Transformation and migration of phosphorus in excess sludge reduction pretreatment by alkaline ferrate oxidation combined with anaerobic digestion

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Abstract

Recently, more and more attention has been paid to the strong oxidation ability of newly prepared potassium ferrate (NAPF) in sludge reduction process, but less attention has been paid to the change of phosphorus in this process. The feasibility of phosphorus migration and transformation during excess sludge reduction pretreatment using NAPF pre-oxidation combined with anaerobic digestion was investigated. After 70 mg/g suspended solids NAPF pretreatment and 16 days anaerobic digestion, the solid-phase volatile suspended solids decreased by 44.2%, and much organic matter had been released into the liquid-phase and then degraded during digestion by indigenous microorganisms. As the sludge pre-oxidation process was performed, solid-phase organic phosphorus and chemically combined phosphorus also released into the liquid-phase as PO$_4^{3-}$, peaking at 100 mg/L. During anaerobic digestion, the Fe$^{3+}$ in the liquid-phase was gradually reduced to Fe$^{2+}$, and then formed Fe$^{2+}$-PO$_4^{3-}$ compound crystals and re-migrated to the solid-phase. The concentration of PO$_4^{3-}$ decreased to 17.08±1.1 mg/L in the liquid-phase after anaerobic digestion. Finally, the phosphorus in the Fe$^{3+}$-PO$_4^{3-}$ compound accounts for 80% of the total phosphorus in the solid-phase. A large number of vivianite crystals in sludge were observed. Therefore, this technology not only effectively reduces sludge, but also increases the proportion of PO$_4^{3-}$ in the sludge in the form of Vivianite.

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**Introduction**

Phosphorus, a nutrient that is required by plants and animals, is a non-metallic resource that is difficult to regenerate (Mayer et al., 2016). Available natural sources of phosphate rock are decreasing continuously due to anthropogenic activities (Jacobs et al., 2017). However, plants and animals also metabolize phosphorous. Phosphorus that enters water bodies is often an important cause of surface water eutrophication (Gross, 2017; Xu et al., 2018b). It is predicted that, once the supply of phosphate rock becomes acutely low, the recovery of phosphorus from waste may become necessary, as this may be one of the feasible solutions to phosphorous shortfalls (van and Brdjanovic, 2014).

Phosphorus has the characteristic of unidirectional fluidity in the biological treatment of municipal wastewater (Nielsen et al., 2019). For this reason, concentrations of phosphorus are high in excess sludge (mass fractions of 4%–9%) (Peng et al., 2018; Xu et al., 2018b). Excess sludge is therefore considered a very promising raw material for phosphorus recovery (CiesliK and Konieczkza, 2017). At present, researches on phosphorus recovery from excess sludge mainly focus on struvite (Li et al., 2019a; Peng et al., 2018). While little phosphorus recovery is practiced in some countries today, as recovered phosphorus generally cannot compete with the relatively low cost of mined phosphorus, due to the complex phosphorus recovery process and strict control conditions (Li et al., 2019a; Mayer et al., 2016). However, compare to struvite, vivianite, an Fe$^{2+}$-PO$_4^{3-}$ compound, has recently received considerable attention due to its relatively simple formation conditions and extremely wide range of applications (Wu et al., 2019). Vivianite, which is a very stable compound, is abundant in the digestion portions of wastewater treatment systems (Wilfert et al., 2018). Therefore, the recovery of phosphorus from sludge as vivianite is an important goal of wastewater treatment research.

The expense of excess sludge disposal accounts for ~50% of total wastewater treatment costs (Zhang et al., 2017). Thus, reduction pretreatment, which decreases excess sludge volume, enhances its stability, and improves its dewatering performance, is necessary in order to decrease sludge treatment costs (Liu et al., 2020b; Wei et al., 2018; Zhang et al., 2017). At present, sludge reduction pretreatment is performed using one or more of the following types of methods (Liu et al., 2020a; Ning et al., 2015; Wang et al., 2014): physicochemical (e.g., heat treatment and ultrasonic pretreatment) (Huang et al., 2016; Mohammadi et al., 2019), chemical oxidation (e.g., with HClO, KMnO$_4$, H$_2$O$_2$, CaO$_2$, CaS$_2$O$_8$, and/or K$_2$FeO$_4$) (Li et al., 2019c; Wang et al., 2019; Wu et al., 2014; Yu et al., 2019), or biochemical (e.g., using cytase) (Lan et al., 2013). K$_2$FeO$_4$, which is a strong, environmentally friendly oxidant, has begun to attract significant attention (An et al., 2017; He et al., 2018b). Importantly, the iron produced during K$_2$FeO$_4$ oxidation also improves flocculation and phosphorus removal during the sludge reduction pretreatment (Chen et al., 2019).

However, previous studies using K$_2$FeO$_4$ for sludge pretreatment have mainly focused on the optimal dosages and related control parameters that result in thorough sludge oxidation (i.e., complete cell lysis and release intracellular organic matter) (Liu et al., 2016; Zhang et al., 2012). In these studies, treatment costs have been largely ignored, and the late-stage treatment and disposal of pollutants in the solid and liquid-phases after oxidation have rarely been taken into account. In a previous study, in order to reduce K$_2$FeO$_4$ dosage while improving the sedimentation and dewatering performance of sludge after oxidation, the sludge aggregates were disintegrated with newly prepared alkaline ferrate (NAPF) via pre-oxidation, and then directly anaerobic digested to reduce sludge volume (Li et al., 2019b). The results showed that this technique not only significantly decreased the required dosage of K$_2$FeO$_4$ several times, but also removed phosphorus from wastewater during anaerobic digestion (Li et al., 2019b). However, the phosphorus transformation processes and the associated mechanisms were not studied in detail. Understanding the existing species of phosphorus compounds in sludge at different stages is conducive to phosphorus recovery. So far, little research has been done on phosphorus release and transformation during sludge reduction, especially in the combined process of NAPF and anaerobic digestion.

In this study NAPF pre-oxidation combined with anaerobic digestion on excess sludge from the secondary settling tank of a municipal wastewater treatment plant was performed, aiming to investigate the migration and transformation of phosphorus between the solid and liquid-phases of excess sludge. After sludge pre-oxidation and anaerobic digestion, the final form and distribution of the phosphorus were determined, and put forward the way and feasibility of recovering phosphorus from the excess sludge as vivianite.

### 1. Materials and methods

#### 1.1. Characteristics of excess activated sludge

The excess sludge was sampled from the sedimentation tank of the municipal sewage treatment plant in Suzhou City, Jiangsu Province, China. This plant adopts A$^2$/O process to remove organic matter, nitrogen and phosphorus from sewage, and add polyferric chloride (PFC) at the end of the process to strengthen the removal of phosphorus, so as to achieve stable phosphorus discharging standard. In order to keep the characteristics of sludge unchanged, the sludge was immediately stored in a refrigerator at 4°C after being taken back. The characteristics of the sludge were: suspended solids (SS) 15,000±312 mg/L, volatile suspended solids (VSS) 8870±264 mg/L, total chemical oxygen demand (TCOD) 11,707±127 mg/L and total phosphorus (TP) 28.19±1.2 mg/L. The concentrations of Al$^{3+}$, Ca$^{2+}$, Fe and Mg$^{2+}$ in sludge are 78±1.1 mg/g, 172.5±7.3 mg/g, 339±5.3 mg/g and 79.5±2.2 mg/g respectively.

#### 1.2. Experimental methods

##### 1.2.1. Pre-oxidation treatment of excess sludge

The excess sludge was divided equally into four 800-mL containers (named as R1, R2, R3 and R4). The concentration of SS in each container is 15,000 mg/L. R1 was the blank control. R2 was the alkaline control, and 10 mol/L NaOH solution was used to adjust the pH to 11. R3 and R4 were pretreated...
with NPAF. The pH of sludge was adjusted to 11, then 70 mg/g SS and 140 mg/g SS K2FeO4 were added respectively. During pre-oxidation, all samples were stirred at 400 r/min with a duration of 1.5 hr (Li et al., 2019b). Then, 200 mL of mixture was taken from each sample to analyze the solid and liquid phases. Duplicate experiments were performed.

1.2.2. Anaerobic digestion of sludge after pre-oxidation treatment
The remaining pre-oxidized sludge from R1, R2, R3 and R4 were continued to be digested in anaerobic bottles without fresh sludge inoculation. The temperature was controlled at 33±1°C. The pH value of all the reactors was not controlled during digestion. The gas produced was collected by gasbag. In order to further analyze the release process of pollutants in sludge and the change of sludge characteristics during anaerobic digestion, the change of solid and liquid substance concentration was continuously measured. Duplicate experiments were performed.

1.3. Analysis methods

1.3.1. Conventional analysis indicators
The SS, volatile suspended solids (VSS), and sludge volume index (SVI) were determined by standard methods (APHA, 2005). The total Fe, Fe3+ and Fe3+ were determined by phanentroline spectrophotometry. NH4+-N, total nitrogen (TN), PO43−-P, total phosphorus (TP), and soluble chemical oxygen demand (SCOD) were measured according to Li et al. (2019b).

1.3.2. Phosphorus fractionation and extraction
To investigate the species and distribution of phosphorus in the excess sludge, as well as its migration and transformation during pretreatment and anaerobic digestion, TP, organic phosphorus (OP), and inorganic phosphorus (IP) were measured according to the Standards in Measurements and Testing (SMT) Programme extraction protocol, which has been widely applied in soils and sediments (He et al., 2016; Pardo et al., 2003). IP comprised weakly adsorbed phosphorus (WA-P), calcium phosphate (Ca-P), iron-aluminum-phosphorus (Fe-Al-P), and residual phosphorus (Res-P). To measure WA-P, phosphorus was extracted with a 0.1 mol/L acetic acid solution (pH 5.2, 80 min). OP, after IP was extracted with 1 mol/L HCl and calcined at 450°C for 3 hr, the obtained phosphorus was extracted with 1 mol/L HCl (3 hr). To measure Fe-Al-P, OP was subjected to three 15 min rinses with 0.1 mol/L PBS and then fixed again using 10% osmic acid. Next, serial dehydration using ethanol of different concentrations was performed for 5 min at each concentration (20%, 40%, 60%, 80%, and 100%). A critical point drying apparatus was used to dry the dehydrated sample. Finally, a scanning electron microscope (FEI Quanta 250, USA) and EDX (Oxford x-act, England) was used to examine the sample.

1.3.4. XRD analysis
The R1, R3, and R4 samples were removed from the anaerobic chamber, dried, and inserted into separate glass capillary tubes. The tubes were sealed at both ends and subjected to XRD (Bruker D8 ADVANCE X-ray diffractometer), using Cu target Kα radiation, a working voltage of 40 kV, a current of 40 mA, a 2θ range of 10–60°, and a step size of 0.02°. After XRD, Jade 6.0 (Materials Data, Inc., USA) was used to compare characteristic peaks in each sludge sample, and the characteristics were compared to PDF standard cards. PDF Understanding the existing species of phosphorus compounds in sludge is conducive to P recovery. Standard card # numbers 75-1186 (Fe3(PO4)(OH)(H2O)3), 81-0463 (FeO(OH)), 83-1764 (FeCO3), and 46-0695 (AlPO4) to determine the main components of each sample.

2. Results

2.1. Sludge reduction using NAPF pre-oxidation and anaerobic digestion
In essence, sludge reduction pretreatment causes the comprehensive release of degradable organic matter, nitrogen, and phosphorus from sludge (Liu et al., 2019). Reduction success is mainly reflected by a decrease in the VSS and volume of sludge, as well as by a corresponding increase in SCOD, TN, and TP in the liquid-phase. Here, the VSS and SVI of the raw sludge were 8870±264 and 149±3.2 mg/L, respectively (Fig. 1a). The solid-phase and liquid-phase characteristics of the sludge differed substantially after different pretreatments. Compared with the solid-phase of untreated sludge (R1), the VSS levels of the alkaline pretreated sludge (R2) and the NAPF-pretreated sludge (R3 and R4) decreased by 8% (to 8164±150 mg/L), 22.9% (to 6842±175 mg/L), and 24% (to 6739±200 mg/L), respectively. Conversely, the SVI of R2, R3, and R4 increased slightly as compared to R1, to 154.7±2.4, 159.5±3.6, 161.9±3.8 mg/L, respectively. However, the liquid-phase concentrations of SCOD and organic nitrogen in R2 increased to 646±14.4 and 57.7±2.3 mg/L, respectively (Fig. 1b). Surprisingly, liquid-phase SCOD concentrations in R3 and R4 were higher than in R2, increasing to 2099.2±21.2 and 2242.5±22.6 mg/L, respectively. The forms of nitrogen in the liquid-phases of R3 and R4 mainly existed as organic nitrogen, and the TN concentrations were 129.6±5.3 and 142.8±5.5 mg/L, respectively (Fig. 1c).
The pretreated excess sludge was directly subjected to anaerobic digestion treatment. After 16 days of operation, the VSS of sludge R1 had decreased slightly (to 8100±100 mg/L), while the VSS levels of R3 and R4 had decreased significantly, to 4952±115 and 4800.4±201 mg/L, respectively. Compared with the solid-phase organic matter levels in the raw sludge, the solid-phase organic matter in R3 and R4 had decreased by 44.2 and 45.9%, respectively. In addition, the precipitability of R3 and R4 had improved significantly, and the SVIs of both sludge samples had decreased, to 95.78±2 mg/L and 90.9±1.9 mg/L, respectively. The SVIs of R3 and R4 were respectively 57.1% and 59.3% of the SVI of the raw sludge.

After 16 days of digestion, although a large volume of organic matter was removed (as indicated by the large volume of gas produced; data not shown), the concentrations of SCOD in the effluents of R3 and R4 (3011.8±28.8 and 3241.2±31.2 mg/L, respectively) remained higher than the initial stage of digestion due to hydrolysis of solid organics (Fig. 1b). The organic nitrogen in R3 and R4 was also hydrolyzed during digestion, primarily forming NH₄⁺-N. The post-digestion concentrations of NH₄⁺-N in R3 (199.5±4.7 mg/L) and R4 (205.4±10.4 mg/L) were greater than those of R2 and R1. In R3 and R4, NH₄⁺-N accounted for 90.1% and 80.7%, respectively, of TN (Fig. 1c).

2.2. Migration and transformation of phosphorus and Fe in sludge during the reduction pretreatment process

2.2.1. Migration and transformation of phosphorus and Fe during NAPF pretreatment

The concentrations of PO₄³⁻ and TP in the liquid-phase of untreated R1 were very low (1.16±0.1 and 1.36±0.2 mg/L, respectively (Fig. 2); After the alkaline pretreatment of R2, the concentration of PO₄³⁻ increased to 28.24±2.1 mg/L, while TP increased to 29.63±1.2 mg/L. After the NAPF pretreatment of R3 and R4, the concentrations of PO₄³⁻ were 46.5±2.2 and 67.2±3.3 mg/L, and the concentrations TP were 60.2±2.2 and 79.1±3.2 mg/L, respectively (Fig. 2a). In the liquid-phases of R2, R3, and R4, the ratios of PO₄³⁻ to TP were 95.3%, 77.2%, and 85%, respectively. Meanwhile, compared with the raw sludge, the liquid-phase of R2, R3 and R4 after alkaline and NAPF pretreatment contains a large number of Fe, total Fe concentration were 122.5±3, 415.3±15 and 556.6±21 mg/L, respectively (Fig. 3a).

To quantify changes in phosphorus form and concentration in sludge after NAPF pretreatment, various solid inorganic phosphorus and organic phosphorus were determined in the solid-phase. TP was 28.19±1.2 mg/g SS in the raw sludge, and primarily consisted of inorganic phosphorus (16.1±0.2 mg/g
SS Fe-Al-P, 4.22±0.3 mg/g SS Ca-P, and 1.6±0.26 mg/g SS Res-P), with low levels of OP (2.3±0.1 mg/g SS) and WA-P (3.95±0.18 mg/g SS) (Fig. 4). Phosphorus levels in all pretreated sludges were much lower than phosphorous levels in R1. In R2, the concentrations of Fe-Al-P and Res-P were 11.26±0.5 mg/g SS and 0.99±0.21 mg/g SS, respectively; these values were lower than those of R1. There were no significant differences in the concentrations of other phosphorus species between R1 and R2. After pretreatment, the concentrations of phosphorus in the solid-phase of R3 were lower than levels in R2: Fe-Al-P, OP, and Res-P in R3 were 7.1±0.2, 1.45±0.05 and 0.88±0.05 mg/g SS, respectively. The concentration of WA-P in R3 was higher than that in R2 and R1 due to the large volume of combined phosphorus released. The volume of PO₄³⁻ released by R4 (which was treated with a higher NAPF dose) was not significantly greater than the volume released by R3. Alkaline-pretreated R2, NAPF-pretreated R3, and NAPF-pretreated R4 released 25.4%, 44.1%, and 48.5%, respectively, of the TP present in the raw sludge (ignoring WA-P).

2.2.2. Migration and transformation of phosphorus and Fe during digestion
To further reduce the sludge after NAPF pretreatment as well as to improve sludge sedimentation and dewatering performance, the pretreated sludge was directly input into the anaerobic digestion reactor for digestion. After 16 days of digestion, phosphorus levels in the solid-phases and liquid-phases changed noticeably (Figs. 2, 4): PO₄³⁻ and TP levels liquid-phase increased to 13.5±2.2 and 13.77±1 mg/L in the R1, respectively, while PO₄³⁻ and TP levels in the R2 liquid-phase decreased to 17.78±1.5 and 20.21±1 mg/L, respectively. In contrast, the concentration of PO₄³⁻ in the liquid-phases of
R3 and R4 increased significantly on the first day of anaerobic digestion to 100±5.1 and 132.6±6.5 mg/L, respectively. During anaerobic digestion progressed, the PO₄³⁻ in the liquid-phases of R3 and R4 continued to decrease as the organic matter was further degraded. After 16 days of digestion, the PO₄³⁻ concentrations of R3 and R4 were 17.08±1.1 and 4.25±0.8 mg/L in the liquid-phases, respectively, and the TP concentrations were 18.85±1 and 5.22±0.3 mg/L, respectively. Meanwhile, in the liquid phase of R2, R3 and R4, the concentration of iron ions decreased significantly, and the total iron concentration was 13±2, 25.4±2.3 and 51.1±4 mg/L, respectively (Fig. 3a).

The OP concentrations in all solid-phase sludges decreased to 0.33–0.4 mg/g SS after digestion (Fig. 4). After digestion, the Fe-Al-P in solid-phase R2 increased to 15.1±0.4 mg/g SS. The WA-P in the solid-phases of R3 and R4 decreased to 2.07±0.1 and 1.6±0.15 mg/L, respectively, while Fe-Al-P increased to 21.2±0.6 and 22±0.48 mg/L, respectively. After digestion, Fe-Al-P levels in R3 and R4 were respectively 80% and 81.3% of Fe-Al-P levels in the whole sludge. Compared with Fe-Al-P levels in raw sludge, the concentrations of Fe-Al-P after NAPF pre-treatment and anaerobic digestion increased to 31.7% in R3 and 36.7% in R4.

### 2.3. Phosphorus species in digested sludge

To understand the phosphorus species distributions in solid-phase sludge after anaerobic digestion, especially Fe-P distributions, the solid-phase sludge was characterized with SEM+EDX and XRD. The SEM analysis showed an abundance of crystalline substances in the solid-phase sludge (Fig. 5). For example, in sludge R4, the EDX surface scan identified these solids materials as primarily Fe-P compounds, with iron, aluminum, calcium, and magnesium mass fractions of 13.9%, 1.5%, 1.5%, and 0.4%, respectively. The individual element diagrams of the EDX surface scan indicated that distributions of iron, phosphorus, and oxygen on the sludge surface were similar, while those of calcium, aluminum, and magnesium differed considerably. As abundant S²⁻ was produced during the anaerobic process and easily formed FeS precipitates with iron, the distribution of sulfur was also characterized. The result showed that the mass fraction of sulfur in the sludge was only 0.4%. However, an analysis of iron ion valences in the sludge indicated that, after anaerobic digestion, above 95% of the iron in the sludge was Fe²⁺ (Fig. 3b). XRD analysis of R1, R3, and R4 showed that the observed crystals had strong diffraction intensities at 2θ (i.e., 11.18°, 13.15°, 20.86°, 26.64°, and 40.5°). These diffraction intensities were very similar to those of vivianite crystal [PDF standard card #75-1186 (Fe₃(PO₄)₂·H₂O)], but very dissimilar to the diffraction intensities of other possible compounds [e.g., FeO(OH), FeCO₃, and AlPO₄, determined based on PDF standard cards] (Fig. 6).

These results therefore suggested that, after anaerobic digestion, PO₄³⁻ migrated from the liquid-phase to the solid-phase, and eventually formed vivianite.

### 3. Discussion

#### 3.1. Effects of NAPF pre-oxidation combined with anaerobic digestion on sludge reduction pretreatment

At present, K₂FeO₄ sludge reduction uses the strong oxidizing properties of K₂FeO₄ in an acid-base environment to disintegrate sludge aggregates, rupture cells, and promote the release of large volumes of organic matter from the solid-phase to the liquid-phase (Liu et al., 2016; Zhang et al., 2016). Ye et al. (2012a) showed that the volume of the sludge solid was reduced by 31%, when the dosage of K₂FeO₄ was 810 mg/g SS. However, the market price of K₂FeO₄ may reach $6000/ton. Relying solely on the oxidizing properties of K₂FeO₄ to reduce excess sludge requires a large volume of chemicals, implying an inevitable increase in sludge treatment costs. Moreover, the addition of large amounts of K₂FeO₄ narrows the particle size distribution in the sludge (He et al., 2018a). Indeed, only when the dosage of K₂FeO₄ is greater than 650 mg/g SS, sludge flocs can be flocculated with sufficient Fe(OH)₃ to improve sedimentation performance (Ye et al., 2012a). Therefore, without the sufficient dosages of floculants and dehydration skeletons, small amounts of K₂FeO₄ reduce sludge sedimentation and dewatering performance. In this study, the aim was not to maximally reduce the sludge volume, and thus small amounts of K₂FeO₄ (70 mg/g SS and 140 mg/g SS) were used for pretreatment oxidation. However, organic matter was still released in large quantities during the oxidation process, and the VSS levels of both R3 and R4 were reduced to about 25%. This reduction was significantly greater than was observed in the alkaline-pretreated R2, indicating that, during NAPF pretreatment, the small amount of K₂FeO₄ was highly oxidative and disintegrated the sludge aggregates.
After anaerobic digestion of the directly oxidized sludge, the VSS levels in the solid-phases of sludges R3 and R4 were again lower than the VSS level of R2. This indicated that NAPF pretreatment rendered the sludge more easily degraded by anaerobic digestion. The reason might be that during pretreatment, NAPF disintegrated the extracellular polymeric substance (EPS) structures of the sludge aggregates instead of oxidizing microbial cell structures (Ye et al., 2012b). Thus, the exposed cells can better hydrolyze the organic matter. Indeed, NAPF pre-oxidation combined with anaerobic digestion reduced VSS levels in the sludge about 45%. This reduction was significantly greater than was observed using oxidation techniques that rely on K₂FeO₄ alone. Thus, the combination of NAPF pre-oxidation and anaerobic digestion not only reduced the dosage of K₂FeO₄ required, but also improved the reduction of solid-phase sludge. The performance of R4 after pretreatment with 140 mg/g SS K₂FeO₄ did not differ significantly from that of R3, indicating that the optimal dosage of K₂FeO₄ for sludges was 20 mg/g SS, and that increasing K₂FeO₄ dosage did not necessarily result in a proportional increase in reduction. However, the relationship between optimal K₂FeO₄ dosage and sludges with different characteristics requires further study.

After NAPF pretreatment, sludge SVI increased noticeably, indicating the deterioration of sludge sedimentation performance. However, after anaerobic digestion, sludge SVI decreased significantly. This suggests that anaerobic digestion enabled exposed, viable microorganisms to use the disintegrated EPS for secondary growth and coagulation. Indeed, anaerobic digestion might help rescue the sedimentation performance of sludges affected by NAPF oxidation.

### 3.2 Migration and transformation of phosphorus during sludge reduction

Currently, biological phosphorus removal is performed following the theory of “anaerobic phosphorus release–aerobic excess phosphorus absorption” (Nielsen et al., 2019). That is, phosphorus in wastewater is transferred to the solid-phase using phosphorus-accumulating organisms (PAOs) and dis-
charging excess sludge. Due to the instability of biological phosphorus removal, PFC or polyaluminium chloride (PAC) is used to increase the phosphorus removal rate and ensure that phosphorus levels in the effluent meet quality standards (Rong et al., 2014; Toor and Kim, 2019). Thus, phosphorus in wastewater is eventually transferred to excess sludge. During sludge reduction, OP is generally released back into the liquid-phase. Due to PFC-enhanced phosphorus removal was adopted in the wastewater treatment process, the phosphorus in the residual sludge used here was chemical phosphorus (Zhang et al., 2019). After alkaline pretreatment, the TP concentration in the liquid-phase increased significantly (Fig. 2).

It can be inferred from the change of phosphorus species concentration in alkaline pretreated solid sludge that the phosphorus fraction mainly comes from the release of Fe-Al-P and Res-P. Xu et al. (2018a) significantly reduced combined IP levels in sludge at pH 13, and concluded that this reduction was primarily due to the dissolution of Al(OH)3 and AlPO4. Although it is difficult to accurately separate and identify Fe-P and Al-P in sludge, but aluminum content of the Fe-Al-P in the sludge used here was low, so an alkaline environment was more conducive to the release of Fe-P from the sludge. After NAPF pre-oxidation, the concentrations of IP and OP in the liquid-phase increased significantly; the relative concentrations of IP and OP decreased as NAPF dosage increased. However, increased NAPF dosages resulted in the increased release of Fe-Al-P, reducing Fe-Al-P concentrations in the sludge after pretreatment. This might be because, as the sludge aggregate disintegrated, more OP bound in the sludge EPS was released into the liquid-phase. Simultaneously, some Fe-Al-P also dissolved into the liquid-phase due to alkaline exposure. It was thus likely that NAPF pretreatment not only enhanced the release of combined phosphorus in an alkaline environment, but also released some of the OP in the sludge. Therefore, the increased phosphorus concentration in the liquid-phase was due to the combined effects of alkali and K2FeO4.

At present, anaerobic digestion is commonly used in the sludge reduction pretreatment (Chen et al., 2018). During anaerobic digestion stage, the increase in liquid-phase phosphorus is mainly due to the release of phosphorus from dead microbial cells and PAOs (Ju et al., 2005). The concentration of PO43− was only 13.5±2.2 mg/L in the liquid-phase, with much PO43− remaining in solid form in the sludge, after direct anaerobic digestion of raw sludge (R1). This suggests that only digestion is not conducive to the efficient recovery of phosphorus from sludge. The alkaline-pretreated sludge (R2) showed a slight decrease in liquid-phase PO43− during anaerobic digestion, probably because the acid produced by digestion caused the pH of the reactor to decrease. This decrease might have stimulated the re-precipitation of Fe-Al-P, consistent with the observed changes in Fe-Al-P concentration in the solid-phase sludge. Wu et al. (2017) and Zou et al. (2018) showed that an alkaline environment was not only conducive to sludge digestion, but also enhanced the release of phosphorus from the sludge. During the initial stage of anaerobic digestion of the alkaline-pretreated sludges (R3 and R4), not only was a large amount of OP converted into IP, but the concentration of PO43− in the liquid-phase also increased significantly. This indicated that additional OP had been released from the solid-phase. After NAPF pretreatment, the liquid-phase contained a high concentration of Fe3+ (Fig. 3a), which in the early stage of anaerobic digestion did not form a compound with the PO43− released from the sludge. However, the Fe3+ did not precipitate in the solid-phase, indicating that the Fe3+ were primarily present as hydroxyl compounds in the early stage of anaerobic digestion and acted as flocculants (Li et al., 2019b). In anaerobic digestion, much of the Fe3+ in the sludge was converted into Fe2+ (Fig. 3b). At the same time, the pH gradually decreased during anaerobic digestion (Appendix A Fig. S1), much of the Fe2+.PO43− in the liquid-phase formed compounds and precipitated in the solid-phase.

### 3.3. Feasibility and recovery of vivianite as the main Fe-P mineral in the reduction process

Vivianite is a stable Fe-P compound crystal (Ksp = 10−36) that is found in many wastewater treatment systems (Wilfert et al., 2016). Compared with the recovery of phosphorus in the form of struvite, vivianite forms at a wider range of pH values (6–9), and has a higher phosphorus concentration (up to 28.3%). More importantly, vivianite has more possible applications than struvite (Wu et al., 2019). Studies have shown that vivianite forms in wastewater treatment systems if several conditions are met. First, there must be sufficient iron ions. Wilfert et al. (2018) showed that when the molar ratio of iron to phosphorus in water is greater than 2.5, the competition between sulfide and phosphate to ferrous can be better avoided; under this condition, the phosphorus in the sludge mainly existed as Fe-P. Second, the reducing environment must be conducive to the conversion of Fe3+ to Fe2+ by iron-reducing bacteria. Wang et al. (2018) found that Geobacter sp. was selected as the main functional microorganism and presented higher vivianite recovery rates (20%–48%) than sewage biomass (7%–33%). Third, the pH of the environment must enable Fe2+ and PO43− to form a compound precipitate; pH > 3 leads to the hydrolysis of vivianite, while pH > 10 cause the iron ions to com-

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*Fig. 6 – XRD characterization of solid-phase crystals in sludge after anaerobic digestion.*
bined with OH\(^{-}\) and form flocs (Wong et al., 2002). Li et al. (2018) studied the effects of different pH values on iron species during the anaerobic fermentation of sludge, found that iron in the solid-phase was primarily present as vivianite at pH 6.0.

The most abundant metallic ion in the sludge examined herein was iron, and the concentrations of Ca\(^{2+}\), Al\(^{3+}\), and Mg\(^{2+}\) were relatively low. In addition, the solid-phase phosphorus compounds in the raw sludge were dominated by combined phosphorus, primarily Fe-Al-P. SEM-EDX indicated that many crystals existed in the solid-phase sludge, largely Fe-P compounds. XRD was used to determine whether these crystals were vivianite. A comparison of the XRD results with the vivianite standard card indicated that the crystals observed in the sludge were mainly vivianite. Therefore, NAPF pretreatment and anaerobic digestion not only reduced solid-phase sludge, but the oxidized products of K\(_2\)FeO\(_4\) provided sufficient iron source for the formation of vivianite. In addition, the anaerobic digestion process created an appropriate reducing environment, which facilitated the conversion of Fe\(^{3+}\) to Fe\(^{2+}\) by microorganisms, and promoted the formation of vivianite. Thus, this method of sludge reduction not only increased vivianite formation, but also effectively increased relative proportion of vivianite in the sludge.

Nevertheless, the effective separation of vivianite crystals from sludge must be considered. Methods used to date include gravitational, super-gravitational, and magnetic separation (Prot et al., 2019). However, sludge composition is relatively complicated, and vivianite is both small and not particularly abundant. Thus, these separation techniques have been difficult to popularize. However, the techniques described herein not only released OP in the sludge during the early stage of anaerobic digestion, but also released the original chemical combined phosphorus in the sludge during NAPF pretreatment. This significantly increased the recovery of phosphorus from sludge, especially in sludge with high chemical phosphorus. More importantly, during the initial stage of anaerobic digestion, the liquid-phase contained high concentrations of Fe\(^{3+}\) and SCOD in addition to PO\(_4^{3-}\). Therefore, the proportion of vivianite in the solid-phase can be effectively increased by separately treating the initial digestion-produced liquid using sludge-water separation. This process may be more conducive to the later recovery of vivianite than existing techniques for separating vivianite from sludge.

### 4. Conclusion

NAPF pre-oxidation combined with anaerobic digestion process not only can achieve efficient sludge reduction, but also can provide the substrate and environment for recycling phosphorus in the form of vivianite. NAPF pre-oxidation enhanced the dissolution and the release of phosphorus from solid-phase into the liquid-phase. Anaerobic digestion promoted the conversion of the NAPF oxidation product from Fe\(^{3+}\) to Fe\(^{2+}\) by using organic carbon, creating an anaerobic environment that promoted the formation of vivianite. Vivianite solid gradually migrated to solid-phase Fe-P compound (increased from 16.1 to 21.2±0.6 mg/g SS, and accounting for 80% of the TP in the sludge).

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### Appendix A Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.02.022.

### References


