Impacts of Wet Thermal Treatment on Heavy Metals Speciation in Contaminated Waste Activated Sludge Using a Modified Sequential Extraction Scheme

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The mobility and the bioavailability of heavy metals in waste activated sludge were determined according to their total content and chemical speciation. A modified three-step sequential extraction procedure was used to determine the total content and metal speciation distribution pattern of various heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) pretreated at a temperature of 100 °C to 200 °C. It was found that the organics solubilization was enhanced at higher temperature, increased by 1.75, 183 and 3.03 folds over the soluble chemical oxygen demand (SCOD) at 100 °C. The total contents of Cd, Pb and Zn exceeded the threshold value established in GB/T standard 23486 (2009), as a function of pH, due to the pollution from the local nonferrous metals industry. For most cases, the impacts of thermal pretreatment on the species distribution were limited and obscure. Cr was the only element showing a potential risk of metal mobilization, such that its residual fraction shifted towards oxidizable fraction at higher treatment temperature. The speciation distribution pattern of Ni, Cr, Cu, and Zn showed potential risks of contamination due to their bioavailability, mobility, or toxicity.

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INTRODUCTION

With the rapid progress of industrialization and urbanization, over 6,030 municipal wastewater treatment plants (WWTPs) in China generated a total of at least 6.25 million tons of waste activated sludge (dry weight) per year (Ministry of Environmental Protection 2015). However, trace metals present in wastewater will accumulate on the biofilms of waste activated sludge through physical, chemical, or biological processes. The concentration and speciation of heavy metals in waste activated sludge presented considerable variations as a result of different wastewater sources; the industrial source of pollutants in wastewater was especially responsible for the potential contaminations of ecosystems *via* heavy metals (Yao *et al.* 2010; Chan *et al.* 2013). Thus, the behavior of heavy metals needs to be carefully investigated throughout the sludge management process.

The full-scale installations of thermal treatment or wet-oxidation were previously applied to improve sludge dewaterability prior to mechanical dewatering, incineration, and final disposal until the 1980s (Zhang *et al.* 2011). However, since Haug *et al.* (1978) investigated the effect of thermal pretreatment on anaerobic biodegradability, thermal

pretreatment at a temperature less than 200 °C has been widely studied as an effective modification of the biodegradability of waste activated sludge before anaerobic digestion; the aim is to improve methane production and optimize the energy balance of the sludge treatment process (Li and Noike 1992; Bougrier *et al.* 2008; Wilson and Novak 2009). In addition to the effects on dewaterability, the impacts of thermal treatment have been fully discussed in terms of the organic solubilization, size distribution, and biodegradability (Eskicioglu *et al.* 2006; Bougrier *et al.* 2008; Carrere *et al.* 2008). However, the influence of thermal treatment on the speciation of heavy metals needs further investigation to identify the potential risk of heavy metal mobilization during sludge pretreatment.

Obrador *et al.* (2001) determined the lability and leachability of trace metals in contaminated waste activated sludge exposed to temperatures of 180, 300, and 400 °C, and found that the trace metals were strongly fixed in the treated sledge, according to the results of sequential metal extraction. Likewise, Sun *et al.* (2010) confirmed its positive effect on metal stabilization, according to the fraction distribution of Pb, Cu, Cd and Zn, in thermal treated sludge (at a temperature of 190 °C), following the subsequential extraction schemes proposed by the Commission of the European Communities Bureau of Reference (known as BCR). However, the discussed temperature range, *i.e.*, greater than 180 °C, exceeded the threshold for optimizing sludge dewaterability and generated refractory meladine compounds (Zhang *et al.* 2016). The BCR schemes and its modifications were well-established procedures to fractionate the metal content into four fractions (acid soluble, reducible, oxidizable, and residual) in waste activated sludge, solids, sediments, and related substrates (Mossop and Davidson 2003; Arain *et al.* 2008; Nemati *et al.* 2011; Zhang *et al.* 2014). Laurent *et al.* (2011) reported that the heavy metals contents in both the soluble and total fractions increased in aerobic process integrated with a 90 °C thermal treatment. To the best knowledge of the authors, the available data is still limited regarding the behavior patterns (total concentration and chemical speciation) of heavy metals in waste activated sludge during thermal pretreatment.

The objective of this study was to evaluate the impact of thermal treatment on the mobility and the bioavailability of heavy metals in waste activated sludge. The duration of thermal treatment had little effect on sludge solubilization; thus, only the impacts of temperature (at a range of 100 to 200 °C) on the total content and speciation of heavy metals were evaluated in this study (Donoso-Bravo *et al.* 2011). A modified BCR sequential extraction, followed by a determination of the metal content in the residual, was applied to fractionate the heavy metals in the sludge (Rauret *et al.* 2000; Mossop and Davidson 2003). Six elements (As, Cd, Cr, Cu, Ni, Pb, and Zn) in the extract were measured *via* inductively coupled plasma optical emission spectrometry (ICP-OES).

EXPERIMENTAL

Materials and Methods

Sample preparation

Dewatered waste activated sludge from the municipal WWTP (127,000 inhabitant-equivalent, with a capacity of 4.4×10^4 m^3/d using a modified Carrousel oxidation ditch process) at Hechi, China, a region famous for its nonferrous metals mining and refining, was used in this study. The moisture of dewatered sludge was reduced to below 60.0% of initial moisture. Raw sludge was stored at a temperature of 4 °C for a maximum duration of 72 h before further utilization. The total solid (TS) and volatile solid (TS) contents of

the wasted activated sludge were determined to calculate the dilution factor to obtain the raw sludge slurry (TS = 1000 mg·L^{-1}) with distilled water in a food processor (WBL25B26, Midea Limited, China).

The supernatant of raw sludge and thermal treated sludge were separated at 6000 rpm for 20 min in a JW-1042 centrifuge (Jiawen, China), and filtered (50 μm, Watman) before further analyze. The precipitates were air-dried at ambient temperature for 28 d in plastic trays packed with paper. The air-dried caky samples were crushed with a glass roller and sieved through a 2 mm sieve before digestion or extraction.

Thermal treatment

Thermal pretreatment was conducted using an electric-heating reactor (HK-ZZ01, Hengke Instruments, China), equipped with four identical hydrothermal synthesis vessels (HSV) inside the reaction chamber. The chamber, filled with 2 L of water as a thermal conductor, would keep rotating during the treatment to guarantee a minimum temperature-gradient in the reaction chamber. Waste activated sludge slurry (500 mL for each vessel) was filled in the HSV and tightly sealed. The thermal treatment temperature was set and controlled at 100, 135, 165, and 200 °C *via* a proportional integral derivative (PID) regulation controller. Thermal treatment was conducted for 30 min once the target temperature was reached. Treated sludge was stored at a temperature of 4 °C for a maximum period of 48 h before further analysis.

Analytical Methods

Instrumentation

An ICP-OES (Agilent 725-OES, Santa Clara, CA) equipped with a Babington nebulizer was used to determine the concentration of heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn). A glass, double-path spray chamber and a standard quartz torch were operated with the following parameters for element determination: a RF power of 1.0 kW, plasma gas at a rate of 15.5 L·min^{-1}, auxiliary gas at a rate of 1.45 L·min^{-1}, atomization gas at a rate of 0.75 L·min^{-1}, and a peristaltic pump flow rate of 10 r/min.

Sequential extraction procedure

Sequential extraction was performed according to a modified BCR procedure (Rauret *et al.* 2000). After the sequential extraction, the residue was digested with aqua regia to determine the residual metal content. The procedures can be briefly introduced as the following steps and are explained in Table 1.

Step 1: 40 mL of acetic acid was added to 1.0 g of the air-dried sample and shaken for 16 h at ambient temperature. The extract was separated from the residual *via* centrifuging.

Step 2: 40 mL of hydroxylammonium chloride was added to the residue from step 1, and the extraction was performed again as above.

Step 3: the residue from step 2 was treated with hydrogen peroxide twice, evaporated to near dryness, and then 50 mL of ammonium acetate, adjusted to a pH of 2 with nitric acid, was added and the extraction was performed again as above.

Step 4: the residue from step 3 was digested according to the procedure of pseudo-total metal digestion.

Table 1. Modified BCR Sequential Extraction Procedures

Step	Fraction	Target phase(s)	Modified BCR schemes (Rauret *et al.* 2000)
1	Acid soluble	Soluble species, carbonate, cation exchange sites	0.11 mol·L^{-1} of acetic acid
2	Reducible	Iron and manganese oxides	0.5 mol·L^{-1} of hydroxylammonium chloride at a pH of 1.5
3	Oxidizable	Organic matter and sulphide	8.8 mol·L^{-1} of hydrogen peroxide followed by 1.0 mol·L^{-1} of ammonium acetate at a pH of 2 with concentrated nitric acid
4*	Residual	non-silicate bound metals	Aqua regia
Note: * Step 4 was not included in original BCR			

Total metal digestion

Microwave-assisted digestion (WMX-III-B, Honghai) was conducted to determine the aqua extractable metal (pseudototal metal) concentrations. First, 1 g of air-dried sludge was digested with aqua regia (5 mL of HNO_3 and 15 mL of HCl) in each PTFE digester. After cooling, the digest was filtered (50 µm, Whatman) into a 100 mL volumetric flask and diluted to the mark with distilled water (Mossop and Davidson 2003).

Quality control

The residual fraction was not suggested in the original BCR procedure; however this step is useful for quality control, since the sum of steps 1 through 4 can be compared with results of a separate aqua regia digestion, according to Eq. 1,

$$\text{Recovery } (\%) = [(C_{Acid} + C_{Red} + C_{Oxi} + C_{Residue})/C_{total}] * 100\% \quad (1)$$

where C_{Acid}, C_{Red}, and C_{Oxi} were the contents of the acid soluble, reducible, and oxidizable fraction extracted in the three-step BCR sequential extraction, respectively, $C_{Residue}$ is the metal content in the residue, and C_{total} is the total content obtained from total content digestion (mg/kg, dry weight) (Nemati *et al.* 2011).

Analytical Methods

The following parameters were analyzed before and after the thermal pretreatment: the soluble chemical oxygen demand (SCOD), ammonia (NH_4^+-N) content, alkalinity, pH, and volatile fatty acid (VFA) content. The VFA was determined using the five-point titration method (Lahav and Morgan 2004). The SCOD, TS, VS, pH, and alkalinity were determined according to the standard methods (APHA-AWWA-WEF 1998).

RESULTS AND DISCUSSION

Sludge Characterization

The effects of the thermal treatment on the waste activated sludge were evaluated by the improvements of the readily biodegradable substrates in liquid phase (as shown in Table 2). The sludge disintegration was a highly temperature-dependent process.

Table 2. Physical-Chemical Characteristics of Raw Sludge and Thermal Pretreated Sludge ($Mg \cdot L^{-1}$)

Substrates	pH	SCOD	NH_4^+-N	VFA	Alkalinity
Raw sludge	7.3 ± 0.1	152 ± 32	42 ± 5	66 ± 9	655 ± 27
100 °C	6.5 ± 0.1	6327 ± 784	453 ± 8	1331 ± 139	3501 ± 644
135 °C	6.4 ± 0.1	17416 ± 775	530 ± 44	1396 ± 351	2101 ± 142
165 °C	6.2 ± 0.2	17929 ± 923	563 ± 66	1873 ± 675	2051 ± 340
200 °C	6.0 ± 0.1	25543 ± 1374	915 ± 75	2601 ± 363	1747 ± 127
Note: the results are expressed as mean ± standard deviation (n=3)					

The SCOD profiles were correlated with the NH_4^+-N values, which were the by-product of protein degradation. This provided evidence of solubilization and degradation of sludge flocs. First, the considerable increase in sludge solubilization induced by thermal treatment at a temperature of 100 °C might be associated with the organic matter liberalized from the sludge matrix and cellular membrane, during the deflocculation of the sludge matrix at a temperature of 95 °C, as reported by Prorot *et al.* (2011). It was found that the organics solubilization was enhanced at higher temperatures. It was increased by 1.75, 183 and 3.03 folds over the SCOD at a temperature of 100 °C.

There was a rapid ammonia release at a temperature of 100 °C, which was 9.79 times greater than the ammonia from raw sludge. Then, the growth of ammonia reached a plateau phase at a temperature range of 100 °C to 165 °C, slightly increasing from 453 $mg \cdot L^{-1}$ ± 8 $mg \cdot L^{-1}$ to 563 $mg \cdot L^{-1}$ ± 66 mg L^{-1}. It was interesting to note the evidence of organics molecular degradation at a temperature of 200 °C. At this point, ammonia increased by 62.5%, which was attributed to the degradation of protein, which was faster than the increase in the SCOD and VFA, by 42.5% and 38.9%, respectively. These results were consistent with the reports on the vigorous sludge solubilization at temperatures greater than 165 °C (Stuckey and McCarty 1984; Mottet *et al.* 2009).

Total Heavy Metal Content

The application of stabilized waste activated sludge as fertilizer for gardening or contaminated landsite remediation are regulated by the maximum permitted total content of heavy metals, established in GB/T standard 23486 (2009), as a function of the pH of the soil. The total contents of heavy metals obtained *via* aqua regia digestion from the solid phase of the raw sludge and treated sludge, along with the permitted metal content, are listed in Table 3.

For most cases, thermal treatment resulted in a moderated decrease in the total metal content of the waste activated sludge, which can be attributed to the solubilization metals removed along with the supernatant separated during the thermal pretreatment. These results are similar with previous studies, in which most of the metal in the sludge was stable in the solid phase after thermal treatment and the degree of metal released was relative to the energy input of the treatment (Appels *et al.* 2010; Sun *et al.* 2010; Laurent *et al.* 2011).

Table 3. Total Heavy Metal Content in Waste Activated Sludge and Their Threshold Values Established by GB/T Standard 23486 (2009) as a Function of pH

Metals	Threshold Content		Raw Sludge	Treated Sludge			
	pH < 6.5	pH > 6.5		100 °C	135 °C	165 °C	200 °C
As	75	75	39 ± 0.5	36 ± 1	36 ± 1	31 ± 2	33 ± 1
Cd	5	20	5.8 ± 0.5	5.5 ± 0.7	5.6 ± 0.6	5.6 ± 0.6	5.5 ± 0.5
Cr	600	1000	416 ± 34	382 ± 16	329 ± 28	363 ± 57	330 ± 13
Cu	800	1500	258 ± 21	271 ± 6	241 ± 22	231 ± 13	233 ± 17
Ni	100	200	63 ± 5	55 ± 2	58 ± 1	58 ± 1	59 ± 4
Pb	300	1000	313 ± 16	314 ± 7	260 ± 10	303 ± 14	288 ± 30
Zn	2000	4000	3924 ± 142	3539 ± 150	3435 ± 164	3454 ± 85	3580 ± 186
Note: the results are expressed as the mean ± standard deviation in $mg \cdot kg^{-1}$ of dry matter (n=3)							

As shown in Table 3, three of the heavy metals (Cd, Pb, and Zn) in the sludge exceeded the limits, depending on the pH of the soil that the waste activated sludge will be applied to. The waste activated sludge used in this study was substandard to apply in acidic solid (pH less than 6.5) because the total contents were above the limits for Cd and Pb, by up to 48.0% to 58.7% and 1.0% to 4.7%, respectively. Nonetheless, the permitted value of Cd and Pb were more permissive in the alkaline condition, as shown in Table 3. Thus, the concentrations of Cd and Pb were still within the permitted levels of the application area with a pH greater than 6.5. A high concentration of Zn was found in the waste activated sludge, which ranged from 3435 to 3924 $mg \cdot kg^{-1}$ of dry matter, almost two-fold the threshold value for a pH less than 6.5. This was attributed to the fact that the average total Zn content in the raw sludge was on the edge of the permissive threshold value when the pH was greater than 6.5, reaching 3924 $mg \cdot kg^{-1}$.

Based on the total heavy metals contents in the waste activated sludge, it can be concluded that the application of waste activated sludge or its downstream product from this WWTP has the potential for heavy metal contamination by Cd, Pb, and Zn; especially in the cases when the soil pH value is below 6.5. Previous study pointed out that the migration of heavy metals between solid-liquid phase mainly depended on the temperature. The percentage of all heavy metals (except Cu) in mobile (acid-soluble/exchangeable and reducible) forms decreased after microwave-assisted thermal hydrolysis treatment (Qiu *et al.* 2021). The general conclusion was in line with the present study. But, the heterogeneity of wasted activated sludge has to be emphasized that the impact of pre-treatment on selected heavy metal could be diverse, as a result of their diversified nature.

Speciation of Heavy Metals

The regulations of waste activated sludge application as fertilizer for gardening or contaminated landsite remediation are based on the total heavy metal contents (Table 3). However, the total content in the solid is a poor indicator of bioavailability, mobility, or toxicity; these properties basically depend on the different chemical forms of binding between trace metals and solid phases of the samples (Nemati *et al.* 2011). Hence, the modified BCR sequential extraction protocol was used to partition the metal in the waste activated sludge. Table 4 shows the results of the sequential extraction schemes for the raw sludge and treated sludge, along with a reasonable recovery index (87.2% to 104.2%)

comparing the values in this study with values in the literature (Mossop and Davidson 2003; Nemati *et al.* 2011). The speciation distribution patterns of the heavy metals are illustrated in Fig. 1.

Table 4. Extractable Heavy Metal Contents in the Sludge for Each Step in the Modified BCR Scheme

Sludge	Fraction	As	Cd	Cr	Cu	Ni	Pb	Zn
Raw	Acid soluble	6.4 ± 0.4	1.2 ± 0.2	1.6 ± 0.1	2.7 ± 0.2	15 ± 1.6	79 ± 7.7	120 ± 4.2
	Reducible	3.5 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	2.3 ± 0.5	19 ± 2.2	29 ± 0.8	1276 ± 45
	Oxidizable	2.4 ± 0.1	0.5 ± 0.05	162 ± 16	121 ± 6	11 ± 1.2	46 ± 0.8	851 ± 38
	Residual	25 ± 0.3	3.2 ± 0.3	198 ± 18	127 ± 14	19 ± 1.1	136 ± 6.9	1461 ± 133
	Sum	37 ± 1.0	5.8 ± 0.5	362 ± 34	252 ± 21	63 ± 6.1	291 ± 16	3708 ± 221
	Recovery (%)	96.0	94.3	87.2	97.8	101.4	92.7	94.5
100 °C	Acid soluble	8.2 ± 1.1	1.4 ± 0.3	1.4 ± 0.1	3.6 ± 1.1	11 ± 0.2	66 ± 8.0	126 ± 32
	Reducible	5.7 ± 0.9	0.6 ± 0.1	0.5 ± 0.2	1.9 ± 0.4	14 ± 0.4	26 ± 5.1	1179 ± 45
	Oxidizable	5.7 ± 0.5	0.7 ± 0.1	172 ± 4.9	135 ± 2.6	10 ± 0.3	39 ± 3.4	904 ± 38
	Residual	17 ± 1.4	2.2 ± 0.3	177 ± 11	118 ± 2.6	15 ± 1.1	150 ± 13	1337 ± 149
	Sum	37 ± 3.8	5.5 ± 0.7	350 ± 16	258 ± 6.6	51 ± 1.9	282 ± 30	2973 ± 223
	Recovery (%)	102.8	87.9	91.7	95.3	92.1	89.%	100.2
135 °C	Acid soluble	6.7 ± 0.7	1.5 ± 0.4	1.1 ± 0.3	3.3 ± 0.6	11 ± 0.6	64 ± 10	53 ± 14
	Reducible	4.6 ± 0.7	0.8 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	17 ± 0.8	21 ± 8	1057 ± 126
	Oxidizable	5.4 ± 0.4	0.7 ± 0.1	163 ± 15	115 ± 1.3	11 ± 0.8	38 ± 6	897 ± 113
	Residual	17 ± 1.7	2.3 ± 0.1	149 ± 11	99 ± 9.9	17 ± 1.1	125 ± 11	1249 ± 84
	Sum	34 ± 3.4	5.6 ± 0.6	313 ± 27	218 ± 11.9	57 ± 3.3	248 ± 36	3257 ± 357
	Recovery (%)	95.3	92.9	95.3	90.3	98.1	95.2	94.8
165 °C	Acid soluble	6.2 ± 0.7	1.3 ± 0.2	1.2 ± 0.2	4.6 ± 0.1	11 ± 0.1	69 ± 7	33 ± 12
	Reducible	3.7 ± 0.5	0.9 ± 0.1	0.4 ± 0.1	0.7 ± 0.1	16 ± 0.9	25 ± 9	964 ± 67
	Oxidizable	3.0 ± 0.6	0.5 ± 0.1	189 ± 25	121 ± 7.8	11 ± 0.2	39 ± 3	938 ± 47
	Residual	16 ± 1.1	2.5 ± 0.5	130 ± 25	114 ± 17.4	18 ± 0.3	149 ± 4	1478 ± 73
	Sum	29 ± 2.8	5.6 ± 0.6	321 ± 50	241 ± 25	55 ± 1.5	282 ± 24	3413 ± 187
	Recovery (%)	92.5	93.3	88.4	104.2	96.4	93.1	98.8
200 °C	Acid soluble	6.2 ± 1.1	1.4 ± 0.3	1.1 ± 0.2	4.1 ± 0.5	10 ± 0.5	55 ± 7	21 ± 5
	Reducible	4.8 ± 0.6	0.7 ± 0.1	0.5 ± 0.1	0.9 ± 0.1	12 ± 1.8	23 ± 9	827 ± 72
	Oxidizable	2.5 ± 0.3	0.8 ± 0.1	209 ± 17	107 ± 9	12 ± 0.9	27 ± 5	891 ± 18
	Residual	19 ± 0.4	2.6 ± 0.5	109 ± 5	104 ± 11	21 ± 1.3	177 ± 17	1484 ± 108
	Sum	33 ± 2.4	5.5 ± 0.6	320 ± 22	217 ± 21	55 ± 4.4	281 ± 38	3529 ± 222
	Recovery (%)	99.3	100.9	96.8	92.9	93.5	97.6	90.0
Note: the results are expressed as the mean ± standard deviation in mg/kg of dry matter (n=3)								

Arsenic

The largest quantity of arsenic in the raw sludge remained in the residual of the sequential extraction, and the proportion of As in each step of the sequential extraction was not fundamentally changed by thermal treatment. However, its proportion in the residual fraction experienced a tiny U-bend curve as additional As was liberated into the more bioavailable forms by approximately 20% at a temperature of 100 °C and bound to the low risk residual fraction at higher temperatures. Meanwhile, the minority chemical fractions associated to the acid soluble, reducible, and oxidizable phases remained relative stable.

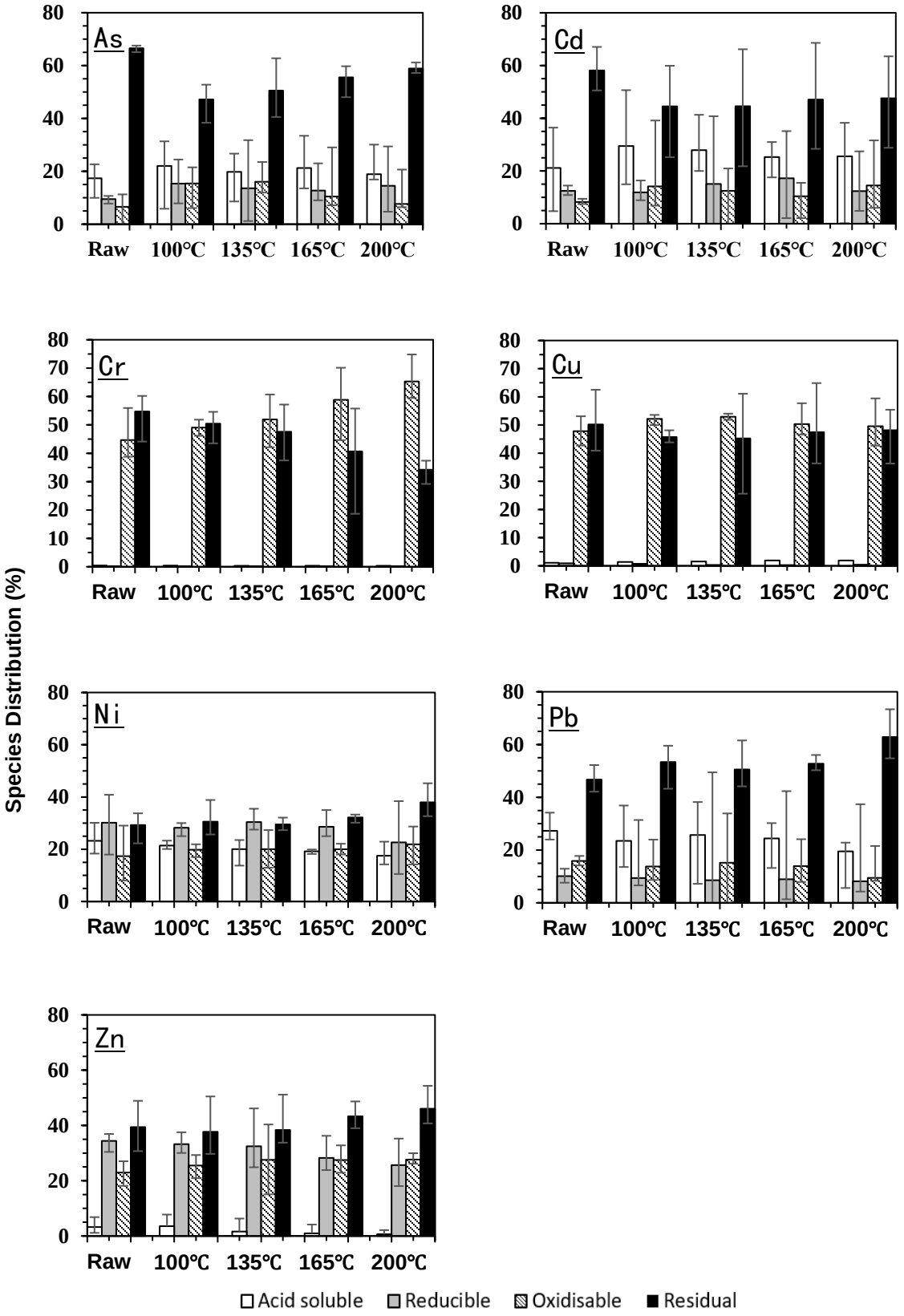

Fig. 1. Speciation distribution of the heavy metals in the raw sludge and treated sludge at different temperatures, using the modified BCR sequential extraction procedure

Cadmium

It was worthy of note that 9.4% to 13.4% of the Cd associated with the residual fraction was converted to acid-soluble and oxidizable forms (as shown in Fig. 1). Heavy metals that are present on the cell surface of the biofilms in the sludge are easily dissolved by acidic solutions (Yoshizaki and Tomida 2000). That means that the potential risk of Cd migration was definitely increased for treated sludge owning to the thermal treatment, in which release the organic content, as well as heavy metals, provided extra surface for ion absorption. Not to mention that the total Cd content was definitely beyond the limit of acidic soil, in which the pH was lower than 6.5 (GB/T 23486-2009).

Chromium and copper

Chromium and Cu were basically greater than 97% of the total elemental content and found in the oxidizable and residual fraction in all cases. For the treated sludge, Cr had shown a clear transformation from the residual fraction to the oxidizable fraction, which indicated that the stable Cr trapped in the crystalline structure was liberated during the thermal treatment. It also indicated that the Cr ion was bound to organic substances (increased from 38.9% in the raw sludge to 63.2% in sludge treated at 200 °C), which would release the metal in oxidant conditions. This result suggested that cobalt would become more mobilizable when the treatment temperature increased. Contrarily, the majority of Cu, which was obtained in the oxidizable (46.0% to 52.4%) and the residual fraction (40.8% to 49.5%), was almost unaffected by the thermal treatment, and the share of the acid soluble fraction was almost negligible, despite the fact that its share slightly increased as the temperature increased. The results of the total content showed that the concentrations of Cr and Cu were below their threshold values, but the fact that a high portion of Cr and Cu were bound to oxidizable fractions was still noticeable.

Nickel

The total concentration of Ni maintained stable during the thermal process at 55 $mg \cdot kg^{-1}$ to 59 $mg \cdot kg^{-1}$, and the metal distribution of nickel was relatively balanced in the sequential extractions, *i.e.*, the reducible and the residual fractions were slightly ahead of the others. However, at a treatment temperature of 200 °C, the reducible fraction of Ni that bound with Fe/Mn oxides, slightly dropped from 27.6% to 21.2%, which were stabilized into the residual fraction. As such, Ni showed a potential risk based on its distribution pattern that more that 64.5% of the Ni was in the acid soluble, reducible, and oxidizable fractions.

Zinc

For zinc, its residual fraction gradually increased from 39.4% to 46.1% when the sludge was treated at higher temperatures, which indicated that the risk of metal migration was generally suppressed by the treatment. However, the high amount of zinc (greater than 56.3%) in the reducible and oxidizable fraction might attribute to the potential threats of zinc release during land application, *e.g.*, anoxic and reductive underground environments or oxidative atmospheres on the surface. The obvious conclusion was that any approach of land utilization of the waste activated sludge from this WWTP should be banned in soil with a pH greater than 6.5, and a careful assessment of the risk of zinc contamination should be undertaken before its application in alkaline conditions.

Lead

The highest share of Pb was retained in the residual fraction in all tested sludge samples, and the secondarily fraction was extracted in the acid soluble form. Those two parts accounted for 74.0% to 82.4% of the total content altogether and an increase in the treatment temperature lead to an increase in the amount of lead distributed in the residual phase (46.7% to 62.9%).

CONCLUSIONS

As thermal treatments including wet oxidation or thermal pretreatment have a growing number of applications in waste sludge treatment, this work has provided a comprehensive understanding about the impact of thermal treatment on the mobility and the bioavailability of the seven heavy metals. The modified BCR sequential extraction provides a valuable data for further risk assessment of biomass utilization from the aspects of the form and content of heavy metals in wasted activated sludge.

1. The total contents showed that limited amounts of heavy metals that bounded to the solid phase of waste activated sludge were liberated into the aqueous solution phase during the thermal process. For the waste activated sludge used in the present study, its Cd, Pb, and Zn content exceed the threshold value for soil with a pH less than 6.5. In fact, the Zn content was also at the edge of the content limit for soil with a pH greater than 6.5.
2. Results from the modified BCR sequential extraction showed that, except for Ni, over 40% of the heavy metals were retained in the residual solids fraction after the extraction sequence in the raw sludge and treated sludge. For most cases, the impacts of the thermal pretreatment on the species distribution were limited and obscure, though Cr was the only element that showed a potential risk of metal mobilization, *i.e.*, its residual fraction shifted towards the oxidizable fraction at higher treatment temperatures.
3. It was worthy of note that the distribution patterns of Ni, Cr, Cu, and Zn showed that these elements were more vulnerable to environmental variation in sludge management. The actual implications of the thermal treatment on heavy metal needs further inspection to determine its long-term impacts on anaerobic digestion, composting, or land application.

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