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Review

Effect of pyrolysis temperature on characteristics, chemical speciation and risk evaluation of heavy metals in biochar derived from textile dyeing sludge

Xingdong Wang[a], Chunxing Li[a], Zhiwei Li[a], Guangwei Yu[a], Yin Wang[a,b,*]

[a] CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[b] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

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ABSTRACT

Textile dyeing sludge (TDS) was pyrolyzed at temperature ranging from 300 to 700 °C to investigate characteristics and to evaluate the risk of heavy metals (Zn, Cu, Cr, Ni, Cd, and Mn) in biochar derived from the TDS. The analyzation of characteristics and potential environmental risk evaluation of heavy metals were conducted by the BET-N_2, FTIR, and BCR sequential extraction procedure. The results showed that the pyrolysis treatment of the TDS contributed to the improvement of the pH value and specific surface areas with increasing pyrolysis temperature. Conversion of the TDS to biochar significantly decreased the H/C and O/C ratios, resulting in a far stronger carbonization and a higher aromatic condensation for the TDS derived biochar. The total contents of Zn, Cu, Cr, Ni and Mn in biochar increased with pyrolysis temperature owing to the thermal decomposition of organic matter in the TDS; but for Cd, the portion distributed in the biochars decreased significantly when the temperature increased up to 600 °C. However, using BCR sequential extraction procedure and analysis, it was found that pyrolysis process promoted changes in the chemical speciation and biochar matrix characteristics, leading to reduce bio-available fractions of heavy metals in the biochars. The potential environmental risk of heavy metals decreased from considerable risk in the TDS to low risk or no risk in biochar after pyrolysis above 400 °C. This work demonstrated that the pyrolysis process was a promising method for disposing of the TDS with acceptable environment risk.

1. Introduction

Textile dyeing sludge (TDS) is the inevitable byproduct generated from textile dyeing wastewater treatment plants. In recent decades, the production of the TDS has mushroomed due to the rapid expansion of the textile dyeing industry (Liang et al., 2013; Vanhulle et al., 2008). According to the China Environment Statistical Yearbook in 2016, approximately 4.65 million tons of the TDS (approximately 80% moisture content) were produced in China (Man et al., 2018). Compared with sewage sludge, the TDS usually contains more toxic organic matter (e.g. perishable organics, dyeing agents, additives, polycyclic aromatic hydrocarbons-PAH, aromatic amines) and heavy metal (e.g. Zn, Cu, Cr, Ni, etc.) (Man et al., 2018; Sohaimi et al., 2017; Xie et al., 2018). These poisonous and harmful substances in the TDS, especially heavy metals (e.g., Zn, Cu, Cr, Ni, Cd, etc.), have strong biological toxicities, causing serious environmental problems, and resulting in unknown harm to humans and wildlife (Schwarzenbach et al., 2006). In China, the main approaches for disposing of the TDS include the use of landfills and incineration (Chen et al., 2012; Xie et al., 2018). However, landfill disposal is becoming increasingly difficult to implement due to limited landfill sites and the risks of polluting farmland and drinking water. Although the TDS incineration can thoroughly degrade organic pollutants, reduce volume, kill pathogens and generate energy, this method has gradually been prohibited because of its high potential risk of secondary pollution and stringent regulations. Therefore, it is imperative to explore other appropriate disposal technologies for the safe management of the TDS.

Pyrolysis technology is the thermal cracking of organic material in the absence of oxygen and at a pyrolysis temperature between 300 and 900 °C (Han et al., 2014). In recent years, pyrolysis has been developed as a sustainable treatment technique for sludges with different properties and from different sources because it has the potential to simultaneously target energy recovery, nutrient recycling, heavy metals immobilization and environmental protection (Chen et al., 2015). This treatment can minimize the volume of sludge, kill eggs of parasitic organisms, degrade pathogens, and produce the renewable syngas,

* Corresponding author at: CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
E-mail address: yinwang@iue.ac.cn (Y. Wang).

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Table 1
Characteristics of the TDS and its biochars.

	TDS	BC-300	BC-400	BC-500	BC-600	BC-700
Yield (wt%)	/	80.85 ± 1.38c[a]	73.12 ± 0.62b	69.02 ± 0.75b	66.81 ± 1.01ab	60.96 ± 0.96a
Ash content (wt%)	51.21 ± 1.35a	63.57 ± 1.17b	68.40 ± 0.98bc	71.35 ± 0.71c	75.03 ± 1.26cd	78.65 ± 1.57d
pH value	7.28 ± 0.08a	7.40 ± 0.05a	8.73 ± 0.04a	10.20 ± 0.10b	10.99 ± 0.07bc	12.35 ± 0.12c
C (wt%)	20.22 ± 0.26d	17.89 ± 1.00c	15.05 ± 0.51b	14.20 ± 0.24ab	13.70 ± 0.18ab	12.28 ± 0.02a
H (wt%)	3.65 ± 0.06e	1.85 ± 0.12d	1.10 ± 0.03c	0.72 ± 0.01b	0.54 ± 0.01ab	0.42 ± 0.01a
N (wt%)	2.26 ± 0.13d	1.71 ± 0.24d	1.11 ± 0.15c	0.83 ± 0.06bc	0.39 ± 0.02ab	0.12 ± 0.01a
S (wt%)	4.31 ± 0.09a	4.60 ± 0.14a	5.32 ± 0.03b	5.55 ± 0.02b	5.96 ± 0.07c	6.62 ± 0.10d
O[b] (wt%)	18.36	10.39	9.01	7.35	4.39	1.92
Molar H/C	2.16	1.24	0.88	0.61	0.47	0.41
Molar O/C	0.68	0.44	0.45	0.39	0.24	0.12
Surface area (m^2/g)	6.44	23.83	21.99	27.13	31.44	65.56

TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.
[a] Lowercase letters after the numerical values show significant differences within each row of data ($p < 0.05$, n = 3).
[b] By difference, O = 100 − (C + H + N + S + Ash).

liquid biofuel and low-priced biochar (Méndez et al., 2014). The biochar derived from pyrolysis of sludge pyrolysis is generally alkaline, with well-developed pore structures and nutrient contents. Sludge derived biochar has been widely used as a soil fertilizer, soil remediation reagent, and cost-effective sorbent (Chen et al., 2008a; Sohi, 2012; Xiao and Chen, 2017). Overall, the application of the pyrolysis method is an effective approach for sludge management, establishing a sustainable energy system and enhancing societal sustainability.

In recent years, heavy metals have attracted increasing attention owing to their adverse impacts on the global environment and human health. Thus, the chemical behavior and bio-availability of heavy metals in sludge during the pyrolysis process have been intensively studied (Jin et al., 2017; Kistler et al., 1987; Li et al., 2018b; Shao et al., 2015). Researches have shown that the majority of toxic heavy metals in sludge were still concentrated in the sludge biochar during the pyrolysis process due to their higher thermal stability than organic substances (Devi and Saroha, 2014; Liu et al., 2018, 2017). Although it is essential to monitor the total heavy metal concentration in sludge, more importantly, identifying the chemical speciation of heavy metals in sludge, since heavy metal speciation largely determines heavy metal mobility, bio-availability, and eco-toxicity (Huang et al., 2018; Legros et al., 2017). Various researches have extensively investigated the toxicity of heavy metals in sludge biochar under various pyrolysis conditions and have found that pyrolysis promotes the transformation of the mobile fraction of heavy metals to more stable forms (Devi and Saroha, 2014; Shao et al., 2015). Jin et al. (2016) observed that most of the heavy metals existed in the oxidizable and residual forms in the biochars after the pyrolysis of the sludge at temperatures ranging from 400 to 600 °C (especially at 600 °C). Our previous study also indicated that heavy metals in the sludge can be substantially migrated from bio-available fractions into the relatively stable fractions during sludge pyrolysis (Li et al., 2018a; Wang et al., 2016), thus lowering the bio-availability of the heavy metals and the potential and direct environmental risks of the sludge biochar. However, most literature focused on municipal sewage sludge, paper making sludge and lignocellulosic waste to investigate the factors influencing the migration and risk assessment of heavy metals during the pyrolysis process, with a few studies concentrating on the heavy metals behavior of the TDS.

The TDS had a lower content of Pb but higher contents of Cr and Ni than sewage sludge, and the chemical fraction distribution of heavy metals in the TDS varied greatly depending on the raw materials, pH and heat-drying method (Liang et al., 2013). During the TDS incineration, a higher temperature and the CaO additive had a positive effect on the crystallization of heavy metals (Lin et al., 2014). Furthermore, Zhang et al. (2017) found that the leaching characteristics of heavy metals in the biochar derived from the TDS can satisfy the requirements of national standards (GB 5085.3-2007, China) and will not pose a threat to the environments. However, the distribution and detailed chemical speciation of heavy metals and the effects of treatment conditions during the TDS pyrolysis have been barely studied thus far.

Therefore, the main objectives of this study were to (1) investigate the pyrolysis process and the effect of pyrolysis temperature on biochar characteristics, (2) evaluate the total concentrations and chemical speciation of heavy metals in biochars produced from the pyrolysis of the TDS at different pyrolysis temperatures (300–700 °C), and (3) assess the potential environmental risk of heavy metals leaching from biochar to the environment.

2. Materials and methods

2.1. Materials

The TDS was obtained from a printing and dyeing plant in Zhejiang Province, located in the southeastern part of China. Before the experiments, the wet TDS sample was dried for 24 h at 105 °C in a drying oven to remove the moisture content and then crushed and sieved to fine particle size (0.043–0.15 mm) and stored in a desiccator. The ash content, pH value and ultimate analyses of the oven-dry TDS are listed in Table 1.

2.2. Experimental apparatus and procedure

Pyrolysis of the TDS was conducted in a homemade pyrolysis and carbonization experimental apparatus included a high-pressure gas source, a horizontal quartz tube with a surrounding electrically heated furnace, and an acetone trap for gas absorption derive (Fig. S1). In each experiment, 20.0 g of oven-dried the TDS was first inserted into a quartz tube, which was purged with argon gas of 99.99% purity for 60 min to wipe out the oxygen gas before pyrolysis and then 100 ml min^{-1} argon gas was maintained during the entire pyrolysis process. The pyrolysis temperature was increased from room temperature to the target temperature at a rate of 10 °C min^{-1}, and the target temperatures were maintained for 60 min. The resultant biochars were noted as BC-X, where the prefix “BC” referred to biochar produced from the TDS, and the infix “X” referred to the required temperature. All pyrolysis experiments were replicated in triplicate, and the replicate samples obtained in each experiment were homogeneously mixed and then the mixed samples were stored in desiccators for further use.

2.3. Characterization of biochar

The biochar yield was calculated according to the weight of the feedstock and obtained biochars. The ash contents of the TDS and its biochars were determined by using the standard GB/T 12496.3-1999. The pH value was measured with a pH meter (Denver, UB-7, USA) and at a ratio of 1:20 (W/V) (Jin et al., 2016). The elemental analyses of C, H, N, and S were analyzed with an elemental analyzer (VARIO MAX,

Germany). The BET surface areas of the samples were determined using N_2 adsorption-desorption isotherms at 77 K using a surface apparatus (Micromeritics ASAP 2020). The surface functional groups of the samples were obtained using a Fourier transform infrared (FTIR) spectrometer (NicoletiS10, ThermoFisher, USA). The oven-dried sample was mixed with KBr at a ratio of 1:100 in an agate mortar and then the resulting mixed powder was pressed into pellets for analysis. The spectra were recorded in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.4. Analysis of heavy metals

2.4.1. Total concentrations and chemical speciation of heavy metals

The three-step BCR sequential extraction procedure was adopted for the sequential extraction of the heavy metals in the TDS and its biochars (Chen et al., 2014). Briefly, 0.50 g of the oven-dried samples was added to 50 ml polypropylene centrifuge tubes and sequentially extracted by the following steps: F1, acid-soluble/exchangeable fraction: 20 ml acetic acid (0.1 M) for 16 h at 25 °C; F2, reducible fraction: 20 ml hydroxylamine (0.1 M, pH 2.0) for 16 h at 25 °C; F3, oxidizable fraction: first, 5 ml hydrogen peroxide (30%, v/v) for 1 h at 25 °C, next, another 5 ml hydrogen peroxide (30%, v/v) for 1 h at 85 °C and dried in a water bath, last, 25 ml ammonium acetate (1 M, pH 2.0) for 1 h at 25 °C. For F1–F3, a portion of the extracted liquids was digested to remove dissolved organics with a mixture of concentrated acid (H_2O_2:HNO_3 = 1:1, v/v) on a hot plate at 100 °C and then diluted to a constant volume (50 ml) with HNO_3 (2%) before analysis. The untreated samples and extracted solid residues were digested with a mixture of concentrated acid (HNO_3:$HClO_4$:HF = 5:5:2, v/v) by using the microwave digestion instrument. Each of the digestion solutions was filtered and diluted for concentration analysis. The heavy metals concentrations in the untreated samples, extracted liquids, and extracted solid residues were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent Technologies, 7500CX, Santa Clara, CA).

In this study, the residual rate of heavy metals in the biochar was proposed as a parameter to determine the enrichment degree of heavy metals in the TDS during pyrolysis, which can be calculated using the following equation:

$$R\% = \frac{BCx \times Y}{TDSx} \times 100 \quad (1)$$

where R is the residual rate of heavy metal in the biochar (%), BC_X is the total concentration of heavy metal in the biochar (mg kg^{-1}), Y is the biochar yield (%), TDS_X is the total heavy metal concentration in the TDS (mg kg^{-1}), and x is a type of heavy metal.

2.4.2. Leaching experiment

The leachability of heavy metals in the TDS and its biochars directly relates to their availability and toxicity, and can be assessed by the toxicity characteristic leaching procedure (TCLP) (Devi and Saroha, 2014; Wang et al., 2016). TCLP simulates landfill condition by using the glacial acetic acid solution (pH: 2.88, liquid/solid ratio, 20:1). The leaching tests were extracted in polyethylene tubes and shaken for 18 h at 200 rpm in a shaking incubator. The supernatant was subsequently separated by centrifugation, and then digested with H_2O_2/HNO_3 and filtered through 0.22-μm membrane filters for heavy metals analysis.

2.4.3. Potential ecological risk index (RI)

The potential ecological risk index (*RI*) proposed by Hakanson based on the total concentration, number, toxicity and sensitivity of heavy metals was used to evaluate the degree of potential risk of heavy metals pollution in the TDS and its biochar using the following equations:

$$C_f = C_m/C_n \quad (2)$$

$$E_r = T_r \times C_f \quad (3)$$

$$RI = \sum E_r \quad (4)$$

where C_f is the contamination factor of an individual heavy metal; C_m and C_n are the potential mobile fractions (F1 + F2 + F3) and the stable fraction (F4) of the heavy metals, respectively; E_r is the potential ecological risk factor for the individual heavy metal; T_r values is the toxic factor of the individual heavy metal, and the values for each heavy metal are in the order of Zn (1), Cu (5), Cr (2), Ni (6), Cd = 30, and Mn (1) (Hakanson, 1980); *RI* is the potential ecological risk index of the overall contamination. Five E_r categories and four *RI* classes have been defined and were listed in Table S1. The concentrations of the BCR fractions of heavy metals in the TDS and its biochar are shown in Table S2.

2.5. Statistical analyses

All experiments were conducted in triplicate, and the results were expressed as only the mean values ± SD (standard deviation). The statistical package SPSS 22.0 was used to perform statistical analyses. The data were calculated to analysis of variance procedures and those means were separated using the protected least significant difference (LSD) test at $P < 0.05$.

3. Results and discussions

3.1. Characterization of the TDS and its biochars

The characterization of the TDS and its biochars produced at different temperatures, including the yield, ash content, pH value, ultimate analysis, and specific surface area, are summarized in Table 1. As the pyrolysis temperature increased from 300 to 700 °C, the TDS biochar yield significantly declined from 80.85% to 60.96% due to the decomposition of organic substances in the TDS during the pyrolysis process (Agrafioti et al., 2013; Yuan et al., 2015). Compared with the TDS (51.21 wt%), the ash content in the biochars clearly increased as the pyrolysis temperature increased. Similar results were also reported by other researchers (Agrafioti et al., 2013; Chen et al., 2014), suggesting that most of the inorganic constituents in the sludge were enriched in the biochar during the pyrolysis process (Chen et al., 2015; Jin et al., 2016). The pH value of the TDS was close to neutral (7.28). During the pyrolysis process, the alkali salts in the TDS were released from the pyrolytic structure, and the amount of acidic surface functional groups decreased with the decomposition of the oxygen-containing functional groups at a higher pyrolysis temperature (Yuan et al., 2011; Zheng et al., 2013), resulting in the pH value of the biochar gradually increasing from neutral to alkaline as the pyrolysis temperature increased. The alkaline nature of the biochars produced from the TDS at high pyrolysis temperatures suggested that the TDS derived biochar application as an amendment to acid contaminated soil will have additional beneficial effects.

Pyrolysis of the TDS reduced the contents of C, H, N, and O in the resultant biochars, with lower C, H, N, and O contents in biochars after pyrolysis at higher temperatures (Table 1). The main reason for this result was the continuous decomposition of volatile matter in the TDS during the pyrolysis process (Li et al., 2018b). The contents of remaining C, H, N and O were only 12.28 wt%, 0.42 wt%, 0.12 wt%, and 1.92 wt% in the BC-700, respectively. However, the S content of the biochars showed an increasing trend as the pyrolysis temperature increased. The ratio of molar H/C and O/C can be used as a carbonization degree parameter to characterize the degree of organic aromaticity of the biochar. It can be seen that the ratio of molar H/C and O/C in the biochar decreased as the pyrolysis temperature due to both the demethylation and decarboxylation reactions during the pyrolysis process (Zhu et al., 2014), implicating a far stronger carbonization and a higher aromatic condensation for the TDS derived biochar (Cayuela et al., 2015; Chen et al., 2014). This higher aromaticity biochar can be resistant to decomposition in soil for many years (Huang et al., 2017).

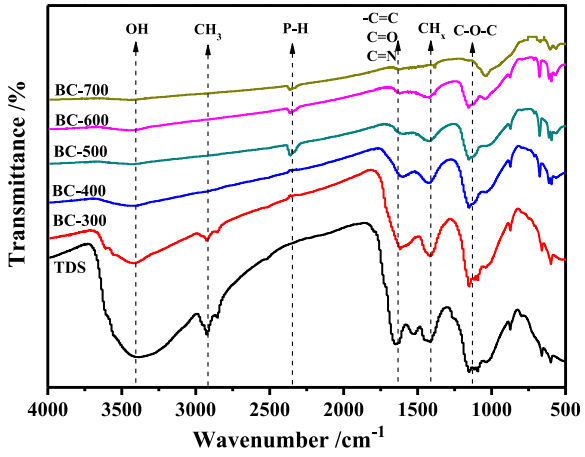

Fig. 1. FTIR spectrum of the TDS and its biochars. TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.

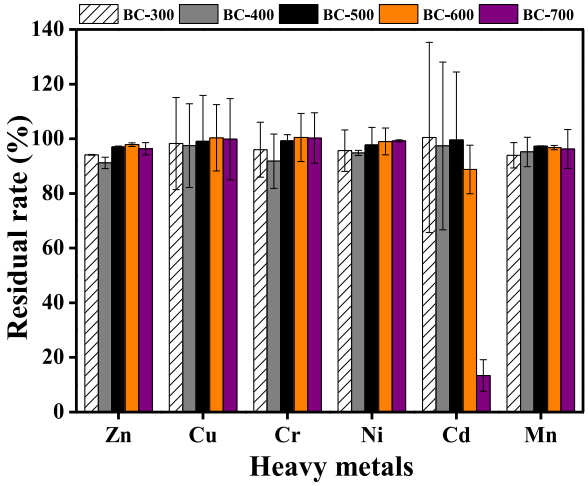

Fig. 2. Percentage of the heavy metals distributed in biochars. BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.

The surface area of the biochar was mostly correlated with the pyrolysis temperature (Li et al., 2017). The surface areas of the TDS and its biochars were 6.44, 23.83, 21.99, 27.13, 31.44 and 65.56 m^2/g, respectively (see Table 1), suggesting that the surface area in the biochars increased significantly with an increase in pyrolysis temperature due to the aggravation of the degree of carbonization.

3.2. FTIR spectra analysis

FTIR spectra analysis was used to identify the chemical functional groups of the TDS and its biochars obtained at different pyrolysis temperatures (Fig. 1). The peaks at 3405–3443 cm^{-1} correspond to -OH stretching vibration related to water, alcohols, and carboxylic acids. The results indicated that the intensity of -OH stretching of the biochar steadily decreased with an increasing pyrolysis temperature (Fig. 1), suggesting that the large amounts of hydroxyl groups in the TDS were decomposed during the pyrolysis process. The peaks at approximately 2923 cm^{-1} correspond to asymmetrical and symmetrical -CH_3 stretching, showing the presence of aliphatic structures in the TDS (Fig. 1); however, these bands disappeared abruptly after pyrolysis at a higher temperature (i.e., ≥ 400 °C), leaving only an imperceptible vestige. This result indicated that almost all the aliphatic C-H bands were decomposed to carbon dioxide, methane, and other gasses or transformed into aromatic structures when the temperature reached 400 °C during the TDS pyrolysis process (Lu et al., 2013). The band at 2360 cm^{-1} in BC-500, BC-600 and BC-700 might be the P–H phosphine (Jin et al., 2014). The peaks at 1601–1647 cm^{-1} correspond to aromatic rings (C=C stretching vibration) and stretching amide bonds (C=O and -CONH- stretching vibration) caused by the presence of acids, aldehydes and lipids that come from proteins in the TDS (Agrafioti et al., 2013; Jin et al., 2016), and the intensities of the peaks decreased slightly as the pyrolysis temperature increased, indicating that biochar possesses very high carbon aromaticity. The peaks at 1417–1420 cm^{-1} corresponding to aliphatic chains, including CH_3 and CH_2 groups, did not disappear with increasing pyrolysis temperatures because the C–H bonds were very strong (Jin et al., 2016). The strong peaks at 1152–1154 cm^{-1} correspond to the C-O-C aliphatic/stretching ether, which was a slight change irrespective of the pyrolysis temperature due to the different forms of oxygen in the sludge that were transformed into carbon chains with a single bond form of carbon-oxygen during the pyrolysis process (Ho et al., 2017). The band with peaks at approximately 873 cm^{-1} corresponds to aromatic ring and heteroaromatic compounds (Hossain et al., 2011; Huang et al., 2017). The aromatic ring can provide π-electrons and has the potential to strongly bond heavy metal cations (Harvey et al., 2011). The bands below 600 cm^{-1} were described as metal-halogen stretching vibrations in samples (Hossain et al., 2011; Huang et al., 2017). According to the results of the FTIR spectra (Fig. 1), the pyrolysis temperature dramatically influenced the category and intensity of the chemical functional groups.

3.3. Heavy metals analysis

3.3.1. Total concentrations of heavy metals in the TDS and its biochar

The total concentrations of Zn, Cu, Cr, Ni, Cd, and Mn in the TDS and its biochar were listed in Table 2. It was noted that the heavy metal contents decreased as follows: Zn > Mn > Cu > Cr > Ni > Cd. Zn had the highest contents among the heavy metals in the TDS, with a maximum content of 8930 mg kg^{-1}, which may be related to the galvanized pipes used in wastewater treatment plants in China (Chen et al.,

Table 2
Total concentrations of heavy metals in samples and their threshold values for the disposal standards of China.

Samples	Heavy metals (mg kg^{-1})					
	Zn	Cu	Cr	Ni	Cd	Mn
TDS	8930.15 ± 89.34a[a]	262.36 ± 15.37a	251.16 ± 10.22a	183.95 ± 5.03a	0.657 ± 0.078a	1601.20 ± 38.07a
BC-300	10,400.17 ± 97.21b	316.55 ± 20.08ab	297.37 ± 9.88ab	217.32 ± 6.27ab	0.793 ± 0.103a	1859.43 ± 20.75ab
BC-400	11,134.92 ± 69.83c	347.53 ± 18.39abc	314.35 ± 11.37bc	238.57 ± 8.21bc	0.852 ± 0.091a	2082.52 ± 33.62bc
BC-500	12,550.41 ± 93.04d	374.05 ± 23.01bc	360.75 ± 8.78c	260.14 ± 5.08c	0.928 ± 0.055a	2256.54 ± 52.01cd
BC-600	13,080.32 ± 70.55d	392.15 ± 10.55bc	376.82 ± 7.99cd	272.39 ± 2.09cd	0.866 ± 0.042a	2319.54 ± 41.27cd
BC-700	14,109.92 ± 91.39e	426.92 ± 20.02c	411.96 ± 10.11d	299.49 ± 7.44d	0.139 ± 0.027b	2525.01 ± 72.13d
Threshold values[b]	3000	1500	1000	200	20	/

TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.
[a] Lowercase letters after the numerical values show significant differences within each column of data ($p < 0.05$, $n = 3$).
[b] According to the disposal of sludge from municipal wastewater treatment plant-Quality of sludge used in forestland (CJ/T 362-2011).

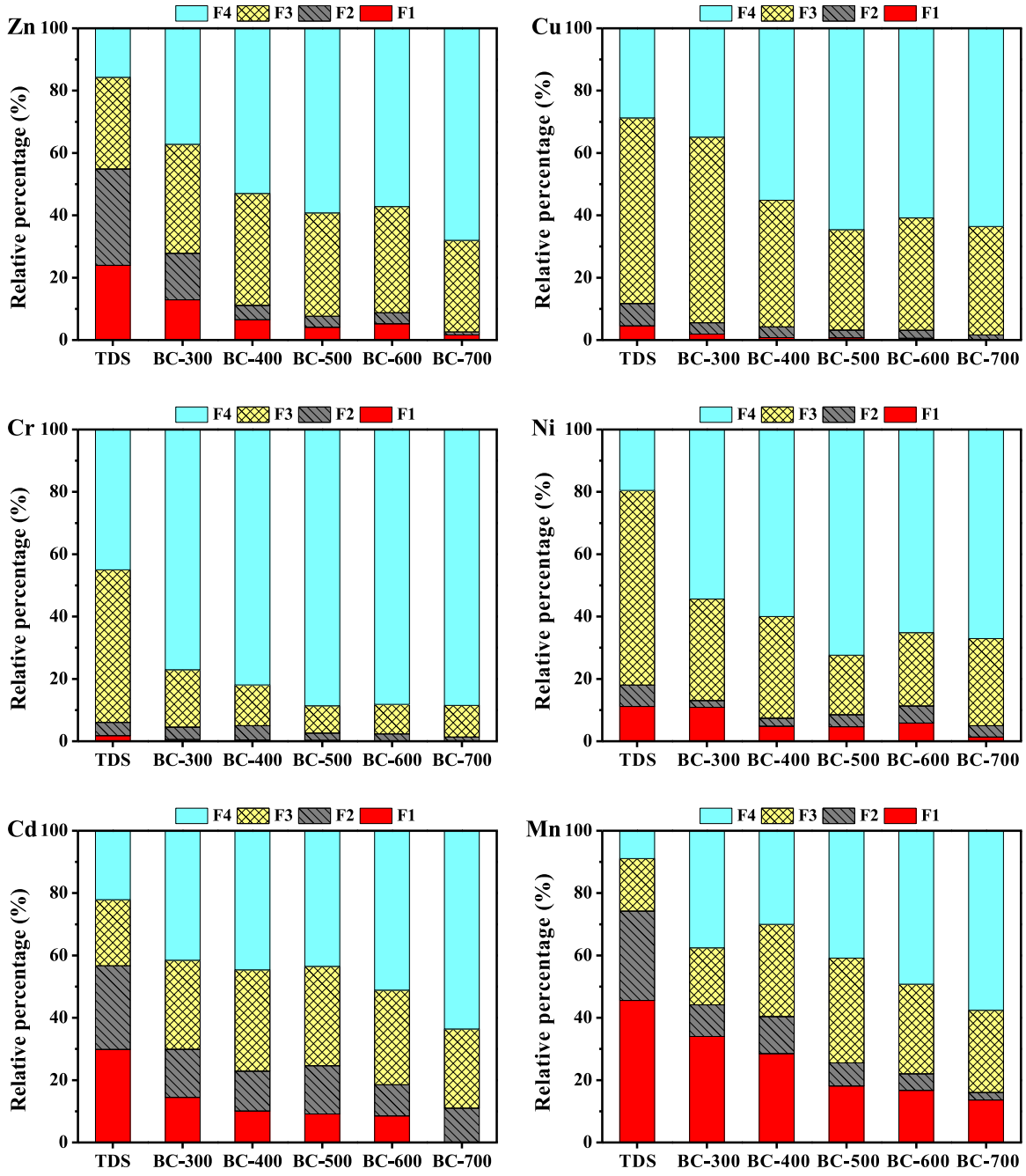

Fig. 3. Fraction distribution of the heavy metals distributed in the TDS and its biochars. TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.

2014; Jin et al., 2016). Compared with the threshold values for sludge used in forestland, all of the heavy metals contents in the TDS were lower than those in the national standard, except for the total contents of Zn, which far exceeded the threshold values. The heavy metals were expected to be mainly distributed in biochar (solid residue) and bio-oil (liquid phase) during the pyrolysis of sewage in the 300–700 °C temperature range (Devi and Saroha, 2014). Fig. 2 showed that the residual rates of Zn, Cu, Cr, Ni, and Mn in the biochars were over 91.19%, 97.49%, 91.81%, 94.82%, and 93.96%, respectively, which suggested that most of heavy metals (except for Cd) mainly accumulated in the biochar after pyrolysis. Accordingly, with the increase in pyrolysis temperature from 300 to 700 °C, the total contents of Zn, Cu, Cr, Ni and Mn in biochars increased due to the lower loss in weight of heavy metals than the loss in weight of organic compounds during pyrolysis (Table 2). For Cd, the portion distributed in the biochars started to decrease when the pyrolysis temperature reached as high as 600 °C, especially for the fraction of Cd distributed in BC-700 (12.92%). It can also be seen from Table 2 that the total content of Cd in the biochar gradually increased with the increase in pyrolysis temperature from 300 to 500 °C, and then decreased suddenly when the pyrolysis temperature continuously increased up to 600 °C. A similar observation was made by other researchers (Chen et al., 2014; Devi and Saroha, 2014; Kistler et al., 1987). This is because the Cd existed mainly as a carbonate in the raw sludge and was easily volatilized and transferred by off-gassing when the pyrolysis temperature increased to 600 °C (Kistler et al., 1987).

3.3.2. Speciation of heavy metals in the TDS and its biochar

Heavy metals bio-availability and eco-toxicity in the environment mainly depend on the heavy metals chemical speciation (Chen et al., 2008b; Leng et al., 2014). The modified BCR was widely used as a sequential extraction method to determine the chemical speciation of heavy metals in samples. In BCR extraction, the bio-availability and mobilization of the heavy metal fractions decrease in the following sequence: F1 > F2 > F3 > F4 (Li et al., 2018b). These heavy metal fractions can be divided into three categories on the basis of their bio-availability (Huang and Yuan, 2016). The F1 and F2 fractions of heavy metals present high bio-availability or direct eco-toxicity, the F3 fraction presents potential bio-availability due to being easy degradability, and the F4 fraction is recognized as a stable nontoxic fraction (Devi and Saroha, 2014).

Fig. 3 illustrated the percentage concentration of the heavy metals in the four BCR fractions in the TDS and its biochars. The main forms of Zn, Cd, and Mn in the TDS were the directly and potentially toxic and bioavailable category (F1 + F2 + F3) (84.27%, 77.88%, and 91.09% for Zn, Cd, and Mn, respectively), indicating the high environmental risk of Zn, Cd, and Mn in the TDS applied to land. A remarkable decline for Zn, Cd, and Mn in the exchangeable and acid-soluble fraction (F1) and the reducible fraction (F2) occurred after conversion of the TDS to biochars via pyrolysis, and a significant gradual increased in the residual fraction (F4) of biochar with increasing pyrolysis temperature from 300 to 700 °C (Fig. 3). For example, the percentage of Zn, Cd, and Mn in the F4 fraction of BC-700 increased by 4.3, 2.8, and 6.5 times, respectively, compared with that in the TDS. The above results suggested that the pyrolysis process can dramatically immobilize heavy metals Zn, Cd, and Mn in the TDS by transforming a large part of the unstable fraction (F1 + F2) into the more stable F4 fractions (Li et al., 2018b). Specifically, the Cu, Cr, and Ni mainly existed in the form of F3 (59.54%, 45.03%, and 63.73% for Cu, Cr, and Ni, respectively) and F4 (28.70%, 54.97%, and 17.91% for Cu, Cr, and Ni, respectively) in the TDS. The pyrolysis process facilitated the transformation of the oxidizable (F3) into the residual fraction (F4) with increasing pyrolysis temperature, and the percentages of Cu, Cr, and Ni in F1 and F2 were slightly lower, indicating that the pyrolysis technology had positive effects on the immobilization of heavy metals in the TDS and that the pyrolysis temperature was an important influencing factor on the immobilization of heavy metals in the biochar.

Recovery of heavy metals in the sequential extraction procedure can be evaluated by comparing the sum of the heavy metals concentration of each fraction determined by the BCR sequential extraction procedure with the total concentrations of heavy metals obtained from the acid digestion procedure. The recovery rates of the modified BCR procedure are shown in Table S2. It can be seen clearly that the sum of each fraction was in good agreement with the total heavy metals concentration with satisfactory recoveries (92.7–105.7%), indicating that this modified BCR sequential extraction procedure used in detecting the speciation of Zn, Cu, Cr, Ni, Cd, and Mn in the TDS and its biochars was exact and reliable.

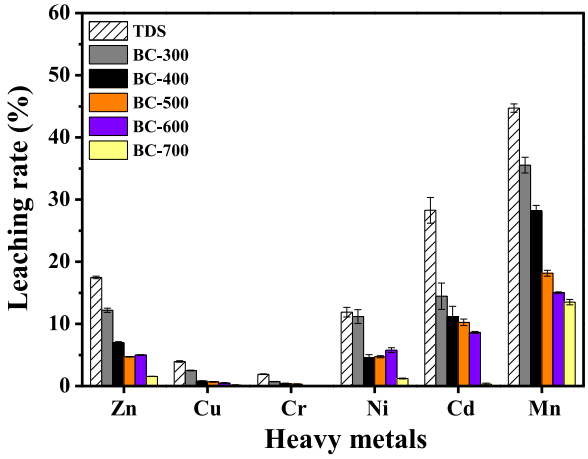

Fig. 4. Leaching rate of heavy metals in the TDS and its biochars. TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature.

3.3.3. Leaching characterization

The leaching characterization of heavy metals was assessed using the TCLP method recommended by USEPA (Wang et al., 2016). The results of the TCLP test for six heavy metals in the TDS and its biochars

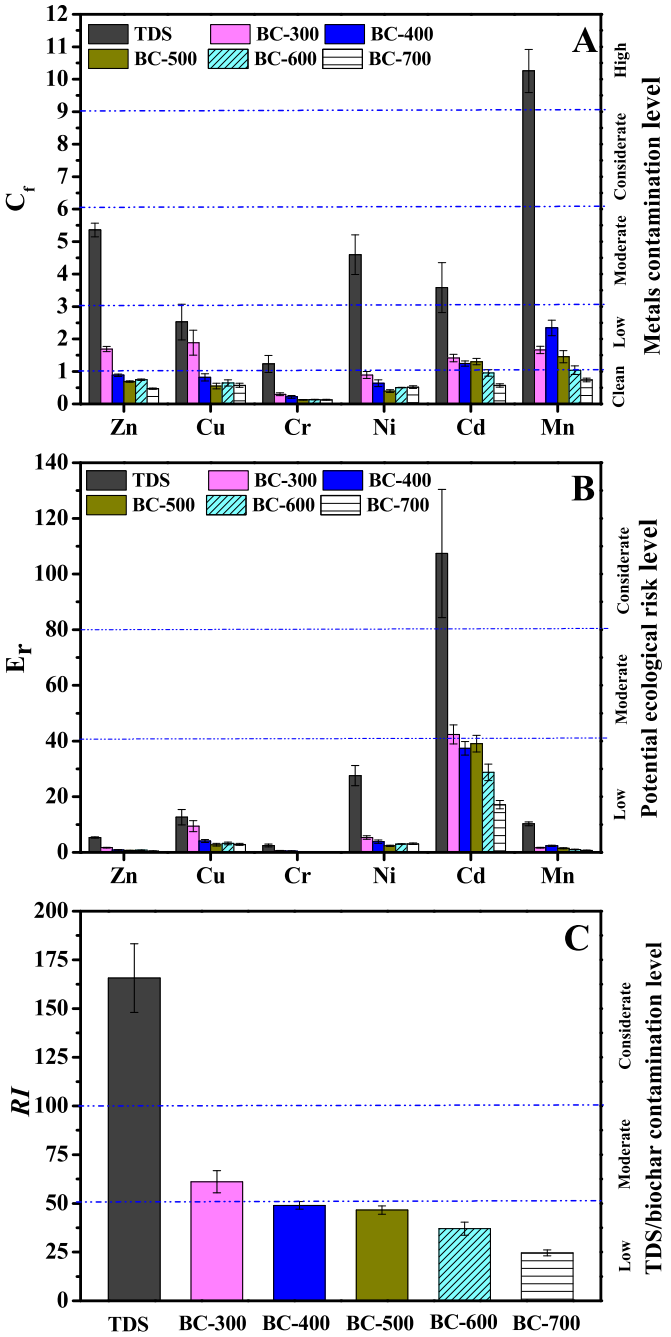

Fig. 5. Ecological risk assessment of the heavy metals in the TDS and its biochars: (A) contamination factor of the individual heavy metal; (B) potential ecological risk factor for the individual heavy metal; (C) the sum of the potential ecological risk index (E_r) of each heavy metals. TDS, raw textile dyeing sludge; BC-X, biochar derived from the textile dyeing sludge pyrolysis at X (°C) temperature;.

were shown in Table S3 and Fig. 4. The leached amounts of heavy metals from the TDS were 1559.51, 10.36, 4.77, 21.88, 0.186 and 715.92 mg kg^{-1} for Cu, Zn, Cr, Ni, Pb and Cd, respectively. The concentrations of heavy metals in the leachate exceeded the threshold values of the USEPA except for Cr and Cd in the TDS. Therefore, these heavy metals in the TDS had very high potential environment risks and can be identified as hazardous wastes according to the USEPA. The leaching potential of the heavy metals in the biochar was found to be suppressed significantly by the pyrolysis process. The concentrations of leached heavy metals from the biochar were remarkably declined after pyrolysis process. Table S3 showed that the amounts of heavy metals (except for Zn) leached from the BC-700 were lower than the USEPA permissible limits. Although the amounts of Zn leached still exceeded the threshold values, those from biochars were decreased significantly. The leaching rate of heavy metals from the TDS and its biochars were shown in Fig. 4. The leaching rate of six heavy metals from the biochar decreased significantly with increasing pyrolysis temperature, clearly indicating the reduced toxicity of leached heavy metals in the biochar after the pyrolysis process. These observations were in accord with the decline in the directly toxic fraction F1 (Fig. 3).

3.3.4. Environmental risk assessment

The bio-availability and eco-toxicity of heavy metals in the TDS derived biochar must be determined to evaluate the environment risk, also the optimal application rate of the sludge biochar to soil for nutrient recycling (Devi and Saroha, 2014; Jin et al., 2017). The values of C_f, E_r and *RI* were determined to clarify the environmental risk level of heavy metals in the TDS and its biochars, and were shown in Fig. 5. The value of C_f for Mn in the TDS was 10.21 (Fig. 5A), indicating a high metal contamination ($C_f > 9$ implies high contamination), and the value of C_f for Zn, Ni, and Cd implied a moderate contamination ($3 < C_f < 6$ implies moderate contamination). That of Cu and Cr in the TDS implied a clean or low metal contamination. While the value of C_f for six heavy metals in biochars declined significantly with the pyrolysis temperature increasing, indicating that pyrolysis process was beneficial for reducing the risk level of heavy metals in the TDS. Consequently, the *RI* value of the six heavy metals in the TDS reached a maximum of 158.98 (Fig. 5C), suggesting a considerable degree of environmental risk of soil and water pollution if directly applied to forestland for nutrient recycling. However, the *RI* value of the biochar was significantly decreased by pyrolysis of the TDS, and the potential environmental risk also declined greatly with increasing of pyrolysis temperature. Remarkably, the *RI* value of the biochar obtained from a higher pyrolysis temperature (≥ 400 °C) was less than 50.00, indicating a very low degree of environmental risk for the utilization of biochar. A similar observation was obtained on pyrolysis of paper mill sludge and sewage sludge at different temperatures (Devi and Saroha, 2015; Jin et al., 2017). Therefore, these results suggested that pyrolysis at a higher temperature was suitable technique for safely treating TDS.

4. Conclusions

In this work, the TDS was pyrolyzed and its biochar was evaluated, and the following results were obtained. The pyrolysis of TDS at different temperatures (300–700 °C) favored the surface area improvement, benefited TDS aromatization and promoted immobilization of majority of heavy metals in the biochar matrix. Furthermore, the accumulated heavy metals migrated from bio-available fractions to the more stable fractions, causing significant reduction in bio-available and leaching potential of the heavy metals in the biochar. The environmental risk evaluation indicated that higher pyrolysis temperature promoted the transformation of eco-toxicity from considerable risk in the TDS to low risk in biochar, resulting in a decrease in the environmental risk of TDS biochar.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2018.10.022.

References

Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. J. Anal. Appl. Pyrolysis 101, 72–78.
Cayuela, M.L., Jeffery, S., van Zwieten, L., 2015. The molar H: Corg ratio of biochar is a key factor in mitigating N_2O emissions from soil. Agric. Ecosyst. Environ. 202, 135–138.
Chen, B., Zhou, D., Zhu, L., 2008a. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42 (14), 5137–5143.
Chen, D., Yin, L., Wang, H., He, P., 2015. Reprint of: pyrolysis technologies for municipal solid waste: a review. Waste Manag. 37, 116–136.
Chen, H., Yan, S.H., Ye, Z.L., Meng, H.J., Zhu, Y.G., 2012. Utilization of urban sewage sludge: chinese perspectives. J. Environ. Sci. Pollut. Res. 19 (5), 1454–1463.
Chen, M., Li, X.-m., Yang, Q., Zeng, G.-m., Zhang, Y., Liao, D.-x., Liu, J.-j., Hu, J.-m., Guo, L., 2008b. Total concentrations and speciation of heavy metals in municipal sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China. J. Hazard. Mater. 160 (2–3), 324–329.
Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y., Ren, L., 2014. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. Bioresour. Technol. 164, 47–54.
Devi, P., Saroha, A.K., 2014. Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. Bioresour. Technol. 162, 308–315.
Devi, P., Saroha, A.K., 2015. Effect of pyrolysis temperature on polycyclic aromatic hydrocarbons toxicity and sorption behaviour of biochars prepared by pyrolysis of paper mill effluent treatment plant sludge. Bioresour. Technol. 192, 312–320.
Han, J., Wang, X., Yue, J., Gao, S., Xu, G., 2014. Catalytic upgrading of coal pyrolysis tar over char-based catalysts. Fuel Process. Technol. 122, 98–106.
Harvey, O.R., Herbert, B.E., Rhue, R.D., Kuo, L.J., 2011. Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. Environ. Sci. Technol. 45 (13), 5550–5556.
Ho, S.H., Chen, Y.D., Yang, Z.K., Nagarajan, D., Chang, J.S., Ren, N.Q., 2017. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. Bioresour. Technol. 246, 142–149.
Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J. Environ. Manag. 92 (1), 223–228.
Huang, H., Yang, T., Lai, F., Wu, G., 2017. Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. J. Anal. Appl. Pyrolysis 125, 61–68.
Huang, H., Yuan, X., 2016. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. Bioresour. Technol. 200, 991–998.
Huang, R., Zhang, B., Saad, E.M., Ingall, E.D., Tang, Y., 2018. Speciation evolution of zinc and copper during pyrolysis and hydrothermal carbonization treatments of sewage sludges. Water Res. 132, 260–269.
Jin, H., Arazo, R.O., Gao, J., Capareda, S., Chang, Z., 2014. Leaching of heavy metals from fast pyrolysis residues produced from different particle sizes of sewage sludge. J. Anal. Appl. Pyrolysis 109, 168–175.
Jin, J., Li, Y., Zhang, J., Wu, S., Cao, Y., Liang, P., Zhang, J., Wong, M.H., Wang, M., Shan, S., Christie, P., 2016. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. J. Hazard. Mater. 320, 417–426.
Jin, J., Wang, M., Cao, Y., Wu, S., Liang, P., Li, Y., Zhang, J., Zhang, J., Wong, M.H., Shan, S., Christie, P., 2017. Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: biochar properties and environmental risk from metals. Bioresour. Technol. 228, 218–226.
Kistler, R.C., Widmer, F., Brunner, P.H., 1987. Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge. Environ. Sci. Technol. 21 (7), 704–708.
Legros, S., Levard, C., Marcato-Romain, C.E., Guiresse, M., Doelsch, E., 2017. Anaerobic digestion alters copper and zinc speciation. Environ. Sci. Technol. 51 (18), 10326–10334.
Leng, L., Yuan, X., Huang, H., Jiang, H., Chen, X., Zeng, G., 2014. The migration and transformation behavior of heavy metals during the liquefaction process of sewage sludge. Bioresour. Technol. 167, 144–150.
Li, C., Wang, X., Zhang, G., Li, J., Li, Z., Yu, G., Wang, Y., 2018a. A process combining

hydrothermal pretreatment, anaerobic digestion and pyrolysis for sewage sludge dewatering and co-production of biogas and biochar: pilot-scale verification. Bioresour. Technol. 254, 187–193.
Li, H., Mahyoub, S.A., Liao, W., Xia, S., Zhao, H., Guo, M., Ma, P., 2017. Effect of pyrolysis temperature on characteristics and aromatic contaminants adsorption behavior of magnetic biochar derived from pyrolysis oil distillation residue. Bioresour. Technol. 223, 20–26.
Li, Z., Deng, H., Yang, L., Zhang, G., Li, Y., Ren, Y., 2018b. Influence of potassium hydroxide activation on characteristics and environmental risk of heavy metals in chars derived from municipal sewage sludge. Bioresour. Technol. 256, 216–223.
Liang, X., Ning, X.A., Chen, G., Lin, M., Liu, J., Wang, Y., 2013. Concentrations and speciation of heavy metals in sludge from nine textile dyeing plants. Ecotoxicol. Environ. Saf. 98, 128–134.
Lin, M., Ning, X.-a., Liang, X., Wei, P., Wang, Y., Liu, J., 2014. Study of the heavy metals residual in the incineration slag of textile dyeing sludge. J. Taiwan Inst. Chem. Eng. 45 (4), 1814–1820.
Liu, T., Liu, Z., Zheng, Q., Lang, Q., Xia, Y., Peng, N., Gai, C., 2018. Effect of hydrothermal carbonization on migration and environmental risk of heavy metals in sewage sludge during pyrolysis. Bioresour. Technol. 247, 282–290.
Liu, T., Liu, Z., Zheng, Q., Lang, Q., Xia, Y., Peng, N., Gai, C., 2017. Effect of hydrothermal carbonization on migration and environmental risk of heavy metals in sewage sludge during pyrolysis. Bioresour. Technol. 247, 282–290.
Lu, H., Zhang, W., Wang, S., Zhuang, L., Yang, Y., Qiu, R., 2013. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. J. Anal. Appl. Pyrolysis 102, 137–143.
Méndez, A., Paz-Ferreiro, J., Araujo, F., Gascó, G., 2014. Biochar from pyrolysis of deinking paper sludge and its use in the treatment of a nickel polluted soil. J. Anal. Appl. Pyrolysis 107, 46–52.
Man, X., Ning, X.A., Zou, H., Liang, J., Sun, J., Lu, X., Sun, J., 2018. Removal of polycyclic aromatic hydrocarbons (PAHs) from textile dyeing sludge by ultrasound combined zero-valent iron/EDTA/Air system. Chemosphere 191, 839–847.
Vanhulle, S., T, M., Enaud, E., Lucas, M., Taghavi, S., Van Der Lelie, D., Van Aken, B., Foret, M., Onderwater, R.C.A., Wesenberg, D., Agathos, S.N., Schneider, Y.J., Corbisier, A.M., 2008. Decolorization, cytotoxicity, and genotoxicity reduction during a combined ozonation/fungal treatment of dye-contaminated wastewater. Environ. Sci. Technol. 42, 584–589.
Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., Von Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313 (5790), 1072–1077.
Shao, J., Yuan, X., Leng, L., Huang, H., Jiang, L., Wang, H., Chen, X., Zeng, G., 2015. The comparison of the migration and transformation behavior of heavy metals during pyrolysis and liquefaction of municipal sewage sludge, paper mill sludge, and slaughterhouse sludge. Bioresour. Technol. 198, 16–22.
Sohaimi, K.S.A., Ngadi, N., Mat, H., Inuwa, I.M., Wong, S., 2017. Synthesis, characterization and application of textile sludge biochars for oil removal. J. Environ. Chem. Eng. 5 (2), 1415–1422.
Sohi, S.P., 2012. Carbon storage with benefits. Science 338 (6110), 1034–1035.
Wang, X., Li, C., Zhang, B., Lin, J., Chi, Q., Wang, Y., 2016. Migration and risk assessment of heavy metals in sewage sludge during hydrothermal treatment combined with pyrolysis. Bioresour. Technol. 221, 560–567.
Xiao, X., Chen, B., 2017. A direct observation of the fine aromatic clusters and molecular structures of biochars. Environ. Sci. Technol. 51 (10), 5473–5482.
Xie, W., Wen, S., Liu, J., Xie, W., Kuo, J., Lu, X., Sun, S., Chang, K., Buyukada, M., Evrendilek, F., 2018. Comparative thermogravimetric analyses of co-combustion of textile dyeing sludge and sugarcane bagasse in carbon dioxide/oxygen and nitrogen/oxygen atmospheres: thermal conversion characteristics, kinetics, and thermodynamics. Bioresour. Technol. 255, 88–95.
Yuan, H., Lu, T., Huang, H., Zhao, D., Kobayashi, N., Chen, Y., 2015. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. J. Anal. Appl. Pyrolysis 112, 284–289.
Yuan, J.H., Xu, R.K., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour. Technol. 102 (3), 3488–3497.
Zhang, H., Gao, Z., Ao, W., Li, J., Liu, G., Fu, J., Ran, C., Mao, X., Kang, Q., Liu, Y., Dai, J., 2017. Microwave pyrolysis of textile dyeing sludge in a continuously operated auger reactor: char characterization and analysis. J. Hazard. Mater. 334, 112–120.
Zheng, H., Wang, Z., Deng, X., Zhao, J., Luo, Y., Novak, J., Herbert, S., Xing, B., 2013. Characteristics and nutrient values of biochars produced from giant reed at different temperatures. Bioresour. Technol. 130, 463–471.
Zhu, X., Liu, Y., Zhou, C., Luo, G., Zhang, S., Chen, J., 2014. A novel porous carbon derived from hydrothermal carbon for efficient adsorption of tetracycline. Carbon 77, 627–636.