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

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15 **Abstract:**

16 This study investigated migration and transformation mechanism of P in waste
17 activated sludge (WAS) during anaerobic fermentation (AF) process and the subsequent
18 hydrothermal conversion (HTC) process. Control of pH during the AF processes was
19 found to be significant, whereby the use of acidic (pH = 5.5) or alkaline conditions (pH
20 = 9.5) facilitated the release of either apatite phosphorus (AP) or non-apatite inorganic
21 phosphorus (NAIP) and organic phosphorus, respectively. At the same pH of 9.5, NaOH
22 promoted the transfer of P into liquid phase, and P in the solid phase was mainly in the
23 form of NAIP. In contrast, Ca(OH)₂ enhanced the incorporation of P into the solid
24 products, with the P mainly in the form of AP. The subsequent HTC process promoted
25 the NAIP transferred to AP, and the bioavailability of P in the HTC solid products was
26 decreased. The P K-edge X-ray absorption near edge structure analysis provided
27 detailed information about the phosphates. It demonstrated that the conversion of
28 Ca₈H₂PO₄·6.5H₂O to Ca₅(PO₄)₃·OH was facilitated by HTC under the alkaline
29 condition. This study sheds lights on transformation mechanism of P speciations during
30 AF and HTC processes, which would provide fundamental information for effective
31 utilization of P in bio-wastes.

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

35

36

37 **1. Introduction**

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

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

50 Anaerobic fermentation (AF) is regarded as an effective way to convert sludge into
51 valuable products (Liu et al., 2016; Wang et al., 2016). For example, large amounts of
52 volatile fatty acids (VFAs) are produced by AF and they are useful raw materials in
53 many chemical and biological reactions (e.g. as a carbon source for denitrification).
54 Many researchers have investigated VFA production during fermentation processes
55 (Esteban et al., 2018; Lin et al., 2009; Yu et al., 2010; Zhang et al. 2009; Zou et al.,
56 2018), and they found that alkaline conditions promoted the production of VFA from
57 WAS. Alkaline AF conditions are usually obtained by the addition of NaOH, while
58 Ca(OH)_2 was also used to adjust the pH of AF process due to the bad dewatering

59 performance of NaOH and its higher cost.

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

68 Some chemical and physical reactions such as precipitation and adsorption relating
69 to P-containing species are pH dependent. Recently, most previous studies just focused
70 on P release behavior of the AF liquid phase. The different P speciations formed under
71 different AF pH and the related transformation mechanism are still unclear, especially
72 with different alkalis (NaOH or Ca(OH)₂). However, it is very important for the further
73 utilization of P in the AF solid phase by investigating the P speciations.

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

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

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

96 **2. Materials and methods**

97 *2.1 WAS*

98 WAS with water content of $98.93 \pm 0.11\%$ was obtained from a secondary
99 sedimentation tank in Quyang waste water treatment plant (located in Shanghai, China)
100 with an anaerobic/anoxic/aerobic process. The main characteristics of WAS are as
101 follows: total suspend solids (TSS) of 10.5 ± 0.9 g/L, volatile suspend solids (VSS) of
102 7.4 ± 0.8 g/L, and pH value of 6.9 ± 0.1 . The ash content of WAS was about 31.0%, and

103 the content of C, H and N were about 30.8%, 5.46% and 31.0%, respectively. The
104 detailed metal element contents of the WAS are illustrated in section 3.3.

105 *2.2 AF treatment with different pH*

106 The AF experiments at different pH were conducted in four 2 L serum bottles with
107 1.6 L WAS. The pH was adjusted to 5.5 and 7.5 by adding HCl and NaOH solution
108 respectively. The AF treatment at pH of 9.5 was adjusted by using either NaOH or
109 Ca(OH)₂. All the serum bottles were flushed with N₂ in order to achieve anaerobic
110 conditions before being sealed. The bottles were maintained in an orbital shaker
111 incubator at a mesophilic temperature of 37 ± 1 °C. The pH was adjusted to the desired
112 value of 5.5, 7.5 and 9.5 every 12 hours. Samples were taken regularly for P and VFAs
113 analyses. After 12 days, the AF products were centrifuged (10,000 rpm for 20 min at
114 *ca.* 25°C) and separated to solid and liquid phases. The liquids were filtered and
115 refrigerated in a 4°C fridge. The solids were dried at 80°C to constant weight for further
116 analyses, and the moisture of solid products were measured. The samples obtained at
117 different AF pH and alkaline additions were labeled as A5.5, A7.5, A9.5 (NaOH
118 condition) and A9.5Ca (Ca(OH)₂ condition), respectively.

119 *2.3 HTC treatments*

120 The AF residues were further used for HTC treatment, which were performed using
121 an autoclave hastelloy reactor with a volume of 250 mL. The reactor was tightly sealed
122 and controlled by a programmable heating device. Previous studies indicated that
123 hydrothermal temperatures greater than 150 °C resulted in the decomposition of some
124 biopolymers and led to the generation of free water (Wang and Li, 2015), and a

125 residence time of 30 min promoted a substantial conversion in the sludge surface
126 properties (Wang et al., 2014). In order to balance financial considerations and HTC
127 performances, AF residues with different pH were treated at 170 °C for 30 min. The
128 HTC products were centrifuged (10,000 rpm for 20 min at *ca.* 25 °C) and separated to
129 solid and liquid phases. The hydrolysates were filtered and refrigerated in 4°C fridge.
130 The solids were dried at 80 °C to constant weight for further analyses, and the moisture
131 of solid phases were measured. Accordingly, samples obtained after HTC process were
132 labeled as H5.5, H7.5, H9.5 and H9.5Ca.

133 *2.4 SMT method*

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

147 available P (Huang et al., 2015; Xie et al., 2011). The concentrations of phosphorus in
148 the supernatants collected after extraction were detected in triplicate via the
149 molybdenum blue method.

150 *2.5 P K-edge XANES Analysis*

151 All P K-edge X-ray Absorption Near Edge Structure (XANES) data were collected
152 at Beijing Synchrotron Radiation Facility (4B7A). The WAS, AF and HTC solid
153 products were ground into fine powders and brushed evenly on the conductive adhesive.
154 Excess powder was subsequently removed in order to achieve a homogeneous thin film.
155 The XANES data were obtained in fluorescence mode using a silicon drift detector.
156 XANES spectra were collected at 2120-2200 eV according to previous literatures
157 (Kruse et al., 2008, 2010). As phosphorus was mostly combined with some metals such
158 as Mg, Fe, Al and Ca in WAS, the following compounds were selected as reference
159 compounds: $\text{Mg}_3(\text{PO}_4)_2$, FePO_4 , AlPO_4 , $\text{Ca}_5(\text{PO}_4)_3\cdot\text{OH}$ (HAP) and $\text{Ca}_8\text{H}_2\text{PO}_4\cdot 6.5\text{H}_2\text{O}$
160 (OCP).

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

164 *2.6 Other characterization analyses*

165 The VFAs contents of different AF liquid samples were detected by GC-FID (GC-
166 2010, SHIMADZU, Japan). The samples were separated by a Stabilwax-DA column
167 (30m \times 0.32mm \times 0.25 μm , PEG-20M, 30 m \times 0.32 mm \times 0.50 μm) with N_2 as carrier gas.

168 The metal concentrations of AF and HTC samples were detected by inductively coupled

169 plasma atomic emission spectrometry (ICP-AES, Optima 8000, Perkin Elmer, USA)
170 and the mean of two replicates are presented. The XPS results were obtained by using
171 an X-ray photoelectron spectrometer (PHI Corporation, Japan, type PHI5000C). The
172 synchrotron radiation XRD data were collected at Beijing Synchrotron Radiation
173 Facility (4B9A). The SEM images were obtained by using a field emission scanning
174 electron microscope (7800F Prime, JEOL, Japan).

175 *2.7 Statistical analysis*

176 The independent variance T tests were conducted to compare the OP contents of
177 WAS and the AF residues. The statistical analyses were performed using the program
178 package SPSS 21 (IBM Corporation, USA) and the significance was assigned at the p
179 < 0.05 level.

180 **3. Results and Discussion**

181 *3.1 Effect of pH on the VFAs and moisture contents of AF and HTC products*

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

185 [Fig. S1](#) presents the VFA contents of WAS fermentation liquids at different pH values.
186 It is observed that the total VFAs concentration of AF supernatants under alkaline
187 conditions (A9.5 and A9.5Ca) were much higher than that of other conditions (A5.5
188 and A7.5) after 12 days fermentation. This is because alkaline condition promoted the
189 hydrolysis of WAS, which provided more soluble substrate to produce VFAs. The main
190 composition of extracellular polymeric substances (EPS) of sludge, protein and

191 carbohydrate were more easily released at alkaline pHs due to the dissociation of acidic
192 groups in EPS and the repulsions between the negatively charged EPS. (Zhang et al.,
193 2009). The increased total VFAs concentrations of sample A9.5 and A9.5Ca were
194 mainly caused by the increase of acetic acid, indicating that alkaline condition could
195 promote the production of acetic acid during the AF process. In addition, the activity of
196 methanogens was reduced under alkaline AF condition. Therefore, the accumulation of
197 VFAs was enhanced under alkaline AF conditions (Zou et al. 2018).

198 Furthermore, it should be notable that the 12 days VFAs concentration (1705.89
199 mg/L) of sample produced using $\text{Ca}(\text{OH})_2$ (A9.5Ca) was much lower than that of A9.5
200 (2617.48 mg/L), which is due to the detrimental effect of Ca^{2+} precipitation on sludge
201 hydrolysis and protein acidification efficiency. (Li et al., 2017).

202 The moisture contents of the AF and HTC solid products after centrifugation are
203 shown in Tab. S1. It was found that after the AF process, the moisture contents were
204 82.28%, 84.61%, 83.41% and 81.60% for sample A5.5, A7.5, A9.5 and A9.5Ca,
205 respectively. After the HTC processes, they decreased to 70.48%, 69.74%, 72.11% and
206 63.20%. It was obvious that HTC significantly enhanced the dewatering performance
207 of AF solid residues. The use of $\text{Ca}(\text{OH})_2$ resulted in the best dewatering performance
208 after the AF and HTC processes, whereby the moisture of sample H9.5Ca decreased by
209 35.73%, when compared with the WAS sample.

210 It is worth mentioning that the dewatering performance under $\text{Ca}(\text{OH})_2$ mediated
211 conditions was better than that of NaOH. This is because $\text{Ca}(\text{OH})_2$ could enhance
212 granulation and it was able to re-flocculate the sludge floc and soluble organic polymers,

213 increase floc density and floc strength, as well as to decrease the amount of bound or
214 inter-floc water (Ahmad et al., 2011; Li et al., 2008). However, Na⁺ released by NaOH
215 can exchange with divalent cations in the WAS, which would weaken the strength of
216 floc structure and deteriorate the dewaterability (Higgins and Novak, 1997).

217 *3.2 P distribution and speciation changes after AF and HTC processes*

218 *3.2.1 P distribution after AF process*

219 After the 12 days AF processes, the distribution of P in solid and liquid products were
220 measured. As shown in Fig.1, the distribution ratios of P in the liquid products with
221 different pH decreased in the order of A9.5 > A5.5 > A7.5 > A9.5Ca. The AF products
222 at the pH of 9.5 with NaOH addition had the highest P distribution in the liquid phase
223 (30.86%), whilst almost all the P was distributed in the solid phase when Ca(OH)₂ was
224 instead used. The P distribution results were predominantly a reflection of the different
225 amounts of P released in the liquid phase. The details are illustrated in Fig.2.

226 Fig.2 highlights the fact that most P was released in the initial 6 days' fermentation,
227 and there was no obvious variation in P concentration after 6 days' fermentation. The
228 release of P at different pH was also in the order of A9.5 > A5.5 > A7.5 > A9.5Ca. The
229 greatest release of P (191.23 mg/L) was achieved at the pH of 9.5 with the addition of
230 NaOH. There are three factors that contributed to this result. Firstly, with the increase
231 of OH⁻, more NAIP of the WAS were released into the AF supernatant, the detailed
232 mechanism is illustrated in section 3.2.3. Secondly, as shown in 3.1, A9.5 generated the
233 largest concentration of VFAs, which provided an efficient carbon source for the P
234 release of phosphorus-accumulating bacteria under anaerobic condition (Huang et al.,

235 [2019](#)). Thirdly, under the alkaline conditions, there is a greater release of OP from WAS,
236 which is also demonstrated in section 3.2.3. OP released from extracellular polymeric
237 substances or microbial cells could be converted to PO_4^{3-} by microbes ([Xie et al., 2011](#)).
238 Interestingly, when $\text{Ca}(\text{OH})_2$ was used, the supernatant had the lowest P concentration
239 (3.05 mg/L) , with large amounts of Ca^{2+} precipitated with the released PO_4^{3-} , which
240 decreased the P concentration in the supernatant. The acidic AF condition (A5.5) gave
241 the second largest P release amongst the four samples. This was mainly attributed to the
242 effect of H^+ , which caused P release from inorganic P (such as Ca-P, Al-P, Mg-P and
243 Fe-P) of WAS. Section 3.2.3 and 3.4 will further verify these results.

244 *3.2.2 P distribution after HTC process*

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

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

263 *3.2.3 Characterization of P speciations after AF process*

264 [Fig.3](#) shows the concentration and proportion of P speciations in the AF residues by
265 SMT method. It can be seen that the TP concentration of the AF residues at the pH of
266 5.5 and 9.5 were both lower than that of the WAS. For sample A5.5, it was mainly
267 attributed to the decrease of IP, which was caused by the dissolution effect of H^+ under
268 acidic conditions. For sample A9.5, it was due to the release of NAIP and OP. The
269 detailed reasons are illustrated in the following parts. Correspondingly, the AF residue
270 at the pH of 7.5 had the largest TP concentration of 30.44 mg/g. It should be noted that
271 the AF supernatant under $\text{Ca}(\text{OH})_2$ mediated alkaline condition had the lowest P
272 concentration, and the P distribution in the solid phase under this condition was the
273 highest. However, the TP concentration of the solid phase was also the lowest observed
274 (23.09 mg/g). This is because the AF solid mass in the presence of $\text{Ca}(\text{OH})_2$ (*ca.* 236 g)
275 was much larger than other conditions (*ca.* 125-140 g), as a results of Ca-associated
276 precipitations. There was a considerable amount of precipitated Ca that did not involve
277 P, such as CaCO_3 (demonstrated in section 3.4) in sample A9.5Ca. Therefore, the solid
278 yield was the largest, but the TP concentration of the solid product generated under

279 $\text{Ca}(\text{OH})_2$ mediated condition was lower than that of other samples.

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

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

299 As shown in [Tab. S4](#), the proportion of Ortho-P/Pyro-P (>70%) was much larger than
300 that of C-O-P in the WAS and AF residues. Therefore, it implied that most P was

301 combined with metal ions and can be regarded as IP. In addition, the proportion of C-
302 O-P decreased with the increase of pH value, indicating that alkaline AF condition
303 promoted the hydrolysis of OP. The results are consistent with the analysis based on
304 SMT method.

305 [Fig.3 \(c\)](#) and [\(d\)](#) show the concentration and proportion of NAIP and AP in different
306 AF residues and the WAS sample. It was observed that the AP concentration (0.47 mg/g)
307 decreased significantly when treated in acidic conditions (pH = 5.5), by comparing with
308 WAS (3.05 mg/g). However, there was no obvious changes for the NAIP concentration.
309 It implied that acidic condition could obviously promote the dissolution of Ca-
310 associated P (AP), in comparison to some other metal associated P (NAIP) during the
311 AF process. Thus Ca-associated P was more sensitive to acidic conditions than other
312 metal-associated P. This can be attributed to the positive effect of H⁺ on Ca-P
313 dissolution, which was enhanced at lower pH and hence resulted in more Ca-P being
314 dissolved ([Latif et al., 2015](#); [Wang et al., 2015](#)). With the increase of pH, the
315 concentration and proportion of AP increased gradually, which implied that alkaline
316 conditions could promote the formation of AP. The AF residue generated with the
317 addition of Ca(OH)₂ had the largest AP concentration (17.17 mg/g) and proportion
318 (94.28%), which was due to the combination of Ca²⁺ and PO₄³⁻ from the supernatant.
319 At the pH of 9.5, the concentrations of NAIP were much lower than that of other
320 samples, which indicated the release of NAIP under higher pH values. Ion exchange
321 effect of OH⁻ was occurred under the alkaline conditions. OH⁻ could dissolve Al-P and
322 combine with Fe³⁺, which had previously been bound to phosphate anions. Following

323 this, P was then liberated from Al-P compounds and Fe-P compounds on account of
324 precipitation-dissolution and ion exchange reactions (He et al., 2016). The chemical
325 equation were as follows: $\text{AlPO}_4 + 4\text{OH}^- \leftrightarrow \text{AlO}_2^- + 2\text{H}_2\text{O} + \text{PO}_4^{3-}$; $\text{FePO}_4 + 3\text{OH}^- \leftrightarrow$
326 $\text{Fe}(\text{OH})_3 + \text{PO}_4^{3-}$.

327 3.2.4 Characterization of P speciations after HTC process

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

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

344 As shown in Fig.4 (c), the concentrations of NAIP and AP increased significantly,

345 with the increase in AP concentration being markedly more pronounced than that of
346 NAIP. It is noted from Fig.4 (d) and Fig. 3 (d) that the proportion of AP increased to
347 3.78% (H5.5), 15.74% (H7.5), 22.15% (H9.5) and 96.04% (H9.5Ca), compared with
348 that of 2.31% (A5.5), 10.43% (A7.5), 15.49% (A9.5) and 94.28% (A9.5Ca) in the AF
349 residues. These results implied that the HTC process promoted the conversion of NAIP
350 into AP, on account of the greater stability of the latter.

351 *3.2.5 P bioavailability analyses of AF and HTC solid products*

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

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

364 *3.3 Metal contents of the AF and HTC products*

365 As mentioned above, the P contained within WAS, AF and HTC solids were mainly
366 in the form of IP, which were combined with metal ions. Therefore, it was necessary to

367 analyze the metal contents of the different samples. The results are shown in [Tab. S6](#).

368 It could be found from the results that the concentrations of Mg, Al, Ca and Fe were
369 much greater than other metals in all the solid samples, suggesting more P combined
370 with such metals. [Tab. S7](#) presents the molar ratios of Mg, Al, Fe and Ca to P, which
371 shows the Al/P ratio was much higher than the others, implying that the Al associated
372 P compounds may occurred most frequently. Furthermore, the concentrations of Na in
373 A9.5 and H9.5 were much higher than the others, which is a consequence of the addition
374 of NaOH for the adjustment of pH. Similarly, the Ca contents in sample A9.5Ca and
375 H9.5Ca were far greater than those of others, which could be attributed to the addition
376 of Ca(OH)₂.

377 Under acidic conditions (pH = 5.5), the concentrations of most metals were decreased,
378 compared with that of WAS. As Na and K associated compounds are more soluble and
379 unstable, the concentration of Na and K decreased much more than others. By
380 comparing the concentration changes of Mg, Al, Ca and Fe, the decrease of Mg and Ca
381 are much larger than that of Al and Fe, indicating that Mg and Ca elements are more
382 sensitive to H⁺. The decreased concentration of Ca was consistent with the decreased
383 amount of AP under acid anaerobic fermentation, which was illustrated in 3.2.3. With
384 the increase of pH value, the metal concentration increased gradually, which was due
385 to the precipitation of metal ion and OH⁻. What worth mentioning was that, except the
386 element of Ca, the other metal concentrations of AF residue under Ca(OH)₂ condition
387 was lower than that of NaOH, even at the same pH value. The main reason was that
388 large amounts of Ca²⁺ could compete with other metal ions to form more Ca associated

389 precipitations.

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

398 [Tab. S8](#) shows the metal concentrations presented in the AF and HTC liquid phases.
399 For the AF samples, almost all the metal concentrations obtained the maximum value
400 at the pH of 5.5, except the Na and Ca concentrations for samples prepared using NaOH
401 and Ca(OH)₂. The metal concentrations mainly follow a decreasing trend with the
402 increase of pH value. The results were consistent with that of the solid products, which
403 was due to the effect of H⁺, leading to more metal ions being dissolved in the liquid
404 phase under the acidic AF condition. After the HTC process, the concentration of metal
405 ions mainly followed an increasing trend, compared with that of the AF liquid products.
406 It indicated that HTC process has a more positive effect on the release of metal ions
407 than that of the AF process. The change trends of the metal concentrations between
408 different HTC liquids were similar to that of the AF liquids.

409 It was found that the Mg concentrations of the liquid samples A9.5Ca and H9.5Ca
410 were much higher than that of sample A9.5 and H9.5. This is because the large existence

411 of Ca^{2+} competed with Mg^{2+} to form precipitates, leading to a greater retention of Mg^{2+}
412 in the liquid phase (Munir et al., 2017). The XANES LCF results in section 3.5 would
413 further verify this phenomenon.

414 3.4 XRD analysis

415 In order to identify the formation of P-containing minerals in different samples, XRD
416 analysis was conducted. As can be seen in Fig. S3, the changes in mineral compositions
417 were apparent after the AF and HTC processes. Fig. S3 (a) shows that the P minerals
418 were mainly associated with Al, Mg, Ca and Fe in WAS. The Ca-associated P minerals
419 disappeared after AF process under acidic conditions (pH = 5.5). An increase in pH (to
420 7.5 and 9.5) (Fig. S3 (b)) resulted in the formation of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaPO}_3(\text{OH})$ in the
421 AF residues, thus indicating that a relatively high pH promoted the generation of Ca-
422 associated P minerals. These results verified the analysis of section 3.2.3, which also
423 showed that the Ca-P content increased with the increase of pH value.

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

429 The AF residues also contained a certain amount of valuable minerals such as
430 vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and struvite $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. Vivianite and struvite
431 precipitations are both regarded as highly efficient methods for the recovery of
432 phosphorus originated from sludge (Law et al., 2019; Munir et al., 2017; Uysal et al.,

433 2010; Wang et al., 2017). Therefore, the AF residue has the potential to be utilized as
434 an agricultural fertilizer, and further techniques should be developed in order to reclaim
435 such minerals.

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

445 The XRD results provide a relatively complete characterization concerning the
446 identity of possible P-containing compounds in the WAS, AF and HTC solid products,
447 as well as some other associated minerals. However, they are highly depended on the
448 crystallinity of mineral components. Some phosphates which were poorly crystallized
449 may be difficult to be identified by XRD. According to the SMT analysis in section
450 3.2.4, the proportion of AP increased significantly after the HTC process, which was
451 due to the higher stability of AP. Nevertheless, XRD analysis suggested that there was
452 no AP existing within the HTC solid products. It may be because the crystalline form
453 of AP was destroyed and not identified by the XRD. Therefore, a more advanced
454 technique such as P K-edge XANES was essential in order to detect the detailed

455 changes of NAIP and AP after the AF and HTC processes.

456 3.5 P K-edge XANES and LCF analysis

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

463 The results indicate that the relative abundances of Ca-associated P (HAP and OCP)
464 decreased from 50.5% (WAS) to 45.7% after the AF conducted at a pH of 5.5 and it
465 increased gradually as the AF pH increased. At the pH of 9.5 (NaOH), the relative
466 abundances of Ca-associated P reached to 60.7%. Large amounts of HAP (59.0%) were
467 generated when Ca(OH)₂ was used in the AF process, and the relative abundance of Ca-
468 associated P was 88.3%. It suggests that Ca(OH)₂ can promote the formation of HAP,
469 including the transformation from OCP to HAP. Furthermore, the relative abundances
470 of AlPO₄ and FePO₄ decreased from 54.2% (A5.5) to 39.3% (A9.5), indicating that the
471 increase of pH value during the AF process could promote the transformation from
472 NAIP to AP. The relative abundances of AlPO₄ and FePO₄ in sample A9.5Ca was only
473 11.7%, which was due to the Ca²⁺ competing with Al³⁺ and Fe²⁺ to generate more HAP
474 precipitation during the AF process. Compared with that of A9.5, pH was not the key
475 factor in the formation of HAP, since the significant presence of Ca²⁺ played an
476 important role in producing HAP. HAP and OCP are related to AP, AlPO₄ and FePO₄

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

480 After the HTC process, the Ca-associated P also increased gradually as the pH
481 increased. The HTC solid sample under Ca(OH)_2 condition had the highest relative
482 abundance of Ca-P (90.7%), including 65.2% of HAP. The relative abundance of HAP
483 is higher than that of the AF residue under Ca(OH)_2 condition (59%). In addition, it
484 could be found that some OCP in AF residues at pH values of 7.5 and 9.5 were
485 converted to HAP after the HTC process. The relative abundance of HAP increased
486 from 0% to 9.9% (H7.5) and 11.2% (H9.5), respectively. The results revealed that HTC
487 process could promote the conversion of OCP to HAP under alkaline conditions.
488 Because HAP is a comparatively more thermodynamically stable product (Bruun, et al.,
489 2016; Huang and Tang, 2016). HAP was not found in the HTC solid product of the AF
490 residue at the pH of 5.5, indicating that HAP could not exist under the acidic
491 hydrothermal condition.

492 In addition, $\text{Mg}_3(\text{PO}_4)_2$ was identified after the HTC process, while it was not
493 presented in AF solid products. This is because HTC process provided a more
494 homogeneous environment for inorganic ions, which increased the activity of the
495 inorganic ions. As a result, the reactions of precipitation, surface absorption and
496 complexation were easily occurred under the HTC process (Huang et al., 2018). Mg
497 was in a relatively high concentration in the WAS and AF residues according to Tab.
498 S6, so $\text{Mg}_3(\text{PO}_4)_2$ was generated in such circumstance. However, $\text{Mg}_3(\text{PO}_4)_2$ was not

499 identified in the HTC sample by $\text{Ca}(\text{OH})_2$ conditions, which can be ascribed to the
500 competitive effect of Ca^{2+} , leading to the accumulation of Mg^{2+} in the liquid phase
501 (Munir et al., 2017). This is consistent with the results of section 3.3.

502 *3.6 Morphology analysis of AF and HTC solid products*

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

516 *3.7 Implication*

517 Global resource and energy shortage promoted the reclamation of some nutrients and
518 critical elements from solid wastes, especially for bio-wastes such as WAS from
519 WWTPs. AF and HTC are considered to be the optimum techniques to achieve the
520 reduction, harmlessness and recycling of bio-wastes. Considerable amounts of P from

521 human life ultimately converged in WWTPs and end up in sludge, which is a great
522 opportunity for P reclamation. Recently, AF process was mainly used to produce VFAs,
523 and researches about HTC were mostly focused on the conversion of C and N
524 compounds. Little is known about the P behavior after the combined processes of AF
525 and HTC. The characterization of P speciations and the corresponding transformation
526 mechanisms that occur during the AF and HTC processes is crucial for the optimization
527 of treatment techniques and further recovery of P from bio-wastes.

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

536 The AF and HTC products obtained by $\text{Ca}(\text{OH})_2$ had the highest P distribution (>
537 99%) in the solid products. The enriched P in the solid products could be further
538 extracted by acid treatment, and subsequently precipitated under alkaline condition to
539 form calcium phosphate ([Heilmann et al., 2014](#)). What worth mentioning is that, the
540 detected CaCO_3 (calcite) in the AF and HTC solid products under $\text{Ca}(\text{OH})_2$ condition
541 was a kind of soil amendment. CaCO_3 can induce metal immobilization by increasing
542 soil pH ([Abd et al. 2013](#); [Houben et al. 2012](#)). Therefore, the AF residue and HTC solid

543 under $\text{Ca}(\text{OH})_2$ condition have the potential to be utilized in soil improvement. Some
544 further studies about the effect of this kind of soil amendment are remain to be
545 investigated.

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

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

560 **4. Conclusions**

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

564 (1) The 12 days VFAs production with NaOH additive ($\text{pH} = 9.5$) was much larger

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

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

571 (3) Acidic AF treatment facilitated the conversion of AP to NAIP and improved the
572 P bioavailability. Alkaline AF condition enhanced the formation of AP, especially with
573 $\text{Ca}(\text{OH})_2$ additive. The following HTC process promoted the conversion of NAIP to AP.
574 The P K-edge XANES analyses verified the SMT results and revealed that the HTC
575 process promoted the conversion of OCP to HAP under alkaline conditions.

576 (4) Some P-associated valuable minerals such as vivianite and struvite were found in
577 the AF residues. CaCO_3 (calcite) was a main mineral in the AF and HTC products under
578 $\text{Ca}(\text{OH})_2$ condition.

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

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589 **Appendix A. Supplementary data**

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

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