGHLIGHTS

- Sewage sludge and anaerobically digested sludge were pyrolyzed to produce biochar.
- Heavy metals Cr, Ni, Cu, As, Cd, and Pb were concentrated in the derived biochars.
- Proportions of heavy metals in the unstable fraction decreased significantly after pyrolysis.
- Pyrolysis treatment obviously alleviated the environmental risk of derived biochars.

GRAPHICAL ABSTRACT



1. INTRODUCTION

As the inevitable byproduct from wastewater treatment, sewage sludge is composed of organic compounds, nutrients, microorganisms, and pollutants (e.g. organic harmful matters, pathogenic organisms and heavy metals) (Singh & Agrawal 2008; Peccia & Westerhoff 2015). Recently, a significant increase of over 4% in the amount of sewage sludge generated annually has been observed due to the growing sewage treatment capacity and increasingly stringent discharge standards in China (Zhou *et al.* 2020). Inadequate treatment and disposal of sewage sludge can cause serious secondary pollution, especially pollution caused by heavy metals in sewage sludge, which can harm human health by contaminating soil and water resource, and finally entering the food chain (Thomsen *et al.* 2017; Chen *et al.* 2019).

Pyrolysis has recently been developed as a potential method for sewage sludge treatment to simultaneously reduce sludge volume, recover energy and immobilize heavy metals (Chen *et al.* 2014; Deng *et al.* 2020). Biochar, the main product of biomass pyrolysis, is generally an alkaline carbon-rich material with porous structure, nutrient contents and abundant functional groups. Biochar derived from sewage sludge has been widely used for the remediation of contaminated soil, adsorption of pollutants and enhancement of anaerobic biogas production (Xiao *et al.* 2018; Ni *et al.* 2019; Ambaye *et al.* 2020). Previous studies have shown that most heavy metals in the raw sewage sludge were still concentrated in the derived biochar after pyrolysis treatment (Udayanga *et al.* 2019; Wang *et al.* 2019), thus the application of biochar derived from sewage sludge may pose a risk to human health and ecological systems due to the non-biodegradable nature of heavy metals. In addition to the total concentrations, the eco-toxicity and bio-availability of heavy metals are also largely determined by the chemical speciation of metals. Previous studies have investigated the chemical speciation transformation of heavy metals in the sludge-derived biochar (Shao *et al.* 2015; Jin *et al.* 2016; Li *et al.* 2018). However, these studies have mainly focused on the chemical speciation and risk assessment of heavy metals in the biochar derived from sewage sludge, with only a few concentrating on the transformation behavior of heavy metals in anaerobically digested sludge during the pyrolysis process. The physicochemical properties of sewage sludge have been known to change significantly during the anaerobic digestion process, such as the content of organic matter, form of inorganic constituents and speciation distribution of heavy metals (Dong *et al.* 2013). However, the influences of these properties on the properties of derived biochar and behavior of heavy metals and are not clearly known due to the complex nature of sewage sludge.

In this study, to investigate the characteristics of derived biochar and evaluate the risk of heavy metals (Cr, Ni, Cu, As, Cd, and Pb), dewatered sewage sludge (DSS) and anaerobically digested sludge (ADS) were converted into biochar through pyrolysis at 550 °C. The physicochemical properties of the biochars derived from these two feedstock materials were characterized.

In addition, the total concentrations and chemical speciation of heavy metals (Cr, Ni, Cu, As, Cd and Pb) in the raw materials and derived biochars were evaluated. The environmental risk of heavy metals was also assessed.

2. MATERIALS AND METHODS

2.1. Biochar preparation

The DSS (TS of 20.71%, VS of 11.35%) and ADS (TS of 16.52%, VS of 5.73%) were collected from a municipal wastewater treatment plant (WWTP) and a sludge treatment plant (STP) located in Tianjin, China, respectively. The WWTP has a treatment capacity of about 400,000 m^3/d and comprises three treatment processes: preliminary, primary, and secondary processes (multistage A/O process). The STP has a treatment capacity of about 800 m^3/d for dewatered input sludge with water content of 80%, and comprises five treatment processes: sludge conditioning, pretreatment, mesophilic anaerobic digestion, dewatering and heat drying. The main feedstocks of this STP are the DSS from the WWTP (over 85%) and partial industrial sludge. The TS and VS of the DSS are prior to pyrolysis, DSS and ADS were dried in an oven at 105 ± 2 °C for 12 hours.

Pyrolysis of DSS and ADS was conducted in a muffle furnace, which was purged with pure nitrogen gas for 60 min to expel oxygen gas before pyrolysis. Next, 20.0 g of sludge sample was inserted into a quartz crucible and sealed to exclude air. The pyrolysis temperature was raised to 550 °C at a rate of 15 °C/min and then held constant for 2 hours. The biochars obtained were cooled at room temperature, milled through a 40-mesh sieve and stored in plastic bags for further analysis. The biochars derived from DSS and ADS were noted as DSS-C and ADS-C, respectively.

2.2. Characterization of biochar

The pH of the biochar was measured with a pH meter (Multi 3510 IDS, WTW, Germany) and at a biochar/:water ratio of 1:10 (w:v). The ash contents of the DSS-C and ADS-C were determined using the standard method (GB/T 28731-2012). The Brunauer–Emmett–Teller (BET) surface areas and pore structure parameter of the biochar samples were determined using a BET apparatus (BET, TRISTAR II 3020, USA). The surface functional groups of the samples were obtained using a Fourier transform infrared (FTIR) spectrometer (FTIR, Nicolet iS10, USA). Changes in surface morphology of the samples were examined using a scanning electron microscope (SEM, JSM-7800F, Japan). Elemental analyses were carried out with an elemental analyzer (EDS, Vario EL Cube, Germany).

2.3. Analysis of heavy metals

For determining the total heavy metal concentration in the sludge and biochar samples, 0.5 g of each sample was digested with 8 ml of H_2O_2 (30%) and HNO_3 (v:v = 1:3) at 180 °C for 35 min using a microwave digestion instrument (CJ/T 221-2005). The digested samples were filtered through a microporous membrane (0.45 μm), and the concentrations of heavy metals in the filtrate were determined using an inductively coupled plasma source mass spectrometer (ICP-MS, Agilent 7700, USA). The chemical fractions of the heavy metals in the sludge and biochar samples were analyzed using the improved BCR method (Rauret *et al.* 1999). In this extraction procedure, chemical forms of heavy metals are classified as acid soluble/exchangeable (FA), reducible (FB), oxidizable (FC), and residual (FD) forms.

2.4. Potential ecological risk index

The potential ecological risk index (E_r) proposed by Hakanson (1980) was widely used to evaluate the contamination and ecological risks of heavy metals in the sludge in the current study. The formulas are as follows:

$$C_f = \frac{C_i}{C_n} \tag{1}$$

$$E_r = T_r \cdot C_f \tag{2}$$

$$RI = \sum E_r \tag{3}$$

where C_f is the contamination factor of individual heavy metals; C_i the heavy metal concentrations in the available (FA + FB + FC) fractions; C_n the heavy metal concentrations in the stable (FD) fractions; E_r the potential ecological risk factor; T_r the toxic response factor for the heavy metal. T_r values of the heavy metals in the sludge are as follows: Cr (2), Ni (5), Cu (5), As (10), Cd (30) and Pb (5) (Hakanson 1980; Huang *et al.* 2011). RI is the total potential ecological risk index

caused by all the heavy metals. The classification criteria of potential ecological risk based on E_r and RI are shown in Table 1 (Jin *et al.* 2016).

3. RESULTS AND DISCUSSION

3.1. Characterizations of the derived biochars

The characterizations of the DSS-C and ADS-C are summarized in Table 2, including the yield, ash content, pH value and elemental analysis. The biochar yield of ADS (60.42%) was clearly obviously higher than that of DSS (48.15%), probably due to higher content of inorganic matter of the ADS resulting from the decomposition of organic substances during the anaerobic digestion process (Ni *et al.* 2019). In addition, high ash content was observed in the DSS-C, indicating that most of the inorganic constituents in the sewage sludge were enriched in the biochar during the pyrolysis process (Jin *et al.* 2016). A previous study showed that carbonates of alkali metals (e.g. Ca, K, Na) were the major alkaline components in the biochar (Yuan *et al.* 2011). The alkali metals could be concentrated in the digested sludge with the transformation of biomass to biogas, which then resulted in the high content of K, Na, Mg and Ca in the ADS-C, compared with DSS-C, as shown in Table 2. Consequently, the ADS-C (pH 10.32) showed relatively higher alkaline nature, compared with the DSS-C (pH 9.24). Since the ratios of molar H/C and O/C were the important parameters to characterize the aromaticity and polarity of the biochar, the higher ratio of molar H/C and O/C in DSS-C (Table 2) implited stronger carbonization and lower aromatic condensation of the biochar derived from DSS.

SEM images (Figure 1) showed that biochar from both sludge samples had rough surfaces and obvious pore structure. However, the pore structures of the DSS-C were more obvious, as can be seen in Figure 1. The results of BET and pore structure analysis presented in Table 3 were consistent with the SEM results. DSS-C showed higher specific surface area (80.67 m^2/g) and higher total pore volume than ADS-C. The micropores were formed during the pyrolysis process as a result of the

Table 1 | Classification criteria of potential ecological risk

C_f	Metal contamination	E_r	Potential ecological risk	RI	Sample contamination
$C_f < 1$	Clean	$E_r < 40$	Low	RI < 150	Low
$1 < C_f < 3$	Low	$40 < E_r < 80$	Moderate	150 < RI < 300	Moderate
$3 < C_f < 6$	Moderate	$80 < E_r < 160$	Considerate	300 < RI < 600	Considerate
$6 < C_f < 9$	Considerate	$160 < E_r < 320$	High	RI > 600	High
$C_f > 9$	High	$E_r > 320$	Very high		

Table 2 | Characteristics of the derived biochars

Parameter	DSS-C	ADS-C
Yield (%)	48.15	60.36
Ash (%)	75.98	60.94
pH	9.24	10.32
C (%)	14.58	25.75
O (%)	8.00	10.61
H (%)	0.66	0.98
Molar H/C	0.53	0.46
Molar O/C	0.40	0.31
K (%)	0.53	0.81
Ca (%)	0.05	0.01
Na (%)	0.21	0.32
Mg (%)	0.28	0.30

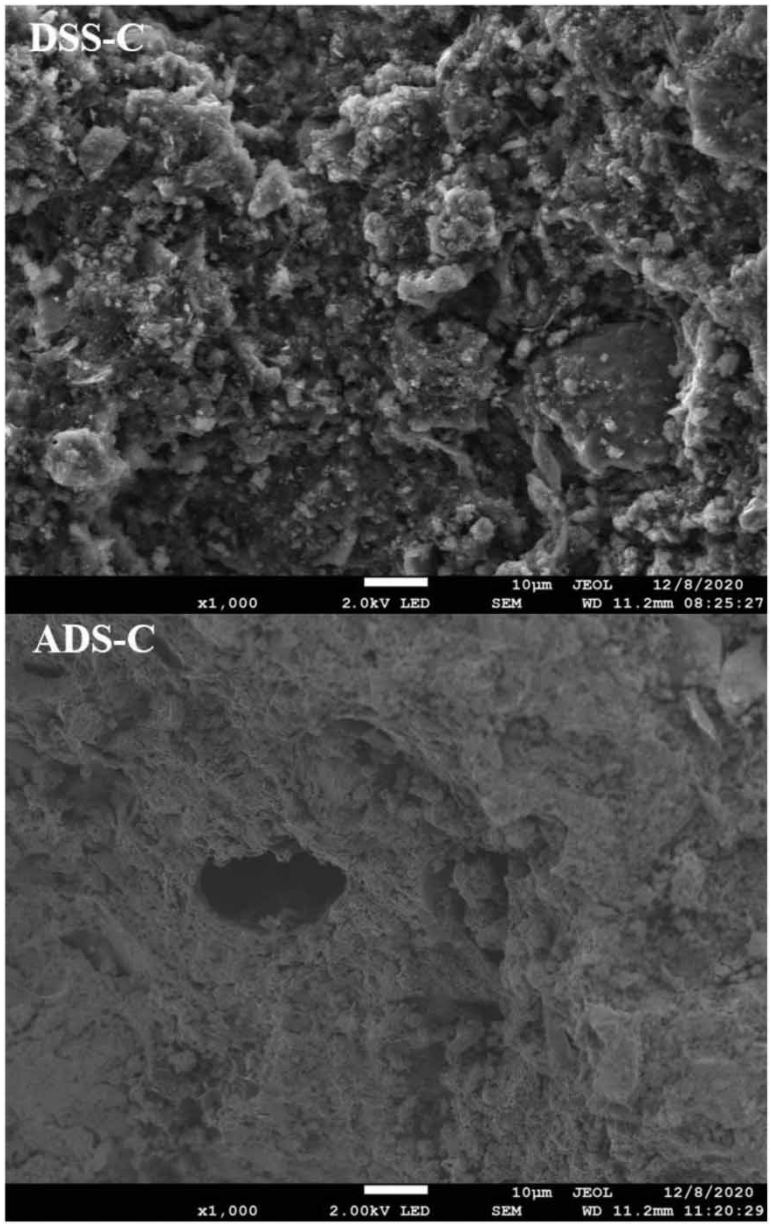


Figure 1 | Scanning electron micrographs of the DSS-C and ADS-C.

Table 3 | BET and pore structure of the derived biochars

Parameter	DSS-C	ADS-C
SSA-N^2 (m^2/g)	80.67	53.45
Volume of micropores <2 nm (cm^3/g)	0.008	0.005
Volume of mesopores 2–50 nm (cm^3/g)	0.069	0.048
Volume of macropore >50 nm (cm^3/g)	0.075	0.085
Total pore volume 1.7–377.9 nm (cm^3/g)	0.153	0.138

evaporation of volatile matters, and micropores could collapse and develop into mesopores or macropores (Zielinska & Oleszczuk 2015). Partial organic matter was been transformed to biogas after anaerobic digestion, resulting in lower volatile matter in the ADS (VS/TS, 34.66%) compared with the DSS (VS/TS, 54.79%). Thus, the mesopores and micropores of DSS-C were more abundant than those of ADS-C. Consequently, the total pore volume of DSS-C was clearly higher than that of ADS-C. The pores in biochar have good adsorption function for heavy metals in the soil and organic pollutants in wastewater (Gul *et al.* 2015). Furthermore, it can also provide a large number of attachment sites for microorganisms in the soil to promote the reproduction of beneficial microorganisms (Ahmad *et al.* 2014).

3.2. Results of FTIR analysis

The infrared peaks of sludge samples and derived biochars are shown in Figure 2. The peaks at 3,430 cm^{-1} correspond to the stretching vibration of -OH in water molecules, alcohols, carboxylic acids, or metal hydroxide. In the FTIR spectra of DSS and ADS, there were peaks before pyrolysis due to aliphatic C-H stretching within the 2,920–2,855 cm^{-1} range, and these organic groups disappeared after pyrolysis, which indicates that organic fatty hydrocarbons were destroyed or transformed to aromatic structures (Jin *et al.* 2016). The bands for aliphatic chains, including CH_3 and CH_2 groups (~1,430 cm^{-1}), also weakened significantly in the DSS-C and ADS-C compared with the sludge samples, but did not disappear due to the high stability of C-H bonds (Zhao *et al.* 2015). The peaks at wave numbers 600–800 cm^{-1} corresponded to the presence of aromatic and heteroaromatic compounds (Hossain *et al.* 2011; Lu *et al.* 2013), which slightly decreased in the ADS-C and disappeared in the DSS-C. This indicated that the aryl C groups in the ADS were relatively stable during the pyrolysis process. The variation of infrared peaks in the sludge and derived biochar showed that the chemical structure of volatile matters in the ADS was more stable than that in the DSS. The bands below 600 cm^{-1} were mainly due to M-X (M-metal, X-halogen) stretching vibrations in both organic and inorganic halogens compounds (Hossain *et al.* 2011), which could be observed in the ADS-C.

3.3. Total concentrations of heavy metals in the sludge and derived biochars

The total concentrations of heavy metals in the DSS, DSS-C, ADS and ADS-C are shown in Table 4. The concentrations of most heavy metals in the ADS were higher than those in the DSS. One of the reasons to explain this phenomenon is that the STP had received partial industrial sludge with high heavy metals (especially Cd) content. The other reason is that heavy metals in the sludge could be concentrated in the digested sludge due to the loss of organic matter during the anaerobic process (Dong *et al.* 2013). Heavy metals in the sludge were further concentrated in the biochars, as can be seen in Table 4.

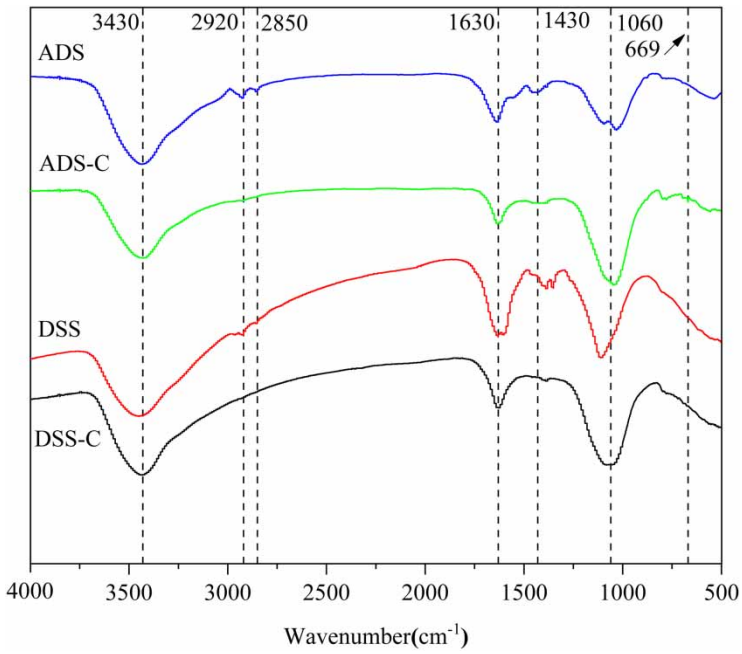


Figure 2 | FTIR spectra of DSS, DSS-C, ADS and ADS-C.

Table 4 | Total concentrations of heavy metals in the sludge and derived biochars

Heavy metals(mg/kg)	DSS	DSS-C	ADS	ADS-C
Cr	147.362	254.064	108.062	144.619
Ni	45.020	76.838	49.970	65.730
Cu	78.146	156.373	271.306	353.210
As	19.859	32.611	21.441	30.317
Cd	1.314	2.123	20.427	32.228
Pb	50.505	59.274	26.637	33.451

Compared with those in the DSS, the concentrations of Cr, Ni, Cu, As, Cd and Pb in the DSS-C increased by 72.41%, 70.68%, 100.10%, 64.21%, 61.57% and 17.36%, respectively, and compared with those in the ADS-C, the concentrations increased by 33.83%, 31.54%, 30.19%, 41.40%, 57.77% and 25.58%, respectively. The increase in the heavy metals' concentration could be attributed to the lower volatilization of heavy metals compared with organic matters, and was in accordance with the yield of the biochars, namely the mass losses during the pyrolysis process. Previous studies (Jin *et al.* 2016; Stefaniuk *et al.* 2016) also indicated that the content of heavy metals was closely related to the mass loss caused by pyrolysis. Pb was reported to be susceptible to volatilization due to the reactions with the carbon compounds in the sludge (Han *et al.* 2017), thus relatively low increase rates of the Pb concentration were observed in both DSS-C and ADS-C.

3.4. Chemical speciation distributions of heavy metals in the sludge and derived biochars

The total concentrations of heavy metals have certain effects on the environmental risk of the treated sludge. However, the bio-availability and toxicity of heavy metals depends more on their chemical forms. In modified BCR extraction, chemical forms of heavy metals are classified as acid soluble/exchangeable form, reducible form (bound to Fe-Mn oxides), oxidizable form (sulfide portion and bound to organic matter), and residual form. The heavy metals in acid soluble/exchangeable and reducible forms showed high bio-availability or direct eco-toxicity; the heavy metals in oxidizable form, showed potential bio-availability; heavy metals in residual form were stable and nontoxic (Devi & Saroha 2014). Figure 3 illustrates the chemical speciation distributions of heavy metals in sludge and derived biochar.

Cr mainly existed in stable forms (oxidizable and residual forms, 77.19%) in the DSS, as shown in Figure 3. After pyrolysis, a slight decrease in the proportion of Cr present in oxidizable form from 32.31% to 25.3% was observed in the DSS-C. However, the proportion of Cr in acid soluble/exchangeable form and reducible form decreased dramatically by 22.81% and 8.10% after pyrolysis, respectively. Correspondingly, the percentage of Cr in residual form increased from 44.88% in the sludge to 66.70% in the DSS-C. Cr in ADS showed higher stability with over 90% of Cr existing in stable forms. After pyrolysis, the percentage of Cr in oxidizable form increased by 11.64%. A slight decrease in the percentage of Cr in residual form was observed in the ADS-C. However, the concentration of Cr increased by 33.83% after pyrolysis. The stabilization of Cr might be attributed to the formation of stable $CaCrO_4$ or $CaCr_2O_4$ through the reaction of Cr^{3+} and CaO produced by the decomposition of $CaCO_3$ in the sludge (Low *et al.* 2015).

Ni was mainly associated with the unstable forms (acid soluble/exchangeable and reducible forms) in DSS and ADS. After pyrolysis, the percentage of Ni in unstable forms decreased from 46.70% (DSS) to 9.31% (DSS-C). The percentage of Ni in residual form increased by 3.62 times in the DSS-C compared with that in the DSS. In the ADS, Ni in unstable forms decreased from 81.60% to 26.79% after pyrolysis. The percentage of Ni in oxidizable and residual forms increased by 4.23 and 1.18 times in the ADS-C, respectively, compared with that in the raw sludge.

Consistent with previous studies, Cu was mainly in oxidizable form in both DSS (86.55%) and ADS (68.04%), which could be attributed to the preference of Cu for organic materials (Wu *et al.* 2016; Zhang *et al.* 2017). With the thermal decomposition of organic matter during the pyrolysis process, the percentage of Cu in oxidizable form decreased from 86.55% to 53.60% in the DSS-C and from 68.04% to 53.17% in the ADS-C. The percentage of Cu in residual form increased by 4.85 and 1.11 times in the DSS-C and ADS-C, respectively, compared with that in the raw sludge. In addition, the percentage of Cu in unstable forms was almost undetectable in the derived biochar (below 1%).

The percentage of As in residual form was 54.37% in the DSS, and increased to 75.03% in the DSS-C, with corresponding reduction of As in acid soluble/exchangeable form (from 17.83% to 0.92%). As also mainly existed in stable forms in the ADS,

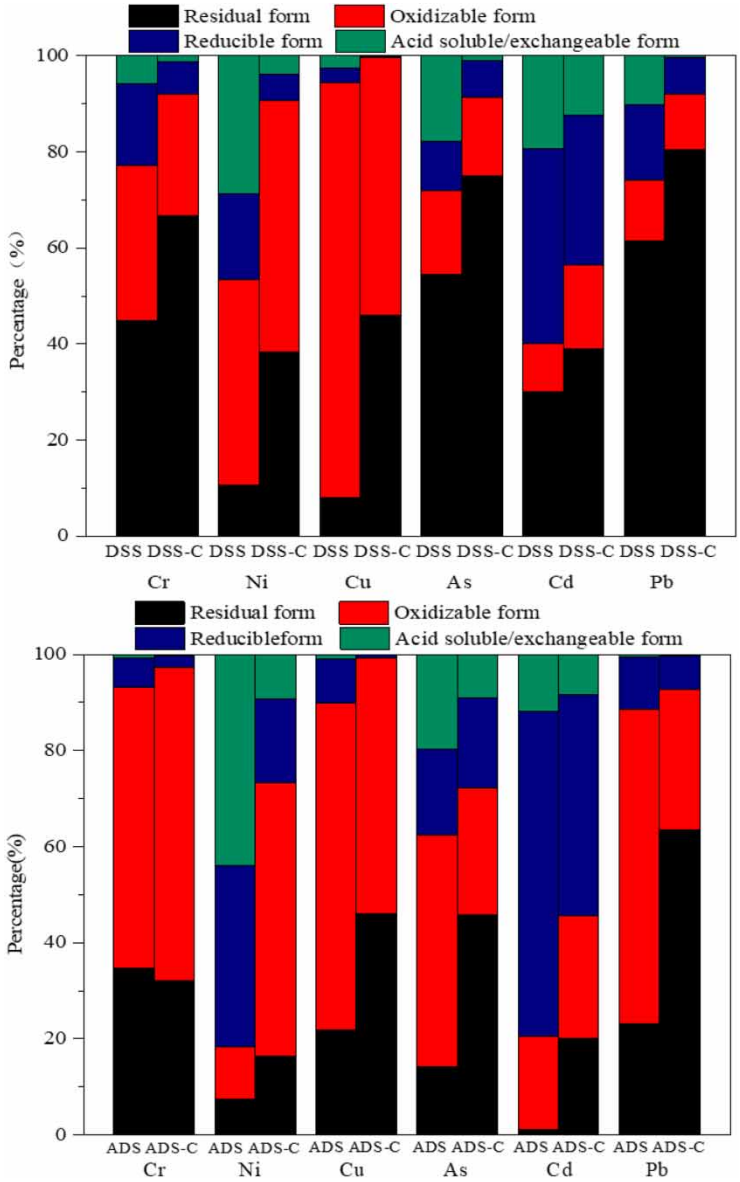


Figure 3 | Chemical speciation distributions of heavy metals in the DSS, DSS-C, ADS and ADS-C.

and pyrolysis caused the reduction of As in reducible and oxidizable forms. Meanwhile, As in residual form increased by 2.20 times in the ADS-C, compared with that in the raw sludge.

Cd mainly existed in unstable forms in the raw sludge with high bio-availability or direct eco-toxicity. Obvious reduction in the percentage of Cd in unstable forms and increase in the content of Cd in residual form were detected in the derived biochars. Cd in stable forms increased by 40.88% in the DSS-C and 121.31% in the ADS-C.

Pb was also in stable forms in the DSS (74.21%) and ADS (88.55%), the percentages of Pb in acid soluble/exchangeable and reducible forms in the DSS decreased by 97.03% and 50.93% respectively after pyrolysis, with the increase of Pb in residual form from 61.39% to 80.40%. Pb in acid soluble/exchangeable form was not detected in ADS and derived biochar. The percentages of Pb in reducible and oxidizable forms decreased by 37.35% and 55.15% respectively in the ADS-C. In addition, Pb in residual form increased by 1.74 times after pyrolysis.

The above results indicated that the pyrolysis process can obviously immobilize heavy metals in the derived biochar by transforming most of the heavy metals in unstable forms and some of the heavy metals in oxidizable form to heavy metals in residual form. The pyrolysis treatment showed positive effects on the reduction of bio-availability and direct eco-toxicity

Table 5 | Ecological risk assessment of heavy metals in the DSS, DSS-C, ADS and ADS-C

		C_f				E_r			
Metal	**T_r**	**DSS**	**DSS-C**	**ADS**	**ADS-C**	**DSS**	**DSS-C**	**ADS**	**ADS-C**
Cr	2	1.23	0.50	1.88	2.12	2.46	1.00	3.76	4.25
Ni	6	8.45	1.61	12.27	5.09	50.70	9.67	73.63	30.52
Cu	5	11.68	1.17	3.57	1.17	58.42	5.86	17.87	5.86
As	10	0.84	0.33	5.99	1.18	8.39	3.33	59.86	11.85
Cd	30	2.32	1.57	92.27	3.98	69.63	47.00	2,768.22	119.37
Pb	5	0.63	0.24	3.32	0.58	3.14	1.21	16.62	2.88
RI						192.75	68.07	2,939.96	174.72

of the heavy metals. However, the concentration of all heavy metals investigated in this study increased significantly in the derived biochar. Thus, the environmental risk of the biochars needed further investigation.

3.5. Evaluation of heavy metals' environmental risk in different sludge and biochar samples

The values of C_f, E_r and RI were determined to evaluate the ecological risk level of heavy metals in different sludge samples and biochars (Table 5). The C_f values of all heavy metals (except Cr in the ADS and ADS-C) were further reduced in the derived biochars due to the transformation of heavy metals from unstable forms to residual form. However, the C_f value of Cr (1.88) implied a low contamination in the ADS, while this value (2.12) in the ADS-C increased slightly after pyrolysis, mainly because of the decreased percentage of Cr in the residual fraction in the derived biochar, as shown in Figure 3. In addition, the environmental risk of Cd (92.27) in the ADS was well above the high-level contamination due to its high concentration and most of Cd in unstable forms in the ADS (Figure 3). In addition, the risk level of Cd was decreased markedly by the pyrolysis treatment to a moderate level (3.98) due to the increased percentage of Cd present in the residual form (Figure 3).

E_r values of Cr, As and Pb in the DSS, DSS-C, Cr, Cu and Pb in the ADS and ADS-C were below 40, indicating the low potential environmental risk. Pyrolysis reduced the E_r values of Ni and Cu in the DSS obviously, indicating the potential ecological risk level reducing from moderate (DSS) to low (DSS-C); while the potential ecological risk level of Ni and As in the ADS decreased from moderate to low; the potential ecological risk level Cd in the ADS decreased from very high to considerable. All the reductions of potential ecological risk levels were shown mainly due to the transformation of metal from unstable forms to stable forms, as shown in Figure 3. However, a slight increase in E_r value of Cr in ADS-C was observed. Because most of the heavy metals were immobilized to some extent in the derived biochars, the RI values of the sludge samples decreased significantly in the generated biochars, indicating a lower level of potential ecological risk than in the raw sludge samples in the environment.

4. CONCLUSIONS

In this study, DSS and ADS were pyrolyzed, and the characteristics of derived biochar, the chemical speciation transformation of heavy metals during the pyrolysis process, were evaluated. ADS-C showed high pH value due to the high content of alkali metals, while DSS-C presented relatively high specific surface area and total pore volume because of the high organic content in the raw sludge. All of the heavy metals detected were concentrated in the biochars by pyrolysis treatment, which resulted in an increase in the single pollution index and NPI. However, pyrolysis could promote the transformation of heavy metals from bio-available (unstable) fractions to stable forms, causing obvious reduction of the potential environmental risks of heavy metals in the derived biochar.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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