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Research article

Effects of lignocellulosic biomass type on nutrient recovery and heavy metal removal from digested sludge by hydrothermal treatment

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ABSTRACT

Sludge is a nutrient-rich organic waste generated from wastewater treatment plants. However, the application of sludge as a nutrient source is limited by its high contents of water and pollutants. In this study, the effects of biomass type on nutrient recovery and heavy metal removal from digested sludge by hydrothermal treatment (HTT) were investigated. Blending biomass with digested sludge for HTT at 180–240 °C increased the recovery of nitrogen in the treated solids. At the HTT temperature of 240 °C, HTT with hardwood sawdust led to the highest nitrogen recovery of 70.6%, compared to the lowest nitrogen recovery of 36.5% without biomass. Blending biomass slightly decreased the recovery of phosphorus compared to those without biomass. Nevertheless, the lowest phosphorus recovery of 91.3% with the use of hardwood sawdust at the HTT temperature of 240 °C was only ~7.0% less than that without biomass. Blending biomass reduced the contents of macro-metals such as Ca, Fe, Mg and Al in treated solids but the metal contents varied with different biomasses. Regarding the heavy metals, the use of rice husk did not decrease the contents of Ni and Co while blending bagasse did not decrease the content of Cr at HTT temperatures of 210 °C and 240 °C compared to the use of other biomasses. The different effects of biomass type on nutrient recovery and heavy metals were likely related to the types and abundances of organic acids such as acetic acid, oxygen-containing functional groups such as C–OH and COOH, oxide minerals such as silica from biomasses and the overall effects of these factors. This study provides very useful information in selection of lignocellulosic biomass for HTT of sludge for nutrient recovery and heavy metal removal.

1. Introduction

Globally, more than 100 million tonnes of raw sludge are produced from wastewater treatment plants per annum (Mateo-Sagasta et al., 2015). Sludge is rich in organic carbon and two primary fertilizer components - nitrogen (N) and phosphorus (P) (Wang et al., 2021; Zheng et al., 2020), and has the potential for soil application as a fertilizer or soil amendment. However, heavy metals present in sludge cause significant food safety concerns due to the potential accumulation of heavy metals in food crops (Liew et al., 2022). In addition, high ash content of sludge may lead to increasing of soil salinity, which may cause phytotoxicity and deterioration of soil quality in a long term (Antonkiewicz et al., 2020). Moreover, sludge contains approximately 70.0%–85.0% moisture content even after dewatering, resulting in high transportation and application costs. Furthermore, high moisture content also reduces sludge stability in long-term storage.

Hydrothermal treatment (HTT) is a relatively simple approach for improving sludge dewaterability and properties (Ebrahimi et al., 2022; Tasca et al., 2019). Through HTT, sludge moisture is reduced, its stability is improved, pathogens are killed, and several heavy metals are selectively removed (Tasca et al., 2019; Wang et al., 2019). However, HTT of sludge alone has drawbacks such as significant loss of nutrients

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into liquid phases, high ash content, and enrichment of some heavy metals in the derived solid products (He et al., 2019; Liew et al., 2021), which reduces the value of sludge as a fertilizer source and restricts its application for soil amendments. Lignocellulosic biomasses, such as crop and wood processing residues, are low-cost, abundant, and organic carbon rich materials. Recent studies have shown that blending biomass with sludge in HTT enhanced sludge dewaterability, increased carbon content, selectively removed heavy metals and improved nutrient recovery (Ebrahimi et al., 2022; Peng et al., 2017; Shi et al., 2013; Wang et al., 2020, 2021; Zhang et al., 2017, 2020). Hence, the addition of biomass to the HTT of sludge will also extend the applications of the derived HTT solids as soil amendment, solid fuel, adsorbent, and others.

Lignocellulosic biomass mainly consists of cellulose, hemicellulose, and lignin. It also contains ash and extractives. Lignocellulosic biomass from different plants can vary significantly in physical structure and chemical compositions. For instance, the cellulose content in lignocellulose differs from 25.0%–65.0%, hemicellulose from 4.0%–37.0% and lignin from 10.0%–30.0% (O'Hara et al., 2011). Some lignocellulosic biomasses such as rice husk have a high ash content up to 25.0% while others such as sugarcane bagasse have low ash contents of less than 5.0% (Ebrahimi et al., 2017; Zhang et al., 2016). Moreover, the contents of water and ethanol extractives, the sugar moieties of hemicellulose (xylose, mannose, arabinose, *etc.*), the types and abundance of lignin subunits also vary (O'Hara et al., 2011; Zhang et al., 2016). HTT of lignocellulosic biomass can lead to the generation of organic acids such as levulinic acid and formic acid from cellulose, and acetic acid through hydrolysis of acetyl groups (Rasmussen et al., 2014). In addition, HTT of lignocellulosic biomass also led to the generation of char-like solid residues having partially carbonized structure containing oxygen-containing functional groups (Titirici et al., 2015).

In the authors' previous study, four common agricultural biomass and forestry residues (include sugarcane bagasse, rice husk, hardwood sawdust, and softwood sawdust) were blended with digested sludge in HTT (Ebrahimi et al., 2022). It was found that the differences in biomass physical structure and chemical composition affected the dewaterability of the derived HTT solid fractions as well as the contents of ash and carbon in the recovered solid fractions (Ebrahimi et al., 2022). In that study, further investigation showed that for the similar biomass type and lower water contents in the derived HTT solid fractions corresponded to higher concentrations of organic acids in the HTT liquid fractions (Ebrahimi et al., 2022). The improved dewaterability was attributed to the hydrolysis of extracellular polymeric substances (EPS) of sludge, especially EPS proteins. At a sludge-biomass total solids (TS) mass ratio of 1:1, the organic acids generated from HTT could lead to reduced water contents of the derived solid fractions (after hydraulic press) to less than 40.0% (Ebrahimi et al., 2022). Moreover, it was also observed that besides the generated organic acids from biomass, biomass type also affected the dewaterability of the derived solid fractions, which was likely due to the different skeleton effects of different biomasses (Wang et al., 2020).

It was hypothesized that apart from the different effects of biomass type on sludge dewaterability, the differences in physical structure and chemical composition of different biomasses can also affect the recovery of nutrients and removal of heavy metals from sludge. The two basic reasons include different leaching effects of organic acids generated in HTT and different adsorption performance of the derived HTT solid residues due to the variations in physio-chemical properties. Moreover, other interactions, such as N-catalyzed transformation by biomass-derived organic acids (Huang et al., 2017; Huang and Tang, 2016; Wang et al., 2021), can also impact the nutrient recovery. Understanding of the effects of biomass type on heavy metal removal and nutrient recovery is important for selecting biomass in HTT of sludge to generate solid residues for different applications. Despite the increasing interest in blending biomass for sludge HTT, the effects of biomass type on the recovery of nutrients and selective removal of heavy metals have not been previously investigated.

Following the authors' previous study on the investigation of the effect of biomass type on deep dewatering of sludge, in the present study, the effects of biomass type on recovery of N, P, macro-nutritional metals, and removal of toxic and heavy metals in HTT derived solids were investigated. Furthermore, since a sludge-biomass TS ratio of 1:1 led to relatively low water contents of resulting solid fractions, only the samples generated at the sludge-biomass TS ratio of 1:1 was investigated. In addition, in this study, recovery and characterization of solid fractions were the focus since potential applications of the solid fractions depend on their properties. The liquid fractions after HTT and mechanical separation were expected to be returned to WWTPs for further treatment and/or use. This study provided useful and fundamental information on selection of lignocellulosic biomass for blending with sludge in HTT to generate treated solids for potential soil or solid fuel applications.

2. Materials and methods

2.1. Materials

Digested sludge used in this study was collected from a local treatment plant in Brisbane (Queensland, Australia), which mainly treats wastewater generated from the urban area. The sludge was generated from anaerobic digestion of primary and waste activated sludge for biogas production. Digestated sludge was dewatered by industrial centrifugation to a water content of ~80% in the wastewater treatment plant. The collected digested sludge samples were kept in a freezer for further use. Sawdust samples (softwood and hardwood) and sugarcane bagasse were purchased from a local timber mill and sugar mill (Gold Coast, Australia), while rice husks were collected from a rice mill in Deniliquin (New South Wales, Australia). Chemicals of analytical grade or above were purchased from Thermo Fisher (Australia) or Sigma-Aldrich (Australia). Table 1 shows the basic properties of the feedstocks.

Table 1
Main physicochemical properties of the feedstocks.

	Raw sludge	Hardwood Sawdust	Softwood Sawdust	Sugarcane bagasse	Rice husk
Moisture (%)	81.7	51.4	25.5	57.5	6.7
Ash (% TS)	24.0	0.4	0.3	4.2	22.5
Cellulose (% TS)	–	54.2	39.8	44.3	34.8
Hemicellulose (% TS)	–	11.6	16.5	23.2	20.3
Lignin (% TS)	–	30.8	37.8	24.7	21.7
Acetyl (% TS)	–	2.4	3.2	5.3	2.5
C (% TS)	39.2	48.9	50.4	43.8	35.3
H (% TS)	6.2	6.0	5.8	5.9	4.7
O (% TS)	22.6	44.6	43.6	45.9	36.2
N (% TS)	6.3	0.1	0.1	0.2	0.4
S (% TS)	1.7	0.0	0.0	0.0	0.9
Ca (g/kg)	21.2	0.8	0.5	0.3	0.8
K (g/kg)	3.3	0.4	<0.1	1.6	5.2
P (g/kg)	27.5	0.1	<0.1	0.2	0.5
Fe (g/kg)	20.6	<0.1	<0.1	0.7	0.1
Al (g/kg)	12.5	<0.1	<0.1	1.0	0.1
Mg (g/kg)	8.4	0.3	<0.1	0.2	0.4
Na (g/kg)	2.4	0.0	0.0	0.1	0.1
Co (mg/kg)	15.8	0.0	0.2	0.6	0.1
Cr (mg/kg)	37.8	0.0	0.0	6.2	3.9
Cu (mg/kg)	595.3	0.7	3.7	1.5	2.3
Ni (mg/kg)	55.8	0.0	0.0	2.7	10.3
Pb (mg/kg)	28.7	0.0	0.0	0.0	0.0
Zn (mg/kg)	802.8	3.8	4.0	10.3	12.6

2.2. HTT experiments

The HTT trials of sludge alone and sludge-biomass mixture (at 1:1 sludge-biomass TS ratio (w:w)) were conducted at temperatures of 180, 210, and 240 °C for 60 min. The biomass and sludge samples were used as received without further sample processing and water addition, which would simulate the operational conditions for industrial application. The detailed reaction conditions were explained previously by the authors (Ebrahimi et al., 2022). It is worth noting that initial water contents in the biomass-sludge mixtures ranged from 69.0% (with bagasse) to 74.0% (with rice husk), depending on the water content in biomass samples. HTT treated sludge samples were collected and solid-liquid fractions separated by an automatic hydraulic press (SpectroPress®, Chemplex Industries, USA) at 24 MPa for 2 min. All the HTT trials were conducted in duplicate.

2.3. Analytical methods

2.3.1. Compositional analysis of treated solid residues

Sample moistures, ash contents, and volatile solids (VS) were measured as described in our previous studies (Cai et al., 2021; Ebrahimi et al., 2022). After HTT and pressing, test samples were dried and then milled using a knife mill through a 2.0 mm mesh. Milled samples were collected for further analysis. 3.0 mg of milled samples were measured in standard capsules for carbon, hydrogen, nitrogen, sulphur, and oxygen (CHNS/O) analysis with the FlashSmart™ Elemental Analyzer (Thermo Fisher Scientific, USA). Elemental compositional analysis was performed in duplicate. To simulate the operational conditions for industrial applications, solid fractions after HTT and mechanical press were directly dried without wash to remove the residual liquids.

The content of heavy metals in dried milled solid was determined by an acid hydrolysis method as previously described (Cai et al., 2021). Briefly, about 60.0 mg of samples were dissolved in an acid mixture of distilled HNO_3, HCl and HF (with a ratio of 1:3:1 v/v), in TFM (modified polytetrafluoroethylene (PTFE)) tubes. After 10 min sonication, the tubes were sealed and then placed in a single reaction chamber microwave system (Milestone Sorisole (BG), Italy) (1500 W, 100 bar and 220 °C). Samples were then placed in a hot block at 85 °C to remove fluorides from the samples. All samples were diluted with 2.0% HNO_3 and the elements determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (PerkinElmer Optima 8300 DV, USA). The analysis was conducted in triplicate.

2.3.2. Determination of elemental composition and surface functional groups of treated solid residues

A portion of the dried sample was crushed into a fine powder and X-ray photoelectron spectrometry (XPS) was used to investigate the surface elements and corresponding functional groups transformation before and after HTT using a Kratos AXIS Supra X-ray photoelectron spectrometer (Shimadzu, Japan). The spectrometer was equipped with a monochromated Al Kα source (1486.7 eV) and a concentric hemispherical analyzer. Calibration and correction were applied for all data to compensate the charge from neutralizer. The ash composition of raw and HTT solids was determined by the X-ray Fluorescence spectroscopy (XRF) (Rigaku SmartLab XRD, Japan) and the results were presented as oxides.

2.4. Calculations

The TS yield, P and N recoveries were calculated based on the following Eqs (1)–(3):

$$TS\ yield\ (\%) = \frac{\text{TS in solid fraction after HTT (g)}}{\text{TS in feedstock (g)}} \times 100 \tag{1}$$

$$P\ recovery\ (\%) = \frac{\text{Total amount of P in solid fraction after HTT (g)}}{\text{Total amount of P in sludge/biomass mixture before HTT (g)}} \times 100 \tag{2}$$

$$N\ recovery(\%) = \frac{\text{Total amount of N in solid fraction after HTT (g)}}{\text{Total amount of N in sludge/biomass mixture beforeHTT (g)}} \times 100 \tag{3}$$

It is worth noting that comprehensive mass balance, which considered the distributions of N and P in solid and liquid fractions (and even gas phase for N) after HTT were not undertaken as this study aimed to recover solid fractions for further applications.

2.5. Statistical analysis

Statistical analysis was applied with the use of IBM SPSS software (version 28.0) when data comparison was required. Statistical analysis was conducted using a one-way analysis of variance (ANOVA) and Post hoc tests for the comparison of mean values between samples. Prior to ANOVA test, homogeneity of data was also checked by the Levenes test. A p-value less than 0.05 ($p < 0.05$) was considered statistically significant.

3. Results and discussion

3.1. Basic feedstock properties

Table 1 shows the basic properties of the sludge and the four biomasses. The sludge sample had a relatively high moisture even after dewatering and high levels of N (6.3%) and P (27.5 g/kg) as well as relatively high levels of general metals and heavy metals. The four biomasses were used as received. The rice husk sample had the lowest moisture of only 6.7%, followed by softwood sawdust (21.0%). Rice husk also had the highest ash content of 22.5%. Hardwood sawdust had the highest cellulose content of 54.2% but the lowest hemicellulose content of 11.6% while rice husk had the lowest cellulose contents of 34.8%. Softwood sawdust had the highest lignin content, followed by hardwood sawdust of 37.8%. Regarding acetyl groups, sugarcane bagasse had the highest content of 5.3%. It was noted that rice husk contained relatively high levels of Cr, Ni and Zn compared to the other biomasses.

Table 2
XPS spectra of relative contents of oxygen functionalities (O1s) at HTT temperatures of 180 °C and 240 °C for untreated sludge, HTT of sludge alone and sludge-biomass solid residues.

Feedstock type		HTT Temp. (°C)	Relative intensities (%)[1]		
			O=C	O–C	C–OH/COOH
Untreated sludge		–	37.7 ± 4.2	47.6 ± 3.2	14.7 ± 2.4
Sludge blended with	No biomass	180	31.8 ± 4.1	44.6 ± 6.5	23.6 ± 3.7
		240	35.3 ± 5.0	42.0 ± 6.1	22.7 ± 3.2
	Hardwood	180	18.1 ± 4.3	46.8 ± 5.2	35.1 ± 4.1
		240	33.9 ± 4.8	45.2 ± 3.7	20.8 ± 2.8
	Softwood	180	26.3 ± 5.2	46.7 ± 3.8	27.0 ± 4.6
		240	25.3 ± 3.8	50.2 ± 5.3	24.5 ± 3.9
	Bagasse	180	29.4 ± 5.0	33.2 ± 5.4	37.4 ± 3.9
		240	30.6 ± 3.3	33.4 ± 5.0	36.1 ± 4.1
	Rice husk	180	36.6 ± 4.4	35.1 ± 3.4	28.3 ± 3.1
		240	31.1 ± 6.0	50.1 ± 4.8	18.8 ± 2.6

Note: 1. O=C, O–C, and C–OH/COOH functional groups were obtained at binding energy of 531.8, 532.8 and 533.5 eV, respectively.

3.2. Effects of biomass type on oxygen-containing functional groups of solid residues after HTT

Oxygen-containing functional groups such as carboxyl groups, lactone/carbonyl groups and hydroxyl groups derived from lignocellulosic biomass play important roles in binding/adsorption of nutrients and metals ions in sludge during HTT (Tasca et al., 2019; Zhang et al., 2017). The types and abundances of these groups are related to biomass composition. As shown in Table 1, the four biomasses used in this study had different compositions. During HTT, a series of reactions such as decarbonylation, decarboxylation, dehydration and depolymerization can happen in lignocellulosic biomass, resulting in generation of furanic and/or cyclic structures with various oxygen-containing functional groups (Titirici et al., 2015; Zhang et al., 2017). In addition, between the components of lignocellulosic biomass (cellulose, hemicellulose, lignin, acetyls, *etc.*) and sludge (protein, lipid, *etc.*), some reactions such as Maillard reaction can also occur, leading to the production of both nitrogen- and oxygen-containing functional groups (Peng et al., 2017; Zhang et al., 2017). It was expected that biomass composition and HTT temperature would impact the types and abundances of oxygen-containing groups of resulting HTT solid residues, thus affecting nutrient recovery and metal removal from digested sludge.

Table 2 shows the types and relative abundances of oxygen-containing functional groups on the surface of solid resides from HTT at 180 °C and 240 °C. At 180 °C, the relative abundance of C–OH and COOH groups of solid residues from HTT of sludge-bagasse and sludge-hardwood mixtures were highest, followed by those from sludge-rice husk and sludge-softwood mixtures. However, those functional groups from HTT of sludge alone was the lowest. At 240 °C, the relative abundance of C–OH and COOH of solid residue from HTT of sludge-bagasse mixture was much higher than all the others. At 180 °C, the relative abundance of C–OH and COOH was likely related to the abundance of carbohydrates (contributing C–OH) in biomass as hardwood and bagasse had the highest contents of carbohydrates. At 240 °C, the relative abundance of COOH might have increased in the total abundance of C–OH and COOH and this increase was associated with the production of carboxylic acids during biomass decomposition and hydrolysis. Sugarcane bagasse had a high content of acetyl groups (Table 1). HTT of sludge-bagasse mixture also led to the highest concentration of organic acids (especially acetic acid) (Ebrahimi et al., 2022), which might result in the integration of carboxylic acid (-COOH) groups to the solid residues. Therefore, C–OH and –COOH groups play important role in the formation of hydrogen bonding network, complexation, and adsorption/binding with cations (Almanassra et al., 2021; Lindholm-Lehto, 2019), which would affect the nutrient recovery and heavy metals removal.

3.3. Effect of biomass type on ash composition in solid residues after HTT

Digested sludge and biomasses contained ashes at different levels (Table 1). For instance, raw and untreated sludge and rice husk had the highest ash contents of 24.0% and 22.5%, respectively, while the ash contents were very low in the two woody sawdust samples. After HTT, the ash contents of all the samples increased compared to those without HTT and the treated samples with higher ash contents were derived from those untreated samples with higher ash contents (Table S1). Furthermore, increasing HTT temperature from 180 °C to 240 °C further increased the ash contents (Table S1).

Table 3 shows the relative abundances of oxide minerals in ashes of untreated sludge and treated samples at 180 °C and 240 °C. Overall, for the same type of sample, the effect of temperature on the relative abundances of oxide minerals was marginal. Furthermore, for the biomass with low ash content, such as hardwood and softwood sawdust samples, the relative abundances of oxide minerals of treated samples were similar to those of untreated sludge and sludge treated without biomass. Due to the high ash contents of sugarcane bagasse and rice husk, the relative abundances of oxide minerals were significantly different from others. It was worth noting that silica was the dominant ash component in the treated solids from sludge-rice husk mixtures due to the high silica content in rice husk. Both inorganic (silicic acid and

Table 3
Relative abundances of oxide minerals in ashes of untreated sludge and HTT-solid residues at 180 °C and 240 °C.

Feedstock type		HTT Temp. (°C)	Content (wt.%)							
			Al_2O_3	CaO	Fe_2O_3	MgO	P_2O_5	SO_3	SiO_2	Other
Untreated sludge		–	10.0	12.9	13.9	5.3	26.7	8.3	17.2	5.7
Sludge blended with	No biomass	180	10.1	12.9	14.0	5.6	27.4	7.6	17.1	5.3
		240	10.3	12.9	14.2	6.5	29.0	6.0	16.4	4.7
	Hardwood	180	10.6	12.9	14.6	5.8	28.0	5.4	17.4	5.3
		240	10.8	12.7	14.7	6.1	28.6	5.3	17.0	4.8
	Softwood	180	11.1	13.2	14.9	5.4	27.6	3.9	18.0	5.9
		240	11.1	12.6	14.9	5.6	27.3	6.4	16.7	5.4
	Bagasse	180	10.8	10.2	13.7	4.0	23.8	4.6	28.0	4.9
		240	10.8	10.3	13.3	4.4	24.1	4.9	27.5	4.7
	Rice husk	180	5.6	6.5	7.4	2.6	14.2	1.2	58.5	4.0
		240	5.8	6.8	7.8	2.9	15.3	1.9	55.6	3.9

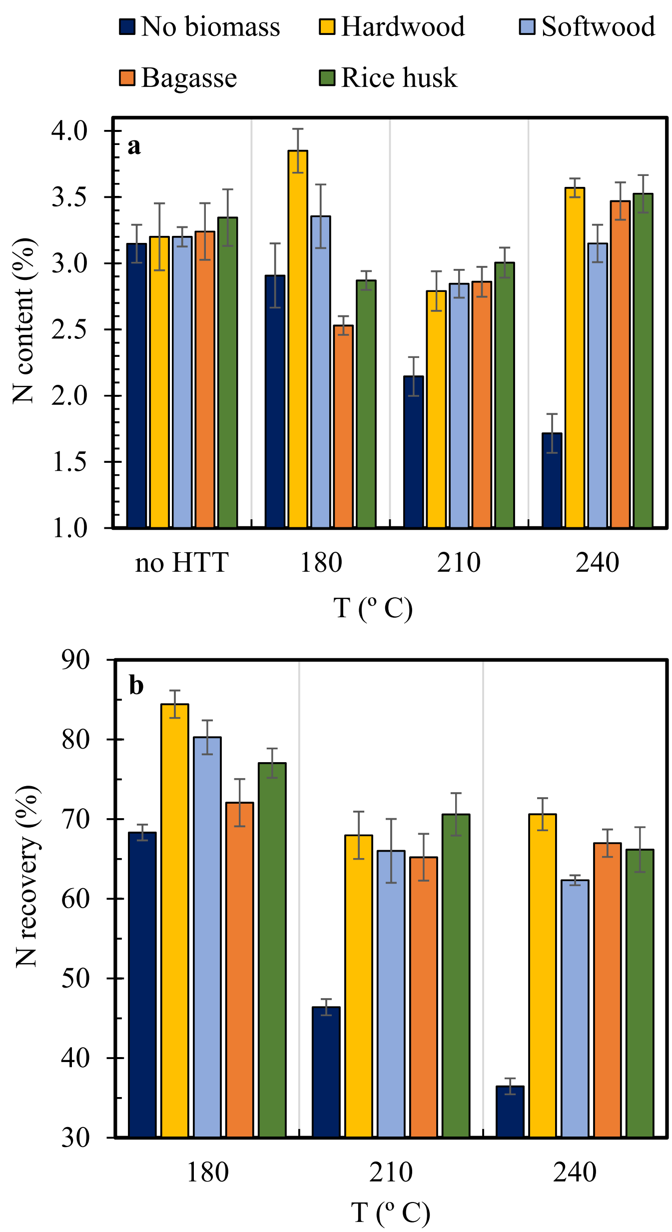

Fig. 1. Content (a) and recovery (b) of N in raw feedstocks and HTT solid residues at different temperatures.

silicates) and organic (*e.g.,* silicate esters) silicates exist in biomass silica structure (Nordin, 1994; Tortosa Masiá et al., 2007; Vassilev et al., 2017), which might influence adsorption of metals during HTT of sludge.

3.4. Effect of biomass type on nitrogen content and recovery

The authors previously studied the effect of biomass type in HTT on sludge dewaterability (Ebrahimi et al., 2022). In the present study, the focus was also on the comprehensive understanding of the effect of biomass type on the physio-chemical properties of dewatered solid fractions, which is important for their applications. Table S1 shows the moisture, TS yield, content of ash and major elements (C, H, N, S and O) after HTT. Except for the elemental composition, other data were published recently by the authors (Ebrahimi et al., 2022). Overall, blending biomass with HTT of sludge at TS ratio of 1:1 improved the dewaterability, decreased the ash contents, and increased the contents of carbon and oxygen of treated solid residues. As previous reported, the dewaterability improvement was largely attributed to the hydrolysis of EPS by organic acids from lignocellulosic biomass (Ebrahimi et al., 2022). Dilution effect led to the reduced ash content of treated solid residues with the use of biomass for HTT, especially at low temperatures though the ash contents were also related to the biomass type and composition (Table S1).

Fig. 1 shows N contents and recoveries in treated solid residues. It should be noted that the N contents of biomass-free samples shown in Fig. 1a were the halved values of the determined values in order to eliminate the dilution due to blending biomass (at a biomass:sludge mass TS ratio of 1:1) for comparison of the N contents of treated sludge-biomass samples. Real N content values of biomass-free samples are presented in Table S1. Without biomass, increasing HTT temperature from 180 °C to 240 °C led to a significant N content reduction from 2.9% to 1.7% compared to the initial N content of 3.2% as shown in Fig. 1a. HTT at 180 °C increased N content in solid residues with woody biomasses compared to that without biomass. Furthermore, HTT at 210 °C and 240 °C increased N contents in solid residues with all the biomasses compared to those without biomass at the same temperatures. Regarding the effect of temperature, without biomass, increasing HTT temperature from 180 °C to 240 °C reduced N content. With biomass, the effect of temperature on N content varied. With woody biomass, the N content decreased with increasing temperature from 180 °C to 210 °C, then increased with increasing temperature from 210 °C to 240 °C. With sugarcane bagasse and rice husk, N content increased with increasing temperature from 180 °C to 240 °C. The N content change with and without biomass at different HTT temperatures was related to (1) reduced N content due to the leaching of N-containing compounds from sludge, *e.g.,* hydrolysis of proteins to soluble small amino acids and peptides, (2) increased N content due to the loss of lignocellulose components especially carbohydrates and also non-nitrogen components in sludge by decomposition, and (3) increased N content due to the binding/adsorption of N-containing compounds (Wang et al., 2021, 2022).

Fig. 1b shows N recoveries with different biomasses at HTT temperatures of 180–240 °C, which considered both the N contents in the solid residues and the yields of TS after HTT. The use of biomass led to the significant N recoveries compared to those without using biomass at all HTT temperature (Fig. 1b). Overall, increasing HTT temperature reduced N recovery though the differences became less obvious at HTT temperatures of 210 °C and 240 °C. At the lowest HTT temperature of 180 °C, the use of two sawdust samples led to the highest N recoveries, which were 12.0%–16.0% higher than that without biomass ($p < 0.05$). Moreover, at the higher HTT temperature of 210 °C and 240 °C, N recoveries with different biomasses were significantly higher than those without biomasses.

The results from the present study were in line with the observations from previous studies, which found that higher N recoveries were obtained with the use of lignocellulosic biomass than HTT of sludge alone (Wang et al., 2021; Zhang et al., 2017). Furthermore, at 180 °C, the trend of N recovery with biomass was in line with N content in Fig. 1a. At 240 °C, N recovery with hardwood appeared to be the highest while its N content level was almost similar to those with rice husk and sugarcane bagasse, due to the differences in the TS yield after HTT.

HTT temperature and biomass type also affected the types and relative abundances of different forms of N. In untreated sludge, N existed as protein-N (34.5%), quaternary-N (14.4%), pyrrole-N (15.2%) and inorganic-N (35.9%) while nitrile-N and pyridine-N were not detected (Ebrahimi et al., 2022). During HTT, protein-N was transformed to different forms of N such as inorganic ammonium salts, quaternary ammonium, nitrile, pyridines, pyrrolidines and pyrazines (Aragón-Briceño et al., 2021; Leng et al., 2021; Wang et al., 2021). A series of reactions including hydrolysis, decarboxylation, deamination, polymerization, and condensation reactions occur during HTT and the detailed transformation mechanisms have been well explained in previous studies (Aragón-Briceño et al., 2021; Leng et al., 2021; Wang et al., 2021).

Table 4
XPS spectra of relative abundances of nitrogen functionalities (N1s) at HTT temperatures of 180 °C and 240 °C for untreated sludge, HTT of sludge alone and sludge-biomass solid residues.

Feedstock type		HTT Temp. (°C)	Relative intensities (%)[1]					
			Pyridine-N	Nitrile-N	Protein-N	Pyrrole-N	Quaternary-N	Inorganic-N
Untreated sludge		–	–	–	34.5 ± 1.6	15.2 ± 2.7	14.4 ± 3.1	35.9 ± 4.2
Sludge blended with	No biomass	180	1.5 ± 0.5	15.6 ± 1.1	47.6 ± 6.2	18.7 ± 2.1	9.6 ± 0.9	7.0 ± 1.1
		240	4.8 ± 0.7	18.1 ± 1.8	20.7 ± 2.4	25.0 ± 3.1	23.2 ± 3.7	8.2 ± 2.0
	Hardwood	180	13.8 ± 0.9	14.0 ± 1.9	22.8 ± 2.6	20.5 ± 4.3	24.9 ± 3.7	4.1 ± 0.5
		240	21.8 ± 1.2	15.6 ± 0.6	6.7 ± 1.0	29.7 ± 5.1	21.5 ± 2.8	4.6 ± 1.2
	Softwood	180	13.2 ± 1.3	13.2 ± 2.0	29.6 ± 3.2	19.3 ± 0.7	20.6 ± 2.0	4.1 ± 0.3
		240	11.6 ± 0.9	26.1 ± 1.4	13.0 ± 2.1	30.7 ± 3.7	5.5 ± 0.8	13.1 ± 2.3
	Bagasse	180	8.4 ± 0.6	14.9 ± 2.5	24.2 ± 3.4	23.3 ± 1.6	24.8 ± 5.2	4.5 ± 1.0
		240	6.4 ± 1.8	35.7 ± 4.8	9.7 ± 3.1	24.1 ± 2.2	22.2 ± 1.2	1.9 ± 0.5
	Rice husk	180	6.6 ± 1.4	23.8 ± 2.0	28.5 ± 2.6	12.8 ± 0.7	16.1 ± 1.1	12.2 ± 1.7
		240	21.0 ± 2.3	24.3 ± 1.2	13.2 ± 2.4	22.8 ± 3.2	10.8 ± 0.4	8.0 ± 2.1

Note: 1. Pyridine-N, Nitrile-N, Protein-N, Pyrrole-N, Quaternary-N, and Inorganic-N groups were obtained at binding energy of 398.8, 399.7, 400.1, 400.6, 401.5 and 402.3 eV, respectively.

Table 4 shows that the types of N and their relative abundances in the solid residues after HTT at 180 °C and 240 °C, respectively. In all the treated samples, the abundance of inorganic-N was reduced significantly from 35.2% in untreated sludge to 2.0%–12.2% in treated solid residues, which was likely due to the removal of inorganic-N by leaching (Ebrahimi et al., 2022). At 180 °C and without biomass, the abundance of protein-N increased in the treated sludge compared to untreated sludge, likely due to more significant loss of inorganic-N. After HTT with biomass, different types of N were fairly evenly distributed, which was attributed to the accelerated deamination of protein-N with the production of other forms of more stable N through polymerization and cyclization. At 240 °C, the relative abundance of protein-N was further reduced though the relative abundance of protein-N in sludge treated without biomass was still the highest. Biomass type also affected the relative abundances of different forms of N. For instance, the solid residue from HTT of sludge-rice husk at 180 °C had relatively low abundances of quaternary-N and pyrrole-N but a high abundance of nitrile-N. After HTT at 240 °C, the relative abundances of different forms of N were further differentiated: the solid residue from HTT of sludge-softwood had the lowest abundance of quaternary-N while the solid residue from sludge-bagasse had the lowest pyridine-N.

The detailed reaction pathways and reaction mechanisms are likely related to biomass composition, functional groups and HTT temperatures. For instance, sugarcane bagasse had the highest content of acetyl groups and HTT led to the highest concentration of organic acids (especially acetic acid) and lowest pH in the HTT liquid (Ebrahimi et al., 2022). As a result, at the low HTT temperature of 180 °C, leaching of inorganic N and hydrolysis of protein-N by organic acids with the use of sugarcane bagasse were more significant than those with other biomasses, leading to the lowest N content (Fig. 1a). At 180 °C and with the use of hardwood sawdust, this was the opposite case (Fig. 1a), which was attributed to the low content of acetyl groups and resulting low concentration of organic acids (Ebrahimi et al., 2022). At higher HTT, the reaction pathways were more complicated, due to the generation of different forms of N and interactions with oxygen-containing functional groups generated in HTT. The available amine-N groups due to the decomposition of sludge protein-N can react with the oxygen-containing functional groups such as C–OH and COOH from biomasses on the surface of HTT solids, thus increasing the N content by activating and introducing multiple N-functional groups (Leng et al., 2020, 2021). For instance, COOH groups can be replaced (through decarboxylation) with the organic N-containing functional groups such pyridine-N and pyrrole-N groups and form multiple heterocyclic rings of N-compounds in the HTT solid fractions (Guo et al., 2016; Leng et al., 2021) as also previously suggested that the higher carbohydrate contents can promote the higher N retention in HTT derived solids (Leng et al., 2021; Li et al., 2019). As shown in Table 2, the oxygen-containing functional groups

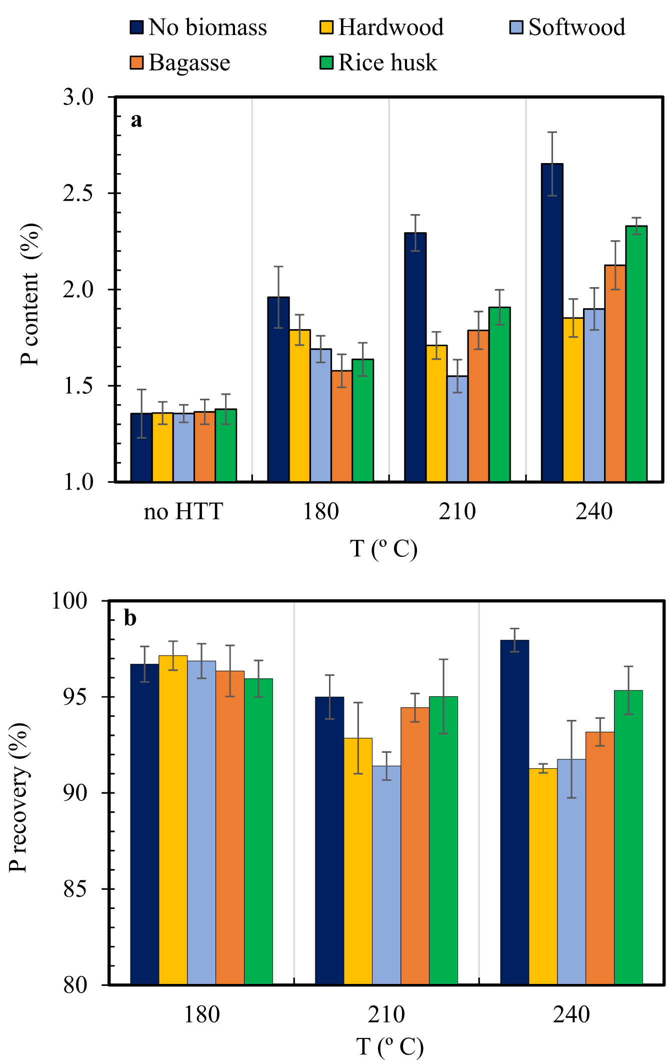

Fig. 2. Content (a) and recovery (b) of P in raw feedstocks and HTT solid residues at different temperatures.

significantly varied among the sludge-biomass solids which in addition to the effect of pH changes in the HTT, also confirms the diverse results of N recovery in HTT solids. Overall, the results showed that biomass helped to immobilize N compared to HTT without biomass and biomass type affected N content and N forms in solid residues from HTT treatment. Oxygen-containing functional groups and acetyl groups (pH changes) from biomass type likely accounted for the difference in N recoveries in HTT solids from sludge-biomass mixtures. Moreover, the N forms likely affect the bioavailability of N, which should be further investigated in future studies.

3.5. Effect of biomass type on phosphorus content and recovery

P and potassium (K) are the other two most important primary fertilizer components for plant growth in addition to N. P in sludge mainly exists as organophosphate (*e.g.,* phytic acid, phosphate mono- or diesters), polyphosphate and inorganic phosphate (Yu et al., 2021). The former two are mainly from the biological removal of P while the latter one is from the chemical removal (Yu et al., 2021). Although the compositions of these phosphates vary depending on the source of sludge, P in organophosphate and polyphosphate in general dominates the total P (Huang et al., 2017). The P content was relatively high in untreated sludge while the level of K was comparably low and therefore it did not elaborate further on the present study.

Fig. 2a shows the P contents in the solid residues after HTT. The presented P contents of biomass-free samples were halved in order to eliminate the dilution effect due to biomass blending. In general, the P contents in solid residues from HTT of sludge-biomass mixtures were reduced compared to that from HTT of sludge alone, which was in line with the results from a previous study on HTT of sludge-pinewood sawdust mixture at a sludge-pinewood TS ratio of 1:1 (Zhang et al., 2017). Furthermore, increasing HTT temperatures from 180 °C to 240 °C resulted in increased P contents in solid residues except for those two from the two woody biomasses. Fig. 2a also shows that biomass type has affected P content. At 180 °C, the solid residue from HTT of sludge-hardwood sawdust had the second highest P content but that from HTT of sludge-bagasse had the lowest P content. At 210 °C and 240 °C, the solid residues from HTT of sludge-sugarcane bagasse had the highest P contents. Fig. 2b demonstrates the P recoveries which have considered both P contents and the yields of solid residues after HTT. In all tested HTT conditions, P recoveries were relatively high, ranging between 91.0%–98.0%. Overall, the trend of P recovery was similar to that of P content (Fig. 2a). At 180 °C, the P recoveries in all the solid residues were similar while at 240 °C, the P recovery in the solid residues from HTT of sludge-rice husk mixture was the highest.

The reasons behind P content change were similar to those for N content change. Like transformation of protein-N to other forms of N, P-containing compounds were also transformed other forms of P during HTT. The detailed transformation mechanisms have been well explained in the recent review papers (Aragón-Briceño et al., 2021; Huang et al., 2017; Yu et al., 2021). Firstly, organophosphate and polyphosphate are hydrolyzed to soluble phosphate along with the solubilization of insoluble phosphate (Huang et al., 2017). Following hydrolysis and solubilization, the presence of a high level of Ca ions in sludge leads to the formation of insoluble $Ca_3(PO_4)_2$ and other calcium-phosphate complexes such as hydroxyapatites ($Ca_5(PO_4)_3(OH)$) (Aragón-Briceño et al., 2021; Huang et al., 2017; Yu et al., 2021; Zheng et al., 2020). Additionally, the presence of high levels of Al and Fe cations not only results in the production of corresponding phosphate salts but also generation of Al/Fe (hydro)oxides, which immobilize phosphate by adsorption (Huang et al., 2017; Yu et al., 2021; Zheng et al., 2020). Other metal cations such as Zn, Mg and Cu can also react with P with the production of insoluble phosphate salts (Aragón-Briceño et al., 2021).

The difference in acetyl content (Table 1), oxygen-containing functional groups (Table 2), and ash content (Table 3) of biomass type were likely the main contributing factors from biomass type which led to different P recoveries outcomes in the derived HTT solids from sludge-biomass mixtures at similar HTT temperatures. For example, the relatively high P content in the solid residue from HTT of sludge-rice husk mixture at 210° and 240 °C (though not significant compared to sugarcane bagasse at 210 °C) was likely related to the formation of apatite in the presence of high levels of silica. Rice husks had a high ash content of 22.4% and the majority of the ash components were silica (Tables 1 and 3). Unlike quartz sand silica, rice husk silica is amorphous and rich in silanols. Silanols are relatively stable under the temperature of 250 °C, especially in the aqueous solutions (Ahmaruzzaman and Gupta, 2011; Potapov and Zhuravlev, 2005). Studies have shown silanols participated in the formation of apatite (Takadama et al., 2000). Oxygen-containing groups such as C–OH and COOH may also participated in the formation of apatite, which might explain the relatively high P content in the solid residue from HTT of sludge-bagasse at 240 °C (Table 2 and Fig. 2a). Moreover, no additional water was added to the HTT process and the differences in the initial water content of sludge-biomass mixtures were less than 5.0%. It is likely that these slight dissimilarities had no significant effect on the total P contents among the sludge-biomass mixtures, especially at the higher HTT temperatures as it was suggested that digested sludge and HTT liquid of sludge have a strong buffering capacity and pH of HTT played an important role in the distribution of total P between solid and liquid products (Huang et al.,

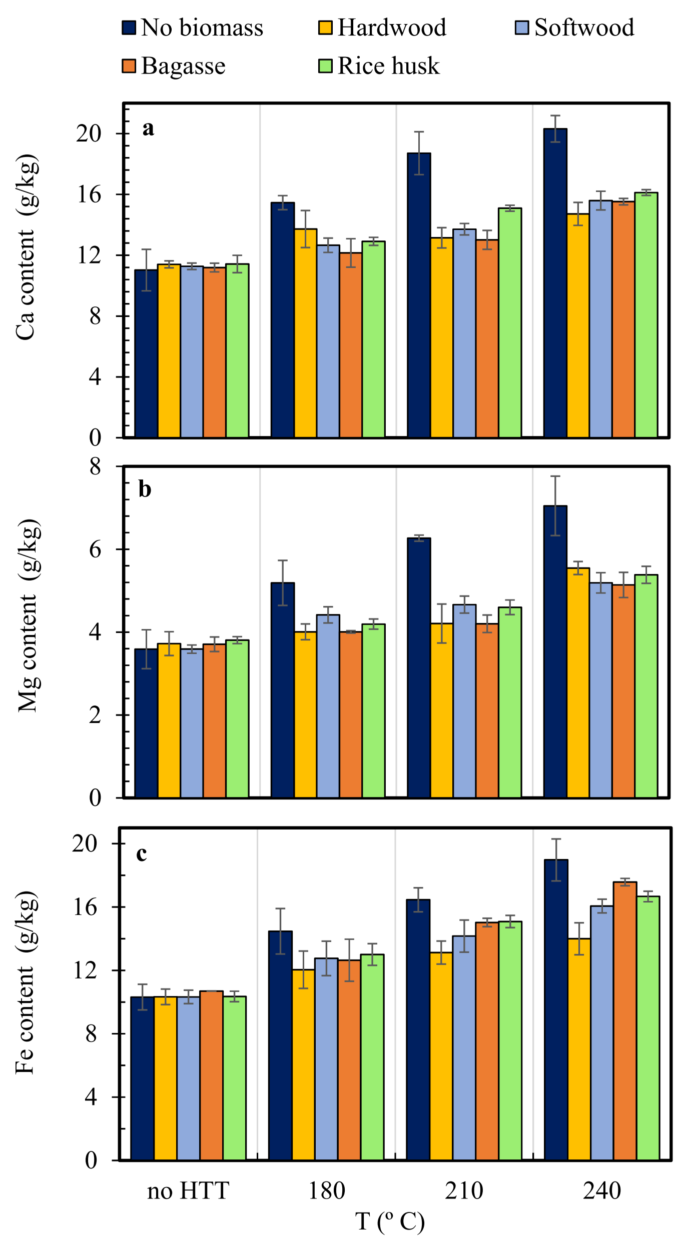

Fig. 3. Contents of Ca (a), Mg (b) and Fe (c) in untreated feedstocks and HTT treated solid fraction at different temperatures.

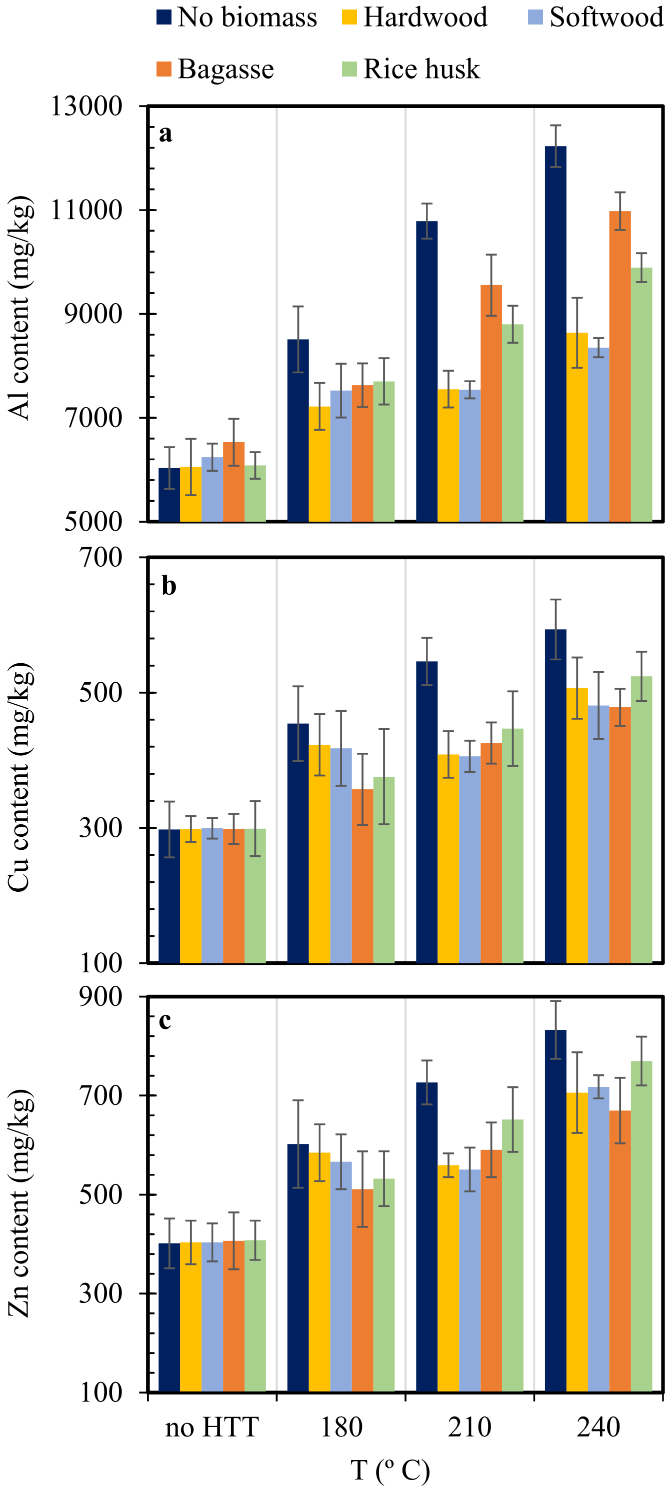

Fig. 4. Contents of Al (a), Cu (b) and Zn (c) in untreated feedstocks and HTT treated solid residues at different temperatures.

2017; Huang and Tang, 2016; Zheng et al., 2020). Although the effect of both biomass type and additional water on the forms of P compounds and their bioavailability as a fertilizer source should be investigated in the future.

3.6. Effect of biomass type on metal contents

In addition to the two-primary fertilizer components (N and P), sludge also contained relatively high levels of Ca, Fe and Mg (Table 1), which are essential macro-nutritional metals required for plant growth. Ca and Mg likely came from the original source of drinking water though Ca may also come from other sources such as neutralization agents. The high Fe content was due to the use of $FeCl_3$ as an odor control agent and a flocculant for sludge thickening in the WWTPs (Rebosura et al., 2020). In addition to these metals, sludge also contains Al and heavy metals such as Zn, Cu and others (Table 1). These metals are generally regarded as toxic to human beings. Among these metals, the contents of Al, Zn and Cu were quite high in untreated sludge (Table 1). The high content of Al was likely from Al-containing coagulants such as aluminum sulfate and aluminum chloride added for wastewater treatment, while the high contents of Zn and Cu were likely from domestic and industrial wastewaters, corrosion of sewerage network, and surface runoff from urbanized areas or roads (*e.g.,* galvanized materials and car washes) (Cantinho et al., 2016; Rebosura et al., 2020).

Figs. 3–5 show the effects of biomass type and HTT temperature on the contents of macro-nutritional metals (Ca, Fe and Mg), the contents of macro-toxic metal (Al) and macro-heavy metals (Zn and Cu), as well as the contents of trace heavy metals (Ni, Cr, Pb and Co), respectively. Again, it should be noted that the presented metal contents of the biomass-free samples were halved in order to eliminate the dilution effect from biomass blending. In general, increasing HTT temperature led to the increase of these metal ions contents and without biomass, the increase was more significant compared to those with biomass. Regarding macro-nutritional metals, the use of hardwood sawdust resulted in the highest Ca content at the lowest HTT temperature of 180 °C but the lowest Ca content at the highest HTT temperature of 240 °C (Fig. 3). In contrast, the use of rice husk led to the highest Ca content at higher HTT temperatures of 210 °C and 240 °C. The use of hardwood sawdust resulted in the lowest Fe contents at all the tested HTT temperatures while sugarcane bagasse led to the highest Fe content at the highest HTT temperature of 240 °C. The effect of biomass type on Mg content varied among biomasses at different temperatures.

Regarding the macro-toxic and heavy metals, the use of two sawdust biomasses led to the lowest Al contents while sugarcane bagasse resulted in the highest contents at HTT temperatures of 210 °C and 240 °C (Fig. 4). In terms of Zn, sugarcane bagasse led to the lower or the lowest contents at the tested HTT temperatures while rice husk resulted in the highest contents at HTT temperatures of 210 °C and 240 °C. Furthermore, the effect of biomass type on the Cu content varied at different temperatures while HTT of sludge with sugarcane bagasse was able to generate solid residues with relatively low Cu contents.

Biomass type also had a significant effect on the contents of trace-heavy metals (Fig. 5). The use of rice husk caused a significant higher Ni content level than the other biomasses at all the tested HTT temperatures. In terms of Cr, HTT of sludge-sugarcane bagasse ended up with the solid residues with the highest Cr contents while rice husk led to the lowest contents at HTT temperatures of 210 °C and 240 °C. For Pb, the effects of biomass type at the lowest and highest temperatures were reversed while almost similar results were observed at the middle temperature of 210 °C for HTT of sludge with different biomass types. Moreover, the use of rice husk led to the highest Co contents at all the tested temperature while softwood sawdust caused the lowest Co contents at the HTT temperatures of 210 °C and 240 °C.

The reasons and mechanisms behind the changes of metal contents were likely to be more complicated than those for N and P due to the overall effects of the biomass-derived functional groups, organic acids, and the interaction with ash components such as silica (Shi et al., 2013). The general mechanisms for the adsorption of metals by biomass and hydrothermally treated biomass have been extensively studied and well summarized in the published review reports (Lindholm-Lehto, 2019; Liu et al., 2021). The major adsorption mechanisms include surface sorption, electrostatic interaction, precipitation and complexation, which are related to surface functional groups, especially oxygen-containing functional groups such as carboxyl (-COOH), lactone/carbonyl (-C=O) and phenolic hydroxyl (-OH) groups (Liu et al., 2021). In addition, the

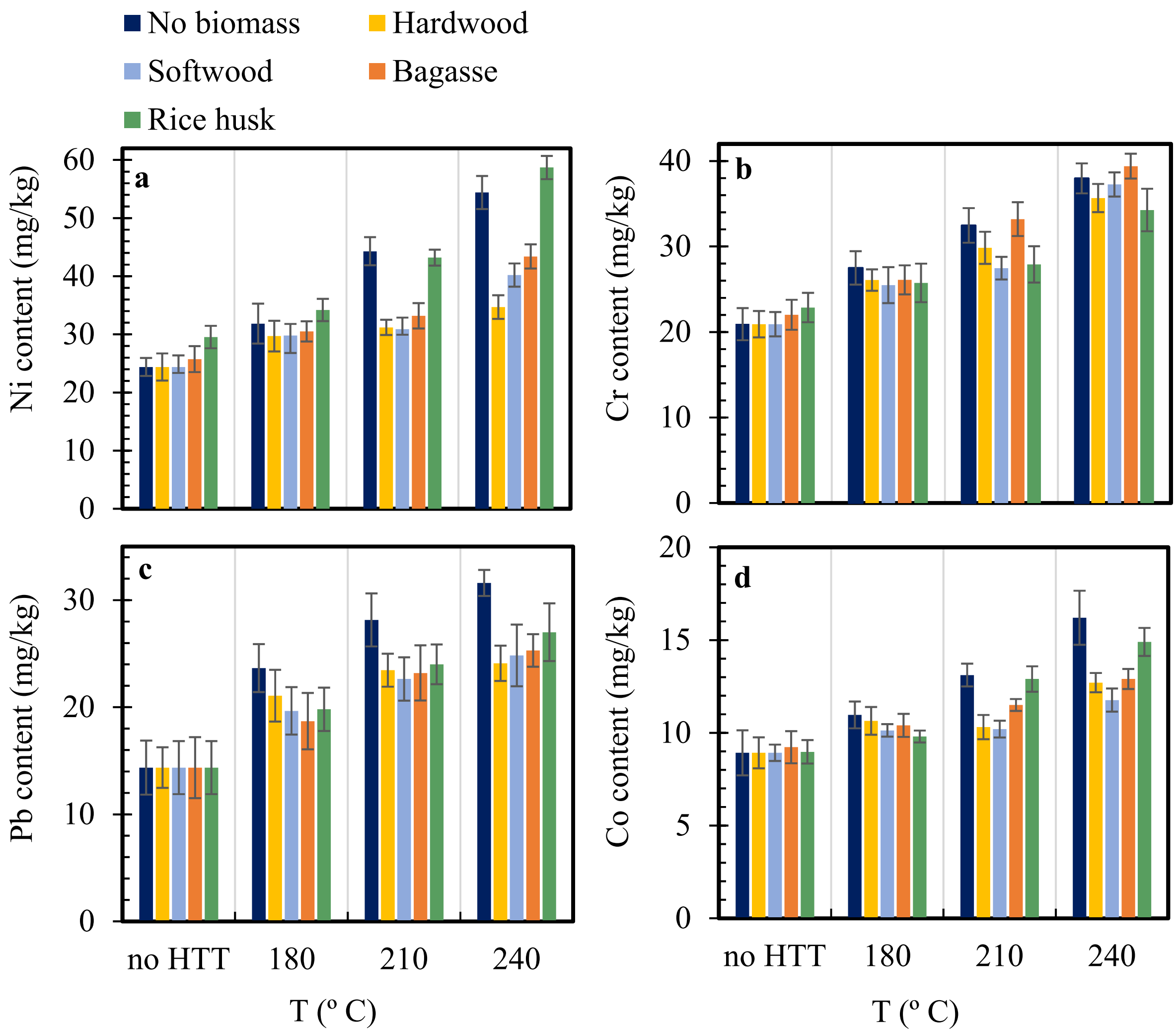

Fig. 5. Contents of Ni (a), Cr (b), Pb (c), and Co (d) in untreated feedstocks and HTT treated solid residues at different temperatures.

silanols in ash silica might also interact with metal ions through complexation. The relative high contents of Ca, Zn, Cu, Ni and Co in solid residues from HTT of sludge-rice husks at 210 °C and 240 °C might be related to the high silica content (Tables 1 and 3) (Ahmaruzzaman and Gupta, 2011). In a previous study (Shi et al., 2013), it was observed that the use of rice husk in HTT of sludge immobilized heavy metals (Cu, Ni, Cr and Cd) and reduced the leaching of heavy metals, which was attributed to the synergistic effect of silicate and other oxygen-containing groups. Moreover, as discussed previously, the high content of Ca was also related to the formation of apatite and associated with the high P recovery, in which silanols might also participate. The high content of Al and Cr in the solid residues from HTT of sludge-bagasse mixture at 210 °C and 240 °C were likely related to the relative high abundance of C–OH and COOH groups (Table 2). Overall, the mechanisms of binding/adsorption of metals are very complicated and the metal content results are the reflection of synergistic effects of leaching effects of organic acids and metal interactions with different functional groups. Nevertheless, the results showed that biomass type affected metal removal in the HTT of sludge.

4. Conclusion

In this study, the effects of biomass types on the contents of nitrogen, phosphorus, and metal ions in digested sludge as well as the recoveries of nitrogen and phosphorus from digested sludge after HTT were investigated. The results showed that the variations in biomass compositions affected the biomass-derived organic acids, such as acetic acid, oxygen-containing functional groups, and ash (*e.g.,* silica), subsequently affecting the recoveries of nutrients and metal ions. Nitrogen contents and recoveries were mainly affected by biomass-derived organic acids and oxygen-containing functional groups. The contents of P and metal ions were determined by the overall effects of leaching by organic acids and interactions with biomass-derived functional groups and silica. This study provided useful information in the selection of lignocellulosic biomass in HTT of sludge for nutrient recovery and heavy metal removal. It is recommended that future studies focus on the investigation of bioavailability of nutrients and metals in the HTT solids for soil applications and the performance of the HTT solids as adsorbents for wastewater treatment or solid fuels for energy generation.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.115524.

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