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Migration and transformation mechanism of phosphorus in waste activated sludge during anaerobic fermentation and hydrothermal conversion

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Abstract:

This study investigated migration and transformation mechanism of P in waste activated sludge (WAS) during anaerobic fermentation (AF) process and the subsequent hydrothermal conversion (HTC) process. Control of pH during the AF processes was found to be significant, whereby the use of acidic ($pH = 5.5$) or alkaline conditions ($pH = 9.5$) facilitated the release of either apatite phosphorus (AP) or non-apatite inorganic phosphorus (NAIP) and organic phosphorus, respectively. At the same pH of 9.5, NaOH promoted the transfer of P into liquid phase, and P in the solid phase was mainly in the form of NAIP. In contrast, $Ca(OH)_2$ enhanced the incorporation of P into the solid products, with the P mainly in the form of AP. The subsequent HTC process promoted the NAIP transferred to AP, and the bioavailability of P in the HTC solid products was decreased. The P K-edge X-ray absorption near edge structure analysis provided detailed information about the phosphates. It demonstrated that the conversion of $Ca_8H_2PO_4 \cdot 6.5H_2O$ to $Ca_5(PO_4)_3 \cdot OH$ was facilitated by HTC under the alkaline condition. This study sheds lights on transformation mechanism of P speciations during AF and HTC processes, which would provide fundamental information for effective utilization of P in bio-wastes.

Key words: Waste Activated Sludge (WAS); Anaerobic Fermentation (AF); Hydrothermal Conversion (HTC); Phosphorus (P); X-ray Absorption Near Edge Structure (XANES)

1. Introduction

Phosphorus is an essential element for the growth and survival of all living organisms. In recent years, phosphorus ore has become a scarce resource due to high fertilizer demand from a global increasing population. In addition, the global distribution of phosphorus ore is uneven (e.g. Morocco and Western Sahara occupy more than 70% of phosphate ore in the world) and could lead to significant fluctuation and instability in the price of the resource (Heilmann et al., 2014; Meng et al., 2019).

As a by-product of waste water treatment plants, large amounts of waste activated sludge (WAS) containing abundant organics are produced. These can cause serious environmental problems if not properly treated. In addition, phosphorus is also accumulated in WAS via biological removal and chemical precipitation from waste water (Fischer et al., 2011; Lin et al., 2003). Thus, WAS can be regarded as a potential source of phosphorus reclamation.

Anaerobic fermentation (AF) is regarded as an effective way to convert sludge into valuable products (Liu et al., 2016; Wang et al., 2016). For example, large amounts of volatile fatty acids (VFAs) are produced by AF and they are useful raw materials in many chemical and biological reactions (e.g. as a carbon source for denitrification). Many researchers have investigated VFA production during fermentation processes (Esteban et al., 2018; Lin et al., 2009; Yu et al., 2010; Zhang et al. 2009; Zou et al., 2018), and they found that alkaline conditions promoted the production of VFA from WAS. Alkaline AF conditions are usually obtained by the addition of NaOH, while $Ca(OH)_2$ was also used to adjust the pH of AF process due to the bad dewatering performance of NaOH and its higher cost.

In addition, P was released from phosphorus accumulating organisms during the AF process, which was also affected by pH (Chen et al., 2019; Zou et al., 2018). Previous studies investigated P release from sludge at different pH. It was found that pH adjustment was the most effective method to release P among different sludge treatment methods (Liu et al., 2019). Shi et al. found that the optimum conditions for P release in biofilm sludge treatment processes were at the pH values of 5 and 10 (Shi et al., 2019a). The results of Latif revealed that low pH (< 5.7) caused a 3.6 times increase in phosphorus release compared to neutral pH (7-7.7) (Latif et al., 2015).

Some chemical and physical reactions such as precipitation and adsorption relating to P-containing species are pH dependent. Recently, most previous studies just focused on P release behavior of the AF liquid phase. The different P speciations formed under different AF pH and the related transformation mechanism are still unclear, especially with different alkalis (NaOH or $Ca(OH)_2$). However, it is very important for the further utilization of P in the AF solid phase by investigating the P speciations.

It should be noted that only 30-40% of the volatile suspended solid (VSS) in WAS were hydrolyzed and utilized for VFA production, and considerable amount of VSS was present in the AF residues (Zhang et al., 2009). The rest part of VSS is difficult to be biologically converted and could be further treated by hydrothermal conversion (HTC). Because HTC is an energy-efficient technique to achieve the reutilization of bio-wastes and enhance the dewatering performance of various sludges (Gao et al., 2019; Wang et al., 2017, 2019).

However, there are no current studies combining AF and HTC for the treatment of WAS, and in-depth investigation on the transformation mechanism of P during the combined processes is extremely limited, which is very important for the further recovery and reutilization of P obtained from WAS.

Based on the above considerations, this research aimed to study the effect of different pH and different alkalis on the changes of P speciations and its transformation mechanism of WAS under the processes of AF and HTC. Since WAS was a complex matrix, different techniques were used to systematically investigate the P speciations. Normally, P speciations are identified by chemical extraction methods, while in-depth analysis has not been conducted. X-ray Absorption Near Edge Structure (XANES) has the specific advantage in identifying phosphates, and XANES linear combination fitting (LCF) could provide detailed information about the relative abundances of different P compounds. This study firstly combined the AF and HTC processes, and focused on the P behavior during the two processes. It will provide some fundamental knowledge on P reclamation and WAS reutilization strategies.

2. Materials and methods

2.1 WAS

WAS with water content of 98.93 ± 0.11% was obtained from a secondary sedimentation tank in Quyang waste water treatment plant (located in Shanghai, China) with an anaerobic/anoxic/aerobic process. The main characteristics of WAS are as follows: total suspend solids (TSS) of 10.5±0.9 g/L, volatile suspend solids (VSS) of 7.4±0.8 g/L, and pH value of 6.9±0.1. The ash content of WAS was about 31.0%, and the content of C, H and N were about 30.8%, 5.46% and 31.0%, respectively. The detailed metal element contents of the WAS are illustrated in section 3.3.

2.2 AF treatment with different pH

The AF experiments at different pH were conducted in four 2 L serum bottles with 1.6 L WAS. The pH was adjusted to 5.5 and 7.5 by adding HCl and NaOH solution respectively. The AF treatment at pH of 9.5 was adjusted by using either NaOH or $Ca(OH)_2$. All the serum bottles were flushed with N_2 in order to achieve anaerobic conditions before being sealed. The bottles were maintained in an orbital shaker incubator at a mesophilic temperature of 37 ±1 °C. The pH was adjusted to the desired value of 5.5, 7.5 and 9.5 every 12 hours. Samples were taken regularly for P and VFAs analyses. After 12 days, the AF products were centrifuged (10,000 rpm for 20 min at *ca*. 25°C) and separated to solid and liquid phases. The liquids were filtered and refrigerated in a 4°C fridge. The solids were dried at 80°C to constant weight for further analyses, and the moisture of solid products were measured. The samples obtained at different AF pH and alkaline additions were labeled as A5.5, A7.5, A9.5 (NaOH condition) and A9.5Ca ($Ca(OH)_2$ condition), respectively.

2.3 HTC treatments

The AF residues were further used for HTC treatment, which were performed using an autoclave hastelloy reactor with a volume of 250 mL. The reactor was tightly sealed and controlled by a programmable heating device. Previous studies indicated that hydrothermal temperatures greater than 150 °C resulted in the decomposition of some biopolymers and led to the generation of free water (Wang and Li, 2015), and a residence time of 30 min promoted a substantial conversion in the sludge surface properties (Wang et al., 2014). In order to balance financial considerations and HTC performances, AF residues with different pH were treated at 170 ºC for 30 min. The HTC products were centrifuged (10,000 rpm for 20 min at *ca*. 25 ºC) and separated to solid and liquid phases. The hydrolysates were filtered and refrigerated in 4ºC fridge. The solids were dried at 80 ºC to constant weight for further analyses, and the moisture of solid phases were measured. Accordingly, samples obtained after HTC process were labeled as H5.5, H7.5, H9.5 and H9.5Ca.

2.4 SMT method

The SMT (Standard Measurement and Testing) method was used to analyze the various P forms contained within the WAS, as well as the AF and HTC products. SMT method has been widely used in the analyses of soil, sediment and sludge samples (Bairq et al., 2018; Huang et al., 2015; Xie et al., 2011). After sequential extraction based on SMT, P in the WAS samples was divided into the following 5 categories: total P (TP), organic P (OP), inorganic P (IP), non-apatite inorganic P (NAIP, i.e. the P fraction associated with oxides and hydroxides of Al, Fe and Mn), and apatite P (AP, i.e. the P fraction associated with Ca). The TP was extracted by 3.5M HCl, and the IP was extracted by 1M HCl. The residue after IP extraction was treated at 450ºC, and then extracted by 1M HCl to test the OP content. As to NAIP and AP, the samples were firstly extracted by 1M NaOH, and the supernatants were further extracted by 3.5M HCl to test the NAIP contents. The residues after the 1M NaOH extraction were further extracted by 1M HCl to test AP contents. The OP and NAIP were regarded as bio-available P (Huang et al., 2015; Xie et al., 2011). The concentrations of phosphorus in the supernatants collected after extraction were detected in triplicate via the molybdenum blue method.

2.5 P K-edge XANES Analysis

All P K-edge X-ray Absorption Near Edge Structure (XANES) data were collected at Beijing Synchrotron Radiation Facility (4B7A). The WAS, AF and HTC solid products were ground into fine powders and brushed evenly on the conductive adhesive. Excess powder was subsequently removed in order to achieve a homogeneous thin film. The XANES data were obtained in fluorescence mode using a silicon drift detector. XANES spectra were collected at 2120-2200 ev according to previous literatures (Kruse et al., 2008, 2010). As phosphorus was mostly combined with some metals such as Mg, Fe, Al and Ca in WAS, the following compounds were selected as reference compounds: $Mg_3(PO_4)_2$, $FePO_4$, $AlPO_4$, $Ca_5(PO_4)_3 \cdot OH$ (HAP) and $Ca_8H_2PO_4 \cdot 6.5H_2O$ (OCP).

Data analyses were performed using the Athena software. All spectra were carefully calibrated, normalized and subjected to linear combination fitting (LCF). All combinations of reference compounds were used to fit each sample.

2.6 Other characterization analyses

The VFAs contents of different AF liquid samples were detected by GC-FID (GC-2010, SHIMADZU, Japan). The samples were separated by a Stabilwax-DA column (30m×0.32mm×0.25μm, PEG-20M, 30 m×0.32 mm×0.50 μm) with N_2 as carrier gas. The metal concentrations of AF and HTC samples were detected by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8000, Perkin Elmer, USA) and the mean of two replicates are presented. The XPS results were obtained by using an X-ray photoelectron spectrometer (PHI Corporation, Japan, type PHI5000C). The synchrotron radiation XRD data were collected at Beijing Synchrotron Radiation Facility (4B9A). The SEM images were obtained by using a field emission scanning electron microscope (7800F Prime, JEOL, Japan).

2.7 Statistical analysis

The independent variance T tests were conducted to compare the OP contents of WAS and the AF residues. The statistical analyses were performed using the program package SPSS 21 (IBM Corporation, USA) and the significance was assigned at the $p < 0.05$ level.

3. Results and Discussion

3.1 Effect of pH on the VFAs and moisture contents of AF and HTC products

It was noted that the enhanced biological phosphorus remove performance lied in the presence of adequate volatile fatty acids (VFAs) in the waste water (Yuan et al., 2011). Therefore, it is necessary to detect the VFAs contents of the fermentation liquids.

Fig. S1 presents the VFA contents of WAS fermentation liquids at different pH values. It is observed that the total VFAs concentration of AF supernatants under alkaline conditions (A9.5 and A9.5Ca) were much higher than that of other conditions (A5.5 and A7.5) after 12 days fermentation. This is because alkaline condition promoted the hydrolysis of WAS, which provided more soluble substrate to produce VFAs. The main composition of extracellular polymeric substances (EPS) of sludge, protein and carbohydrate were more easily released at alkaline pHs due to the dissociation of acidic groups in EPS and the repulsions between the negatively charged EPS. (Zhang et al., 2009). The increased total VFAs concentrations of sample A9.5 and A9.5Ca were mainly caused by the increase of acetic acid, indicating that alkaline condition could promote the production of acetic acid during the AF process. In addition, the activity of methanogens was reduced under alkaline AF condition. Therefore, the accumulation of VFAs was enhanced under alkaline AF conditions (Zou et al. 2018).

Furthermore, it should be notable that the 12 days VFAs concentration (1705.89 mg/L) of sample produced using $Ca(OH)_2$ (A9.5Ca) was much lower than that of A9.5 (2617.48 mg/L), which is due to the detrimental effect of Ca^{2+} precipitation on sludge hydrolysis and protein acidification efficiency. (Li et al., 2017).

The moisture contents of the AF and HTC solid products after centrifugation are shown in Tab. S1. It was found that after the AF process, the moisture contents were 82.28%, 84.61%, 83.41% and 81.60% for sample A5.5, A7.5, A9.5 and A9.5Ca, respectively. After the HTC processes, they decreased to 70.48%, 69.74%, 72.11% and 63.20%. It was obvious that HTC significantly enhanced the dewatering performance of AF solid residues. The use of $Ca(OH)_2$ resulted in the best dewatering performance after the AF and HTC processes, whereby the moisture of sample H9.5Ca decreased by 35.73%, when compared with the WAS sample.

It is worth mentioning that the dewatering performance under $Ca(OH)_2$ mediated conditions was better than that of NaOH. This is because $Ca(OH)_2$ could enhance granulation and it was able to re-flocculate the sludge floc and soluble organic polymers, increase floc density and floc strength, as well as to decrease the amount of bound or inter-floc water (Ahmad et al., 2011; Li et al., 2008). However, Na^+ released by NaOH can exchange with divalent cations in the WAS, which would weaken the strength of floc structure and deteriorate the dewaterability (Higgins and Novak, 1997).

3.2 P distribution and speciation changes after AF and HTC processes

3.2.1 P distribution after AF process

After the 12 days AF processes, the distribution of P in solid and liquid products were measured. As shown in Fig.1, the distribution ratios of P in the liquid products with different pH decreased in the order of A9.5 > A5.5 > A7.5 > A9.5Ca. The AF products at the pH of 9.5 with NaOH addition had the highest P distribution in the liquid phase (30.86%), whilst almost all the P was distributed in the solid phase when $Ca(OH)_2$ was instead used. The P distribution results were predominantly a reflection of the different amounts of P released in the liquid phase. The details are illustrated in Fig.2.

Fig.2 highlights the fact that most P was released in the initial 6 days' fermentation, and there was no obvious variation in P concentration after 6 days' fermentation. The release of P at different pH was also in the order of A9.5 > A5.5 > A7.5 > A9.5Ca. The greatest release of P (191.23 mg/L) was achieved at the pH of 9.5 with the addition of NaOH. There are three factors that contributed to this result. Firstly, with the increase of OH^-, more NAIP of the WAS were released into the AF supernatant, the detailed mechanism is illustrated in section 3.2.3. Secondly, as shown in 3.1, A9.5 generated the largest concentration of VFAs, which provided an efficient carbon source for the P release of phosphorus-accumulating bacteria under anaerobic condition (Huang et al., 2019). Thirdly, under the alkaline conditions, there is a greater release of OP from WAS, which is also demonstrated in section 3.2.3. OP released from extracellular polymeric substances or microbial cells could be converted to PO_4^{3-} by microbes (Xie et al., 2011). Interestingly, when $Ca(OH)_2$ was used, the supernatant had the lowest P concentration (3.05 mg/L) , with large amounts of Ca^{2+} precipitated with the released PO_4^{3-}, which decreased the P concentration in the supernatant. The acidic AF condition (A5.5) gave the second largest P release amongst the four samples. This was mainly attributed to the effect of H^+, which caused P release from inorganic P (such as Ca-P, Al-P, Mg-P and Fe-P) of WAS. Section 3.2.3 and 3.4 will further verify these results.

3.2.2 P distribution after HTC process

Fig.1 also shows the P distribution of different HTC products. The proportions of P in the liquid phases were 10.41%, 7.96%, 11.17% and 0.78% for samples H5.5, H7.5, H9.5 and H9.5Ca, respectively. It was found that more P was distributed in the solid phase after the HTC process, which was due to the enrichment effect of HTC process (Shi et al., 2019b). Even at the same pH of 9.5, sample H9.5 had the largest P distribution in the liquid phase, while sample H9.5Ca had the largest P distribution in the solid phase. It illustrates that alkaline AF residues with NaOH also had the promotion effects on P release during the HTC process, whereas significant precipitation of Ca-P compounds occurred in the solid phase upon the use of $Ca(OH)_2$. The liquid phase under acidic conditions (H5.5) had the second highest P distribution, which demonstrates that acidic AF residues could promote the release of P during the HTC process.

As shown in Tab. S2, the released P in the AF and HTC liquid products were mainly in the form of PO_4^{3-}, which is consistent with previous literatures (He et al., 2016; Liu et al., 2019). In addition, the formation and range of P-containing speciations in the solid phase were more complex than that of the liquid phase (Qian and Jiang, 2014). Therefore, different techniques were performed to systematically characterize these P speciations in the solid phase.

3.2.3 Characterization of P speciations after AF process

Fig.3 shows the concentration and proportion of P speciations in the AF residues by SMT method. It can be seen that the TP concentration of the AF residues at the pH of 5.5 and 9.5 were both lower than that of the WAS. For sample A5.5, it was mainly attributed to the decrease of IP, which was caused by the dissolution effect of H^+ under acidic conditions. For sample A9.5, it was due to the release of NAIP and OP. The detailed reasons are illustrated in the following parts. Correspondingly, the AF residue at the pH of 7.5 had the largest TP concentration of 30.44 mg/g. It should be noted that the AF supernatant under $Ca(OH)_2$ mediated alkaline condition had the lowest P concentration, and the P distribution in the solid phase under this condition was the highest. However, the TP concentration of the solid phase was also the lowest observed (23.09 mg/g). This is because the AF solid mass in the presence of $Ca(OH)_2$ (*ca.* 236 g) was much larger than other conditions (*ca.* 125-140 g), as a results of Ca-associated precipitations. There was a considerable amount of precipitated Ca that did not involve P, such as $CaCO_3$ (demonstrated in section 3.4) in sample A9.5Ca. Therefore, the solid yield was the largest, but the TP concentration of the solid product generated under

$Ca(OH)_2$ mediated condition was lower than that of other samples.

In addition, according to Fig.3 (a) and (b), the proportions of IP (all > 80%) were much larger than that of OP among all samples, indicating that most of the phosphate anion was combined with metal ions in WAS and AF residues. Notably, the OP concentration of the AF residue at the pH of 9.5 with NaOH (2.60 mg/g) was significantly ($p < 0.05$) less than that in the residue produced at pH 5.5 (3.09 mg/g) and WAS (3.22 mg/g), according to the independent variance T test (the details are shown in Tab.S3). The results indicate that more OP was hydrolyzed from WAS under alkaline condition with NaOH mediated, which further verify the reason why sample A9.5 has the largest P release in section 3.2.1. Even though the OP concentration of the AF residue under $Ca(OH)_2$ condition (2.97 mg/g) was also less than that of A5.5 and WAS, there was no significant decrease (p > 0.05). The results provide further evidence that the hydrolysis effect of NaOH is much more pronounced than that of $Ca(OH)_2$.

As shown in Fig. S2, P 2*p* XPS analysis of the WAS and AF samples were conducted. It was readily observed that the P 2*p* peaks of the different samples could be deconvoluted into two components. The peak of 134ev was assigned to C-O-P, which was related to organic phosphorus (Qian et al., 2019). The peak of 133ev was assigned to Ortho-P/Pyro-P, and it was mainly associated with metals, which could be regarded as inorganic phosphorus (Huang et al., 2015). The proportions of peak areas (shown in Tab.S4) can be used to semi-quantitatively analyze the P speciations.

As shown in Tab. S4, the proportion of Ortho-P/Pyro-P (>70%) was much larger than that of C-O-P in the WAS and AF residues. Therefore, it implied that most P was combined with metal ions and can be regarded as IP. In addition, the proportion of C-O-P decreased with the increase of pH value, indicating that alkaline AF condition promoted the hydrolysis of OP. The results are consistent with the analysis based on SMT method.

Fig.3 (c) and (d) show the concentration and proportion of NAIP and AP in different AF residues and the WAS sample. It was observed that the AP concentration (0.47 mg/g) decreased significantly when treated in acidic conditions (pH = 5.5), by comparing with WAS (3.05 mg/g). However, there was no obvious changes for the NAIP concentration. It implied that acidic condition could obviously promote the dissolution of Ca-associated P (AP), in comparison to some other metal associated P (NAIP) during the AF process. Thus Ca-associated P was more sensitive to acidic conditions than other metal-associated P. This can be attributed to the positive effect of H^+ on Ca-P dissolution, which was enhanced at lower pH and hence resulted in more Ca-P being dissolved (Latif et al., 2015; Wang et al., 2015). With the increase of pH, the concentration and proportion of AP increased gradually, which implied that alkaline conditions could promote the formation of AP. The AF residue generated with the addition of $Ca(OH)_2$ had the largest AP concentration (17.17 mg/g) and proportion (94.28%), which was due to the combination of Ca^{2+} and PO_4^{3-} from the supernatant. At the pH of 9.5, the concentrations of NAIP were much lower than that of other samples, which indicated the release of NAIP under higher pH values. Ion exchange effect of OH^- was occurred under the alkaline conditions. OH^- could dissolve Al-P and combine with Fe^{3+}, which had previously been bound to phosphate anions. Following this, P was then liberated from Al-P compounds and Fe-P compounds on account of precipitation-dissolution and ion exchange reactions (He et al., 2016). The chemical equation were as follows: $AlPO_4 + 4OH^- \leftrightarrow AlO_2^- + 2H_2O + PO_4^{3-}$; $FePO_4 + 3OH^- \leftrightarrow Fe(OH)_3 + PO_4^{3-}$.

3.2.4 Characterization of P speciations after HTC process

Fig.4 presents the concentration and proportion of P speciations that were detected following HTC treatment. Fig.4 (a) shows that the TP concentrations of different HTC solid products increased by 35.35% (H5.5), 34.00% (H7.5), 33.19% (H9.5) and 36.18% (H9.5Ca), compared with that of AF solid products. These results suggest the significant P enrichment effect of the HTC process. It was also observed that the increase of TP concentration was mainly attributed to the increase of IP. However, the OP concentrations were decreased, indicating that the hydrolysis of OP took place over the HTC processes. Owing to the relatively low HTC temperature (170 °C), there was still *ca.* 5% OP remaining in the TP of solid products (Fig.4 (b)).

According to the P 2*p* XPS results (Fig. S2), the proportions of Ortho-P/Pyro-P in HTC solid products were higher than that of the AF residues. The percentages of C-O-P in A5.5 (29.60%), A7.5 (26.83%), A9.5 (24.77%) and A9.5Ca (22.54%) decreased significantly to 21.98% (H5.5), 20.67% (H7.5), 17.58% (H9.5) and 14.98% (H9.5Ca) after the HTC process, which suggested that certain amounts of organic phosphorus in the AF residues hydrolyzed and converted to Ortho-P/Pyro-P during the HTC treatment. The results were in agreement with the SMT analyses as discussed above.

As shown in Fig.4 (c), the concentrations of NAIP and AP increased significantly, with the increase in AP concentration being markedly more pronounced than that of NAIP. It is noted from Fig.4 (d) and Fig. 3 (d) that the proportion of AP increased to 3.78% (H5.5), 15.74% (H7.5), 22.15% (H9.5) and 96.04% (H9.5Ca), compared with that of 2.31% (A5.5), 10.43% (A7.5), 15.49% (A9.5) and 94.28% (A9.5Ca) in the AF residues. These results implied that the HTC process promoted the conversion of NAIP into AP, on account of the greater stability of the latter.

3.2.5 P bioavailability analyses of AF and HTC solid products

Some soluble phosphates which could be released and utilized by plants are defined as bio-available P. According to the study of Ruban (Ruban et al., 2001), NAIP and OP are regarded as bio-available P. Because NAIP are easily to be released, absorbed and utilized by organisms. OP could be mineralized by microorganism and release some soluble phosphates. The soluble phosphates may combine with active Fe^{3+}, and then converted to some Fe-P compounds, which could be utilized by organisms.

As shown in Tab. S5, the percentages of bio-available P (OP and NAIP) reached a maximum value under acidic AF conditions (97.99%) and decreased gradually with the increase of pH values. Under the alkaline AF condition with $Ca(OH)_2$, the percentages of bio-available P was the lowest (18.69%). After the HTC process, the proportion of bio-available P were decreased, which can be attributed to the release of OP and the increased contents of AP.

3.3 Metal contents of the AF and HTC products

As mentioned above, the P contained within WAS, AF and HTC solids were mainly in the form of IP, which were combined with metal ions. Therefore, it was necessary to analyze the metal contents of the different samples. The results are shown in Tab. S6.

It could be found from the results that the concentrations of Mg, Al, Ca and Fe were much greater than other metals in all the solid samples, suggesting more P combined with such metals. Tab. S7 presents the molar ratios of Mg, Al, Fe and Ca to P, which shows the Al/P ratio was much higher than the others, implying that the Al associated P compounds may occurred most frequently. Furthermore, the concentrations of Na in A9.5 and H9.5 were much higher than the others, which is a consequence of the addition of NaOH for the adjustment of pH. Similarly, the Ca contents in sample A9.5Ca and H9.5Ca were far greater than those of others, which could be attributed to the addition of $Ca(OH)_2$.

Under acidic conditions (pH = 5.5), the concentrations of most metals were decreased, compared with that of WAS. As Na and K associated compounds are more soluble and unstable, the concentration of Na and K decreased much more than others. By comparing the concentration changes of Mg, Al, Ca and Fe, the decrease of Mg and Ca are much larger than that of Al and Fe, indicating that Mg and Ca elements are more sensitive to H^+. The decreased concentration of Ca was consistent with the decreased amount of AP under acid anaerobic fermentation, which was illustrated in 3.2.3. With the increase of pH value, the metal concentration increased gradually, which was due to the precipitation of metal ion and OH^-. What worth mentioning was that, except the element of Ca, the other metal concentrations of AF residue under $Ca(OH)_2$ condition was lower than that of NaOH, even at the same pH value. The main reason was that large amounts of Ca^{2+} could compete with other metal ions to form more Ca associated precipitations.

After the HTC process, the concentration of Na and K in the solid products decreased significantly. This is because Na and K associated compounds were not stable under HTC process, large amounts of Na^+ and K^+ transferred to the liquid phase. The change trends of Mg, Al, Ca and Fe are similar to that of AF residues. However, the concentrations of these elements in HTC solid products were higher than that of AF residues, which was due to the enrichment effect of HTC process and the changes in physical structure of the solid products. After the HTC process, the solid products became more porous (shown in section 3.6), which would absorb more metal ions.

Tab. S8 shows the metal concentrations presented in the AF and HTC liquid phases. For the AF samples, almost all the metal concentrations obtained the maximum value at the pH of 5.5, except the Na and Ca concentrations for samples prepared using NaOH and $Ca(OH)_2$. The metal concentrations mainly follow a decreasing trend with the increase of pH value. The results were consistent with that of the solid products, which was due to the effect of H^+, leading to more metal ions being dissolved in the liquid phase under the acidic AF condition. After the HTC process, the concentration of metal ions mainly followed an increasing trend, compared with that of the AF liquid products. It indicated that HTC process has a more positive effect on the release of metal ions than that of the AF process. The change trends of the metal concentrations between different HTC liquids were similar to that of the AF liquids.

It was found that the Mg concentrations of the liquid samples A9.5Ca and H9.5Ca were much higher than that of sample A9.5 and H9.5. This is because the large existence of Ca^{2+} competed with Mg^{2+} to form precipitates, leading to a greater retention of Mg^{2+} in the liquid phase (Munir et al., 2017). The XANES LCF results in section 3.5 would further verify this phenomenon.

3.4 XRD analysis

In order to identify the formation of P-containing minerals in different samples, XRD analysis was conducted. As can be seen in Fig. S3, the changes in mineral compositions were apparent after the AF and HTC processes. Fig. S3 (a) shows that the P minerals were mainly associated with Al, Mg, Ca and Fe in WAS. The Ca-associated P minerals disappeared after AF process under acidic conditions (pH = 5.5). An increase in pH (to 7.5 and 9.5) (Fig. S3 (b)) resulted in the formation of $Ca_3(PO_4)_2$ and $CaPO_3(OH)$ in the AF residues, thus indicating that a relatively high pH promoted the generation of Ca-associated P minerals. These results verified the analysis of section 3.2.3, which also showed that the Ca-P content increased with the increase of pH value.

On the other hand, there was an obvious generation of $CaCO_3$ crystalline phase (calcite) in the AF residue with $Ca(OH)_2$ addition (Fig. S3 (c)), thus indicating that the AF treatment with $Ca(OH)_2$ addition promoted the formation of $CaCO_3$, due to the production of CO_2 during the AF process. This also verified that there were some Ca-associated precipitates that did not contain P, as mentioned in section 3.2.3.

The AF residues also contained a certain amount of valuable minerals such as vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ and struvite $NH_4MgPO_4 \cdot 6H_2O$. Vivianite and struvite precipitations are both regarded as highly efficient methods for the recovery of phosphorus originated from sludge (Law et al., 2019; Munir et al., 2017; Uysal et al., 2010; Wang et al., 2017). Therefore, the AF residue has the potential to be utilized as an agricultural fertilizer, and further techniques should be developed in order to reclaim such minerals.

Fig. S3 (d) shows the mineral compositions of the HTC solid products. It suggests that some mineral compositions disappeared after the HTC process, which might be due to the destruction of crystal structures during the HTC process. However, the berlinite ($AlPO_4$) was remained in the HTC solid phase, implying that the berlinite was relatively stable and abundant in the HTC process. This is consistent with the results shown in Tab. S7, which implied that the Al-associated P compounds maybe more abundant than the other speciations. According to the XRD spectrum, $CaCO_3$ was also a main mineral in the HTC product of the AF residue under $Ca(OH)_2$ condition. It indicated that $CaCO_3$ crystal was stable under the conditions of this HTC process.

The XRD results provide a relatively complete characterization concerning the identity of possible P-containing compounds in the WAS, AF and HTC solid products, as well as some other associated minerals. However, they are highly depended on the crystallinity of mineral components. Some phosphates which were poorly crystallized may be difficult to be identified by XRD. According to the SMT analysis in section 3.2.4, the proportion of AP increased significantly after the HTC process, which was due to the higher stability of AP. Nevertheless, XRD analysis suggested that there was no AP existing within the HTC solid products. It may be because the crystalline form of AP was destroyed and not identified by the XRD. Therefore, a more advanced technique such as P K-edge XANES was essential in order to detect the detailed changes of NAIP and AP after the AF and HTC processes.

3.5 P K-edge XANES and LCF analysis

In order to systematically characterize the changes of phosphates during the AF and HTC processes, as well as to validate the results obtained by SMT method, P K-edge XANES and LCF analyses were conducted. Fig.5 presents the linear combination fittings of P K-edge spectra, and the associated LCF factors are given in Tab.S9. All the R factors were lower than 0.02, which meant good fitting results. Fig.6 shows the relative abundances of different phosphates.

The results indicate that the relative abundances of Ca-associated P (HAP and OCP) decreased from 50.5% (WAS) to 45.7% after the AF conducted at a pH of 5.5 and it increased gradually as the AF pH increased. At the pH of 9.5 (NaOH), the relative abundances of Ca-associated P reached to 60.7%. Large amounts of HAP (59.0%) were generated when $Ca(OH)_2$ was used in the AF process, and the relative abundance of Ca-associated P was 88.3%. It suggests that $Ca(OH)_2$ can promote the formation of HAP, including the transformation from OCP to HAP. Furthermore, the relative abundances of $AlPO_4$ and $FePO_4$ decreased from 54.2% (A5.5) to 39.3% (A9.5), indicating that the increase of pH value during the AF process could promote the transformation from NAIP to AP. The relative abundances of $AlPO_4$ and $FePO_4$ in sample A9.5Ca was only 11.7%, which was due to the Ca^{2+} competing with Al^{3+} and Fe^{2+} to generate more HAP precipitation during the AF process. Compared with that of A9.5, pH was not the key factor in the formation of HAP, since the significant presence of Ca^{2+} played an important role in producing HAP. HAP and OCP are related to AP, $AlPO_4$ and $FePO_4$

belong to NAIP. The results obtained by P K edge XANES LCF provided detailed information about the changes of different phosphates and verified the SMT results which were discussed previously.

After the HTC process, the Ca-associated P also increased gradually as the pH increased. The HTC solid sample under $Ca(OH)_2$ condition had the highest relative abundance of Ca-P (90.7%), including 65.2% of HAP. The relative abundance of HAP is higher than that of the AF residue under $Ca(OH)_2$ condition (59%). In addition, it could be found that some OCP in AF residues at pH values of 7.5 and 9.5 were converted to HAP after the HTC process. The relative abundance of HAP increased from 0% to 9.9% (H7.5) and 11.2% (H9.5), respectively. The results revealed that HTC process could promote the conversion of OCP to HAP under alkaline conditions. Because HAP is a comparatively more thermodynamically stable product (Bruun, et al., 2016; Huang and Tang, 2016). HAP was not found in the HTC solid product of the AF residue at the pH of 5.5, indicating that HAP could not exist under the acidic hydrothermal condition.

In addition, $Mg_3(PO_4)_2$ was identified after the HTC process, while it was not presented in AF solid products. This is because HTC process provided a more homogeneous environment for inorganic ions, which increased the activity of the inorganic ions. As a result, the reactions of precipitation, surface absorption and complexation were easily occurred under the HTC process (Huang et al., 2018). Mg was in a relatively high concentration in the WAS and AF residues according to Tab. S6, so $Mg_3(PO_4)_2$ was generated in such circumstance. However, $Mg_3(PO_4)_2$ was not identified in the HTC sample by $Ca(OH)_2$ conditions, which can be ascribed to the competitive effect of Ca^{2+}, leading to the accumulation of Mg^{2+} in the liquid phase (Munir et al., 2017). This is consistent with the results of section 3.3.

3.6 Morphology analysis of AF and HTC solid products

Fig.7 presented the SEM spectra of WAS, AF and HTC solid products. It could be found that the particulars of the WAS sample were in large size, and mainly in the form of bulk structure. The needle-shaped SiO_2 crystals were detected in the WAS sample. After the alkaline AF process, the particulars became smaller, especially for the AF residue under $Ca(OH)_2$ condition (A9.5Ca). Layer shaped mineral precipitations were found in sample A9.5, while there were also some spherical shaped $CaCO_3$ crystals in sample A9.5Ca. After the HTC process, the surface of the solid products (H9.5, H9.5Ca) became rougher, and large amounts of flocculent structures appeared. The specific surface area increased and it was beneficial for the adsorption of phosphates and metal ions. In sample H9.5, needle-rod shaped SiO_2 crystals and layer shaped precipitates were detected. However, sample H9.5Ca was mainly dominated by $CaCO_3$ crystals. The morphological analysis results of WAS, AF and HTC solid products were consistent with the conclusions obtained by the metal ions and XRD analysis.

3.7 Implication

Global resource and energy shortage promoted the reclamation of some nutrients and critical elements from solid wastes, especially for bio-wastes such as WAS from WWTPs. AF and HTC are considered to be the optimum techniques to achieve the reduction, harmlessness and recycling of bio-wastes. Considerable amounts of P from human life ultimately converged in WWTPs and end up in sludge, which is a great opportunity for P reclamation. Recently, AF process was mainly used to produce VFAs, and researches about HTC were mostly focused on the conversion of C and N compounds. Little is known about the P behavior after the combined processes of AF and HTC. The characterization of P speciations and the corresponding transformation mechanisms that occur during the AF and HTC processes is crucial for the optimization of treatment techniques and further recovery of P from bio-wastes.

The present study found that the alkaline AF condition (pH=9.5) achieved via NaOH addition obtained maximum release of P (30.86%) from WAS. The P distributed in the AF and HTC liquid phase could be recovered by some crystallization method to form hydroxyapatite or struvite (Guisasola et al., 2019; Shi et al., 2019b). The AF supernatant under NaOH condition (pH=9.5) also obtained the highest content of VFAs, which could be an effective carbon source for the P release of phosphorus-accumulating bacteria. While some further studies about the detailed functional genes and pathways of the bacteria associated with P transformation during the AF process are still needed.

The AF and HTC products obtained by $Ca(OH)_2$ had the highest P distribution (> 99%) in the solid products. The enriched P in the solid products could be further extracted by acid treatment, and subsequently precipitated under alkaline condition to form calcium phosphate (Heilmann et al., 2014). What worth mentioning is that, the detected $CaCO_3$ (calcite) in the AF and HTC solid products under $Ca(OH)_2$ condition was a kind of soil amendment. $CaCO_3$ can induce metal immobilization by increasing soil pH (Abd et al. 2013; Houben et al. 2012). Therefore, the AF residue and HTC solid under $Ca(OH)_2$ condition have the potential to be utilized in soil improvement. Some further studies about the effect of this kind of soil amendment are remain to be investigated.

Acidic AF conditions (pH = 5.5) generated the highest bioavailable P (OP+NAIP) content (97.99%) in the solid phase, which had potential application as a P fertilizer (Kahiluoto et al., 2015). After the HTC process, the proportion of bio-available P was reduced, especially under alkaline conditions. Concomitantly, the P concentration in the solid phase was increased and the dewatering performance of the solid products were improved. It indicated that the HTC process could enrich phosphorus to the solid phases, which could be further extracted by acid for recycling (Shi et al., 2019b).

In general, treatment using alkaline conditions (NaOH) is beneficial for the generation of VFAs and P recovery from the liquid phase, whereas acidic conditions (pH = 5.5) increased the P bioavailability of the solid phase. The use of $Ca(OH)_2$ improved the dewaterability and enhanced the P enriched in the solid products during the AF and HTC processes. These findings provide fundamental knowledge for the further recovery and recycling of P from bio-wastes, which are of great significance for the recycling of global resource and sustainable development.

4. Conclusions

This study elucidated the variation of P speciations and the related transformation mechanism during the AF and HTC processes at different pH and different alkalis. The main conclusions are as follows.

(1) The 12 days VFAs production with NaOH additive (pH = 9.5) was much larger

than that of $Ca(OH)_2$, whereas $Ca(OH)_2$ can be utilized in order to obtain a more optimal dewatering performance.

(2) Under the alkaline AF condition (pH = 9.5) with NaOH additives, the transfer of P to the supernatant was promoted, due to the dissolution of NAIP and release of OP in the AF solid phase. At the same AF pH value (9.5), $Ca(OH)_2$ fixed more P in the AF and HTC solid products.

(3) Acidic AF treatment facilitated the conversion of AP to NAIP and improved the P bioavailability. Alkaline AF condition enhanced the formation of AP, especially with $Ca(OH)_2$ additive. The following HTC process promoted the conversion of NAIP to AP. The P K-edge XANES analyses verified the SMT results and revealed that the HTC process promoted the conversion of OCP to HAP under alkaline conditions.

(4) Some P-associated valuable minerals such as vivianite and struvite were found in the AF residues. $CaCO_3$(calcite) was a main mineral in the AF and HTC products under $Ca(OH)_2$ condition.

The results obtained have great implications on the recycling of P from bio-wastes, and the methodology could also be applied to investigate the behavior of other elements.

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Appendix A. Supplementary data

Supplementary data related to this article are provided in the supplementary section.

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