



# Phosphorus recovery from sludge by pH enhanced anaerobic fermentation and vivianite crystallization

Changyu Li<sup>a,b</sup>, Yanqing Sheng<sup>a,\*</sup>, Hengduo Xu<sup>a</sup>

<sup>a</sup> Research Center for Coastal Environment Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Chunhui Road 17, Laishan District, Yantai, 264003, PR China

<sup>b</sup> University of Chinese Academy of Sciences, No. 19(A) Yuquan Road, Shijingshan District, 100049, Beijing, PR China

## ARTICLE INFO

Editor: Despo Kassinos

### Keywords:

Anaerobic fermentation  
Phosphorus fraction  
Phosphorus recovery  
Waste active sludge  
Vivianite

## ABSTRACT

Phosphorus (P) shortage is a global issue. However, P recovery from waste activated sludge (WAS) has huge potential. In this study, an innovative method for the recovery of P from WAS via pH adjustment-enhanced anaerobic fermentation (AF) and vivianite crystallization was developed. The results indicate that P could be effectively released from WAS to the supernatant under an appropriate pH during AF. P release efficiency increased by 31.6 % at pH 5.0 and 26.1 % at pH 11.0 compared to the control. Over 99 % of the P in the liquid could be recovered by subsequent vivianite crystallization, and ~60 % total P recovery efficiency was obtained. The scanning electron microscopy and X-ray diffraction analyses showed that the co-precipitation of Ca<sup>2+</sup> and Mg<sup>2+</sup> affected vivianite purity. The recovered vivianite purity from the pH 11.0 supernatant (91.39 %) was higher than the pH 5.0 supernatant (85.44 %) because of lower Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the former. In addition, the heavy metals in the recovered vivianite were lower than their own risk thresholds. This study provides new insights into the recovery of P from WAS by pH adjustment-enhanced AF and vivianite crystallization.

## 1. Introduction

Phosphorous (P) is an irreplaceable biogenic element for living matter and plays a vital role in ecosystems. Rock phosphate is a limited and nonrenewable resource, which might be exhausted in 60–80 years [1]. High P emissions due to agriculture and human activity have caused increasing crises in aquatic environments, especially eutrophication [2, 3]. Therefore, it is important to utilize P resources and enhance P recovery from P-rich wastes [4]. P recovery in wastewater treatment plants has attracted increased attention. During wastewater treatment, ~90 % of P in wastewater is transferred to waste activated sludge (WAS) [5]. Relevant studies showed that P accounts for 2–10 % of the dried WAS [6,7]. Therefore, WAS is a potential P resource.

Anaerobic fermentation (AF) has been widely used to reduce the WAS amount and recover resources and energy from WAS, e.g., volatile fatty acids (VFA) and methane [8]. During AF, some P stored in WAS can be released into liquid solution [9]. However, this released P only accounts for 20–30 % of the total P in WAS without pretreatment [7,10].

Therefore, pretreatment is needed to further promote the efficiency of P release. Previous studies showed that the pH during AF is one of the dominant factors influencing P release as it affects solid P sorption-desorption and precipitation-solubilization [6,11]. The pH of WAS during the AF process is usually close to neutral without acid/alkaline adjustment [12]. Some researchers have reported that an acidic pH (< 5.7) could increase P release by 3.6 times compared with a neutral pH [13], and that if the pH is 4.0, 51 % of the total P would be released from WAS [14]. Furthermore, adjusting the fermentation pH to 11.0 may have tripled the supernatant P concentration in Chen's study [15]. However, the disadvantages of this approach are that heavy metal dissolution is increased under an acid pH and that orthophosphate (PO<sub>4</sub><sup>3-</sup>-P) binds to metal ions to form precipitation under an alkaline pH [16–18]. These issues not only affect P release, they also affect the purity of the P recovered products. Therefore, in order to achieve efficient P recovery, optimal pH selection of the AF process is necessary. In addition, previous studies have indicated that the oxidation reduction potential (ORP) might be a crucial factor controlling the release and

**Abbreviations:** AF, anaerobic fermentation; AP, apatite phosphorus; IP, inorganic phosphorus; NAIP, non-apatite inorganic phosphorus; OP, organic phosphorus; ORP, oxidation reduction potential; PO<sub>43</sub>-P, orthophosphate; TDP, total dissolved phosphorus; TSS, total suspended solid; TSP, total solid phosphorus; VFA, volatile fatty acid; WAS, waste activated sludge.

\* Corresponding author.

E-mail address: [yqsheng@yic.ac.cn](mailto:yqsheng@yic.ac.cn) (Y. Sheng).

<https://doi.org/10.1016/j.jece.2020.104663>

Received 25 September 2020; Received in revised form 20 October 2020; Accepted 22 October 2020

Available online 2 November 2020

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transfer of P from a solid to a liquid in sediments [19]. Thus, it is likely that P release could be further increased by reducing the ORP of WAS.

For P recovery, vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ] crystallization has received attention due to its natural ubiquity, easy accessibility, and foreseeable economic value [20]. In fermented sludge, 70 % of the total P presented in the sludge might be bound in vivianite if enough Fe was provided [21]. Because such a high fraction of P is potentially present as vivianite, P recovery from sludge by vivianite is expected. In previous studies,  $\text{Fe}^{3+}$  in WAS was reduced to  $\text{Fe}^{2+}$  by dissimilatory metal-reducing bacteria and vivianite was generated by *in situ*-induced crystallization in the sludge [22–24]. However, the Fe/P molar ratio in sludge is usually much lower than 1.5 [25], so the external Fe addition is required for efficient vivianite formation considering the high P and low Fe quantities [26,27]. Furthermore, although vivianite could be generated in the sludge, it is difficult to separate fine vivianite particles from sludge [26]. The AF treatment leads to the release and transfer of P from the solid phase to the supernatant. If the released P would crystallize in the supernatant, the products could be easily separate and the feasibility of the P recovery method by vivianite would be greatly enhanced. Several simulated tests indicated that the redox conditions, pH, and microbial community influence the efficiency of the P recovery based on vivianite precipitation [28,29]. However, considering the potential effects of heavy metals, there is a lack of studies on P recovery based on vivianite in fermentation supernatants. Moreover, the influence of other metal ions in WAS on the vivianite formation remains unclear.

The main objectives of this study were as follows: 1) determine the optimal pH of AF for P release and identify its potential mechanisms by P fraction investigation; 2) explore the optimum conditions for vivianite formation with high purity; and 3) assess the feasibility of P recovery based on vivianite precipitation.

## 2. Materials and methods

### 2.1. Description of WAS

The WAS was collected from a secondary sedimentation tank of a municipal wastewater treatment plant (handling capacity 150,000 t/d) in Yantai, China, which is operated using an anaerobic–anoxic–aerobic process. Prior to the treatment, the WAS stabilized by gravitational sedimentation for 2 h at 4 °C. The properties of thickened WAS are shown in Table 1.

### 2.2. P release by AF under different pH conditions

The AF experiments were conducted in eight 1000 mL serum bottles. Each bottle was filled with 800 mL WAS; subsequently the pH was adjusted to 2.0, 3.0, 4.0, 5.0, 10.0, 11.0, and 12.0 using 4 M NaOH or 4 M HCl. One unadjusted bottle was used as the control. Before the AF, the serum bottles were purged with nitrogen gas for 15 min to eliminate oxygen. The bottles were capped with rubber stoppers and placed in an

**Table 1**  
Properties of waste activated sludge for AF.

Parameter	WAS (thickened)
pH	6.91 ± 0.05
TSS (mg/L)	22460 ± 530
Volatile suspended solid (mg/L)	16150 ± 210
Total chemical oxygen demand (mg/L)	21540 ± 320
SCOD (mg/L)	128.33 ± 6.40
VFA (mg/L)	32.5 ± 2.9
TSP (mg/g TSS)	21.47 ± 1.02
TDP (mg/L)	16.62 ± 0.52
$\text{PO}_4^{3-}\text{-P}$ (mg/L)	13.84 ± 0.74
Total Fe (mg/g TSS)	21.8 ± 0.5
Total Al (mg/g TSS)	36.2 ± 0.7
Total Ca (mg/g TSS)	35.1 ± 1.1
Total Mg (mg/g TSS)	17.3 ± 0.3

air-bath shaker (150 rpm) at  $35 \pm 1$  °C for 12 d. Inoculum was not added to these bottles during AF, and therefore WAS was used as both substrate and inoculum in this study. In addition, the pH of each bottle was adjusted every 12 h to ensure a variation of  $\pm 0.2$ . Fermentation supernatants of each bottle were collected every 24 h to measure the total dissolved P (TDP) and  $\text{PO}_4^{3-}\text{-P}$  concentration. As soon as the WAS fermentation was complete, the mixture was centrifuged at 10,000 rpm for 10 min. The supernatant obtained after the centrifugation was used to measure the metal ion, soluble chemical oxygen demand (SCOD), and VFA concentration. The residual sludge was dried in a vacuum freeze drier for 48 h and ground in a mortar to obtain a fine powder for the analysis of the unreleased P fraction present in sludge

### 2.3. ORP-dependent P release experiments

After 12 days of fermentation, sludge in which the pH was unadjusted, sludge at pH 5.0, and sludge at pH 11.0 were selected for ORP-dependent P release experiments. Serum bottle (250 mL) was filled with 200 mL post-fermented sludge and 0.01 g  $\text{NaBH}_4$ . The bottle was placed in an air-bath shaker (150 rpm) at  $35 \pm 1$  °C and the AF was continued for 24 h. Samples were taken at regular intervals to measure the ORP and supernatant P concentrations.

### 2.4. Vivianite precipitation

Although ideal P release efficiency was found at pH 3.0, 4.0, 5.0, and 11.0 (section 2.2), the supernatant had higher  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and heavy metals at pH 3.0 and 4.0, which reduced the purity of the recovered vivianite. Therefore, supernatants with pH 5.0 and 11.0 were selected for vivianite precipitation. In order to enhance the vivianite formation, the supernatants were neutralized from pH 5.0 and 11.0 before precipitation.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution (0.1 M) addition was used as the external source of  $\text{Fe}^{2+}$  during vivianite crystallization. The molar ratio of Fe/P during the crystallization was set at 1.5. To determine the effects of  $\text{Fe}^{2+}$  oxidation for vivianite precipitation, nitrogen ( $\text{N}_2$ ) purging or ascorbic acid addition was used to avoid the oxidation of  $\text{Fe}^{2+}$  during the vivianite precipitation. For the group without  $\text{N}_2$  and ascorbic acid,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution was added to the two supernatants (pH 5.0 and 11.0), respectively, and the pH was then adjusted to 7.0 with agitation for 10 min. After 30 min of sedimentation, the sample was centrifuged at 4000 rpm for 10 min. Finally, the P and metal ion concentrations in the liquid were measured. After centrifugation, the solids were freeze-dried for other analyses. For the  $\text{N}_2$  treatment of the samples, the reactor was flushed with  $\text{N}_2$  during precipitation. For the ascorbic acid treatment, ascorbic acid (0.1 g/L) was added to the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution before precipitation. The remaining steps were the same with the group without  $\text{N}_2$  and ascorbic acid. In addition, the synthesis of vivianite was conducted according to Liu et al. [28]. The procedures are described in detail in the Supporting Information.

### 2.5. Measurement and analysis

#### 2.5.1. Chemical analysis calculation methods

A digital pH meter (PE28-Standard, Mettler) with a combined electrode (LE438) was used to determine the pH values. The ORP of the WAS was measured using a portable meter (HQ30D, HACH). The total suspended solid (TSS), volatile suspended solid, total chemical oxygen demand, soluble chemical oxygen demand, TDP, and  $\text{PO}_4^{3-}\text{-P}$  were measured in accordance with the standard methods [30]. The P fractions in the WAS were determined using the optimized standards, measurements and testing method (SMT; detailed in Supporting Information) [31]. Based on this method, the total solid P (TSP) was divided into solid organic P (OP) and inorganic P (IP); IP includes apatite P (AP, calcium-bound P) and non-apatite inorganic P (NAIP, P bound to aluminum, iron, and manganese oxides and hydroxides). The supernatant after filtration (0.45  $\mu\text{m}$  membrane), WAS, and crystallization

products after microwave-assisted HNO<sub>3</sub>-HF-HClO<sub>4</sub> fermentation were used to measure the total metals. The Al, Fe, Mg, and Ca were determined using an inductively coupled plasma optical emission spectrometer (PerkinElmer NeON 300). The Cu, Zn, Cd, Cr, and Pb concentrations were determined using inductively coupled plasma mass spectrometry (Agilent Technologies, 7700). VFA, composing acetate, propionate, *n*- and *iso*-butyrate, and *n*- and *iso*-valerate were detected by a high performance liquid chromatography unit (Shimadzu LC-20AD, Japan). VFA constituents were separated by an Xtimate Sugar-H column and were measured with an UV detector at 210 nm.

The efficiency of the P release ( $P_{RL}$ ) from WAS was calculated using Eq. (1).

$$P_{RL} = \frac{c_{AF}}{c_{TSS}c_{TSP} + c_0} \times 100\% \quad (1)$$

where  $c_{AF}$  is the PO<sub>4</sub><sup>3-</sup>-P concentration in the supernatant after AF,  $c_{TSS}$  is the TSS (22.46 g/L in this study),  $c_{TSP}$  is the TSP concentration (21.47 ± 1.02 mg/g TSS), and  $c_0$  is the initial TDP concentration in the WAS.

The efficiency of the P recovery ( $P_{RC}$ ) from WAS was calculated using Eq. (2).

$$P_{RC} = \frac{c_{AF} - c_{crystall}}{c_{AF}} \times P_{RL} \quad (2)$$

where  $c_{crystall}$  is the PO<sub>4</sub><sup>3-</sup>-P concentration in the supernatant after the vivianite crystallization and  $c_{AF}$  is the PO<sub>4</sub><sup>3-</sup>-P concentration in the supernatant after AF.

### 2.5.2. Characterization of the recovered precipitates

The micromorphology and elemental composition of the recovered precipitates were analyzed using a high-resolution field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan) and energy-dispersive X-ray micro-analyzer (EDS, EX-350, Horiba, Japan). The precipitates were also examined using X-ray diffraction (XRD). The XRD data were recorded using an X-ray diffractometer (XRD-7000, Shimadzu, Japan) and Cu-K<sub>α</sub> radiation at 40 kV and 30 mA in the 2θ range of 10° to 90°. The scanning speed was 4.0°/min.

### 2.5.3. Statistical analysis

All experiments were conducted in duplicate or triplicate. An analysis of variance was used to evaluate the significance of the results;  $p < 0.05$  was considered statistically significant. The data presented in this study are the mean ± standard deviation.

## 3. Results and discussion

### 3.1. Effects of fermentation pH on P release

#### 3.1.1. Variation of P in the liquid

During the P release batch experiments, TDP and PO<sub>4</sub><sup>3-</sup>-P were used to evaluate the performance of P release. The changes in the TDP and PO<sub>4</sub><sup>3-</sup>-P in the liquid with the fermentation time are shown in Fig. 1. In general, the acid or alkali treatments have a positive impact on the P release during AF, while the effects differ under different pH conditions.

The performance of PO<sub>4</sub><sup>3-</sup>-P release was classified into three types based on the pH and compared with that of the control group. Under pH 2.0 and 12.0, which are regarded as extreme values, the PO<sub>4</sub><sup>3-</sup>-P concentration rapidly increased on the first day and reached 204.0 and 196.8 mg/L, respectively. However, the PO<sub>4</sub><sup>3-</sup>-P stabilized within the next 11 d, suggesting that no further P was released. Under acidic pH conditions (pH 3.0, 4.0, and 5.0), the PO<sub>4</sub><sup>3-</sup>-P concentration increased in the first four days and reached 366.0, 355.2, and 312.1 mg/L, respectively. The maximum PO<sub>4</sub><sup>3-</sup>-P concentration was obtained for the supernatant with pH 3.0 was 2.3 times higher than that of the control group, which indicates that PO<sub>4</sub><sup>3-</sup>-P can be effectively released under acid conditions. Under alkaline pH conditions (10.0 and 11.0), the PO<sub>4</sub><sup>3-</sup>-P

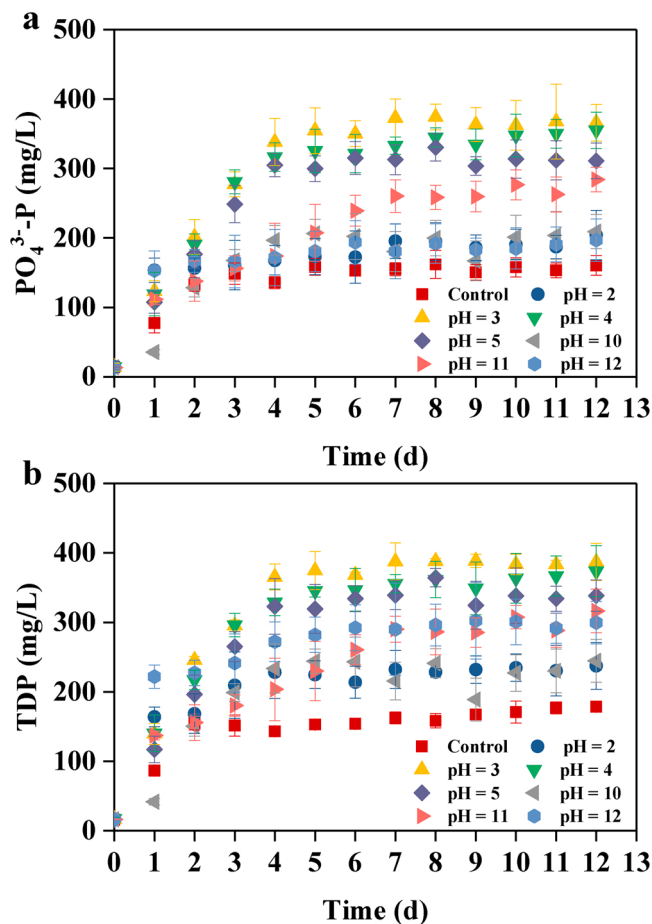


Fig. 1. Performance of the P release under different pH conditions.

concentration reached 209.1 and 284.0 mg/L, respectively, which is higher than that of the control group but lower than that under acid conditions. This proves that acid pretreatment is favorable for high PO<sub>4</sub><sup>3-</sup>-P concentrations in the liquid phase.

Fig. 1b shows that the release of TDP is similar to that of PO<sub>4</sub><sup>3-</sup>-P. Nevertheless, at pH 12.0, the maximum TDP concentration was much higher than that of PO<sub>4</sub><sup>3-</sup>-P. This indicates that over 30 % TDP of supernatant is OP (Fig. S1). The recovery of this type of P by vivianite precipitation will be difficult.

#### 3.1.2. Variations of P fractions in the solid phase

Because the TSS concentration decreased during AF, the variations of P fractions expressed as percentages do not necessarily mean variations in the amount of P species. Therefore, the residual solid P contents of each group were calculated to distinguish the contributions of different P fractions (Fig. 2). The results show that the residual P content has the following order: control > alkali-enhanced > acid-enhanced. This trend is the exact opposite of the TDP trend (increase). Compared with the control, the solid P contents decreased with pH adjustment. As the main component of TSP, IP can be released under both acid and alkaline conditions. Although the IP (AP and NAIP) content decreased, its proportion (>70 %) of the TSP after AF remained high (Fig. 2). The AP proportion decreased with decreasing pH and the minimum proportion (10.3 %) was observed at pH 2.0. But under alkali conditions, AP content remained stable or even slightly increased. This indicates that the alkali condition was not conducive to AP release. The NAIP content increased to 84.98 mg with the pH increase from 3.0 to 10.0 and then decreased to 51.64 mg when the pH increased to 12.0. Except for pH 2.0, the OP content of the residual solid under acidic conditions (~16 mg) was lower than that under alkaline conditions (~20 mg).

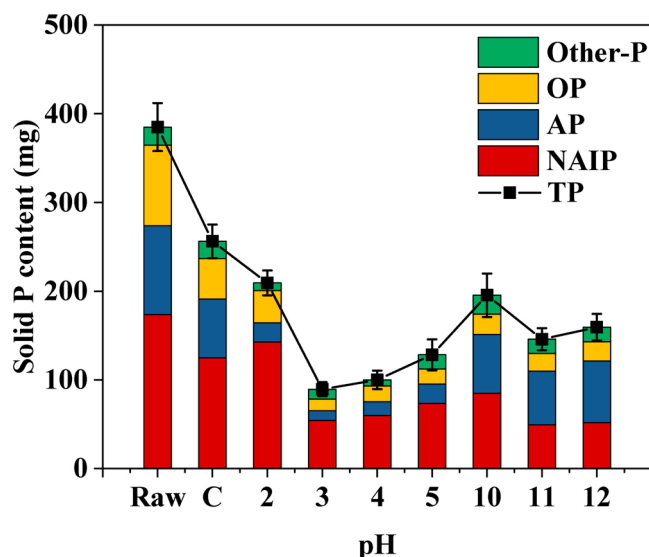


Fig. 2. Distributions of the P fractions in the solid phase after AF (C: control).

### 3.2. Effect of different fermentation pH on the release of metal ions

According to the SMT, most P exists in the metal-bonded state in WAS. The metal ions are released with the P. Because of the affinity between the metal ions and  $\text{PO}_4^{3-}$ , the metal ion release and subsequent co-precipitation were investigated.

#### 3.2.1. Release of common metals under different pH conditions

Fig. 3 shows that pH affects Fe, Al, Ca, and Mg release during the AF process. Specifically, Fe was the sum of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , Al was the  $\text{Al}^{3+}$ , Ca was the  $\text{Ca}^{2+}$ , and Mg was the  $\text{Mg}^{2+}$ , respectively. Overall, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations decreased with the increase in the pH (2.0–5.0). However, at pH 10.0–12.0, the  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  concentrations remained low while the  $\text{Al}^{3+}$  content slightly increased, demonstrating that AP is relatively stable and NAIP can be easily released under alkaline conditions. This is consistent with the results reported in section 3.1, which showed that  $\text{OH}^-$  replaced the site of  $\text{PO}_4^{3-}$  in NAIP at an alkaline condition and caused the  $\text{PO}_4^{3-}$  to be released into the liquid.

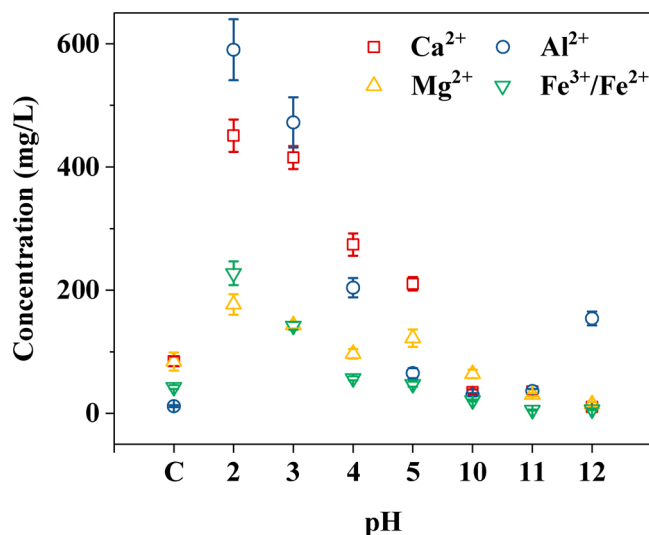


Fig. 3. Effect of the pH on the release of Ca, Mg, Al, and Fe from WAS (C: control).

### 3.2.2. Heavy metal release under different pH conditions

Generally, WAS contains Cd, Cr, Cu, Zn, and Pb, which may transfer to the precipitate product, leading to environmental risks regarding vivianite applications [32]. The heavy metal release before and after AF is shown in Table 2. Compared with the control group, the concentration of dissolved heavy metals significantly increased due to the pH changing. Compared with alkaline pH conditions, the positive effect of the acidic pH on the trace metal release is more notable. Almost no Cd or Pb were detected under alkaline conditions. However, the Cr and Cu concentrations decreased with the increase in the pH, indicating that a low pH enhances the Cr and Cu release. There is no significant correlation between the Zn release and pH.

### 3.3. Effects of fermentation pH on AF performance

The effect of fermentation pH on SCOD and VFA accumulation is shown in Table S1. It is observed that the concentration of SCOD and VFA under the alkaline condition was higher than in the acidic and control groups. The SCOD concentration was 2646.1 mg/L at pH 11.0, while the SCOD concentrations were only 1376.4 and 1284.0 mg/L at pH 5.0 and the uncontrolled pH, respectively. These results are consistent with previous studies on sludge AF [33,34]. It was found that the alkaline condition greatly promoted the transformation of the sludge substrate from a granular state to a dissolved state. The maximum concentration of VFA was 775.7 mg/L at pH 10.0, which is 2.2 and 1.9 times as high as that at pH 5.0 (349.2 mg/L) and at the uncontrolled pH (410.6 mg/L) condition. The activity of acidogenic bacteria is inhibited under acid conditions and results in lower VFA accumulation [35]. Higher VFA accumulation under alkaline conditions was attributed to sludge hydrolysis and the inhibition of methanogen activity [13], which increased VFA production and reduced consumption. Moreover, extreme pH conditions (2.0 and 12.0) were adverse to the AF process and caused lower VFA production. Fortunately, acclimatization and pH tolerance have been previously observed, which may allow digesters to operate effectively despite a weakly acid or alkaline pH [13,36].

### 3.4. P release mechanisms and optimization of AF pH

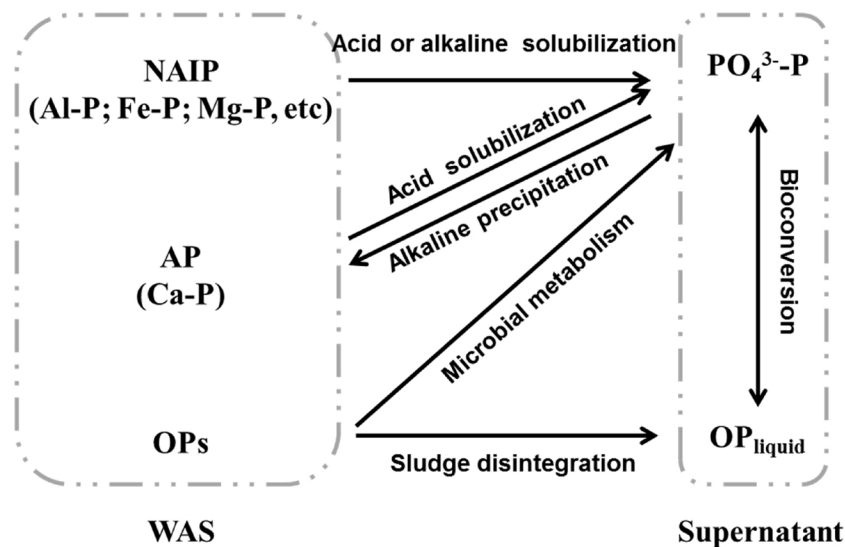
Based on the above results, a schematic diagram of the P release pathways during the AF process under different pH conditions is illustrated in Fig. 4. In WAS, P exists as IP (AP and NAIP) and OP. An alkaline pH enhanced NAIP release but caused AP formation, while an acid pH promoted both AP and NAIP release. OP could be released to liquid by sludge disintegration and converted to  $\text{PO}_4^{3-}$ -P by bioconversion. In addition, OP could also be converted to  $\text{PO}_4^{3-}$ -P directly via microbial metabolism. The details of the P release mechanisms are discussed as follows.

Under acid conditions, a remarkable amount of NAIP and AP was dissolved, and a lower pH led more of them to be released (Fig. 2). This is because the acid pH has a positive effect on the dissolution of the metal bound P [14,37]. When the pH decreased from 5.0 to 3.0, the concentrations of Fe, Al, Ca, and Mg in the liquid phase increased by 180.1 mg/L, 524.9 mg/L, 240.4 mg/L, and 54.7 mg/L, respectively. This demonstrates that metal ion leaching caused by  $\text{H}^+$  led the P-precipitates to become soluble. In addition, OP release decreased as the pH decreased. This may have been because bioconversion was inhibited by the drop in the pH [38]. This was also indicated by the decline in VFA production. Under alkaline conditions, the AP in the solid phase showed slight growth as the pH increased from 10.0 to 12.0. This is because the alkaline pH was favorable for the formation of hydroxyapatite [34]. In contrast, a considerable amount of NAIP was dissolved, and a higher pH led more of it to be released. In NAIP, P was mainly bound to Al and Fe oxides and hydroxides. This part of P would be released as  $\text{OH}^-$  replaced  $\text{PO}_4^{3-}$  at an alkaline condition. An alkaline condition could promote sludge disintegration and increase alkaline phosphatase activity, which contributes to the conversion of OP [38].

**Table 2**

Release of heavy metals from the supernatant before and after AF (mg/L).

Heavy metal (mg/L)	Raw supernatant	pH							
		Control	2.0	3.0	4.0	5.0	10.0	11.0	12.0
Cr	0.032	0.041	0.212	0.365	0.465	0.074	0.020	- <sup>a</sup>	-
Cd	-	-	0.011	0.006	0.003	-	-	-	-
Cu	0.006	0.070	0.367	0.164	0.230	0.100	0.003	-	-
Zn	0.060	0.700	11.120	7.580	1.350	2.200	0.380	1.270	2.160
Pb	-	-	0.352	0.117	0.288	0.040	-	-	-

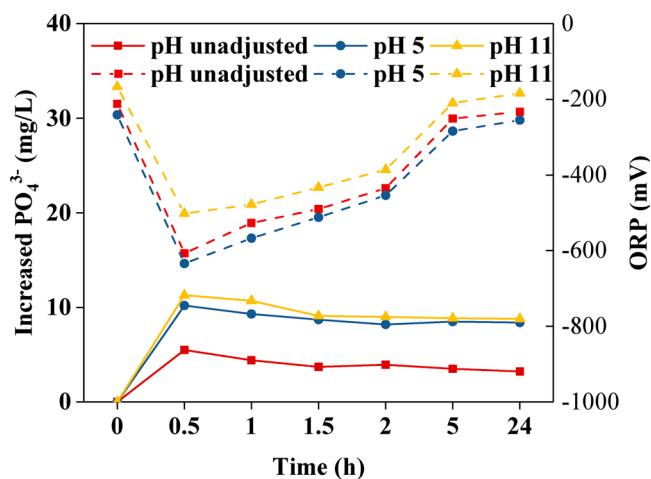
<sup>a</sup> Below the detection limit.**Fig. 4.** Chemical and biological pathways of P release in AF under different pH.

The contributions of different P speciation to P release are very different depending on the pH values. Acid pH enhanced AP and NAIP release while alkaline pH promoted NAIP and OP release. Therefore, pH optimization for P release is related to the P fraction of the WAS [39]. In the sludge in which NAIP and OP account for a high proportion, the promoting effect of the alkaline pH was significant. In contrast, when AP and NAIP account for a high proportion, an acid pH is more efficient.

In this study, suitable pH values for high P release (> 59.0 %) were 3.0, 4.0, 5.0, and 11.0. However, the  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations in the supernatant after alkaline AF are lower than that after acidic AF because of the hydrolysis of metal ions under alkaline conditions. These ions may compete with  $\text{Fe}^{2+}$  for  $\text{PO}_4^{3-}$ , resulting in low purity of the recovered vivianite. The  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations in the supernatant at pH of 5.0 were a quarter of that at pH of 3.0, while the P release efficiency merely declined by 7.0 %. In addition, the heavy metal releases also showed similar trends to  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . Therefore, in order to ensure potential chemical consumption safety and product purity, an AF supernatant of pH 5.0 and 11.0 should be selected for subsequent crystal recovery.

### 3.5. Effect of the ORP on the P release

In this work, prior to experimental manipulation of the ORP, the  $\text{PO}_4^{3-}$ -P concentration in the control supernatant was 160.4 mg/L with an average ORP of -212 mV. The trends of the  $\text{PO}_4^{3-}$ -P concentration and ORP with time are presented in Fig. 5. It shows that the ORP of the control rapidly decreased from -212 to -607 mV with  $\text{NaBH}_4$  addition. The ORP then slowly increased over the next 24 h and finally returned to the initial value. This was caused by the buffer capacity of the WAS. Generally, P bound to Fe is relatively sensitive to alterations of the ORP. Under reducing conditions, Fe oxides will undergo dissolution, causing

**Fig. 5.** The changes of ORP and increased  $\text{PO}_4^{3-}$  concentration with time.

the release of  $\text{Fe}^{2+}$  and loss of P sorption sites [19]. Therefore, the released P may transfer to the supernatant. However, the  $\text{PO}_4^{3-}$ -P concentration in the supernatant (control, pH 5.0, and pH 11.0) only increased by 3.4 %, 2.7 %, and 3.1 %, respectively. This might due to the combination of  $\text{Fe}^{2+}$  and  $\text{PO}_4^{3-}$  to form vivianite under control conditions. However, the combination of  $\text{Fe}^{2+}$  and  $\text{PO}_4^{3-}$  was weak under pH 5.0 and pH 11.0. This means that a normal ORP (~200 mV) during AF contributes to the release of P, but the released P concentration does not notably increase based on further reductions of the ORP of WAS.

### 3.6. P recovery as vivianite

According to results detailed in section 3.3, the separated supernatants (pH 5.0 and 11.0) were used for P recovery. After the vivianite precipitation, the supernatant  $\text{PO}_4^{3-}$ -P concentration was lower than 0.5 mg/L, demonstrating that over 99 % of the  $\text{PO}_4^{3-}$ -P in the supernatant was recovered. Therefore, the total P recovery rate by vivianite precipitation mainly depends on the P release from WAS. The released  $\text{PO}_4^{3-}$ -P at pH 5.0 and 11.0 accounts for 64.5 % and 59.0 % of the total P in WAS, respectively. Therefore, a total of ~60 % solid P could be recovered by vivianite crystallization from WAS.

#### 3.6.1. Prevention of $\text{Fe}^{2+}$ oxidation during vivianite precipitation

In contrast to traditional P recovery methods (struvite and hydroxyapatite), the vivianite crystallization process usually requires more attention because of the risk of  $\text{Fe}^{2+}$  oxidation. Therefore, two approaches ( $\text{N}_2$  and ascorbic acid) were used to protect  $\text{Fe}^{2+}$  during the P recovery. The SEM images of the P recovery products obtained under different conditions are shown in Fig. 6 and Fig. S2. In the pH 5.0 supernatant, the P precipitates obtained using the  $\text{N}_2$  and ascorbic acid approaches both showed clear crystals (Fig. 6). However, the product of the control sample (without  $\text{N}_2$  or ascorbic acid treatment) was a lumpy amorphous substance varying in size (Fig. 6a). The crystallization obtained in the pH 11.0 supernatant also showed similar changes (Fig. S2). These results suggest that both  $\text{N}_2$  and ascorbic acid treatment can promote crystallization by preventing  $\text{Fe}^{2+}$  oxidation.

The crystallinity and structure of the precipitates obtained from the supernatant with pH 5.0 and 11.0 were evaluated using XRD analysis. The XRD pattern of synthetic vivianite is characterized by distinctively strong and sharp diffraction peaks at  $13.16^\circ$ ,  $18.14^\circ$ ,  $27.76^\circ$ , and  $29.85^\circ$  (Fig. 7 and Fig. S3), similar to the standard spectra of vivianite (PDF-79-1928#), indicating the production of pure vivianite. In comparison, the products of the control sample were amorphous (without characteristic peaks). Presumably, these solid products mainly contain co-precipitation products and amorphous Fe oxides with adsorbed  $\text{PO}_4^{3-}$ . The patterns of the recovery products after  $\text{Fe}^{2+}$  protection by  $\text{N}_2$  show

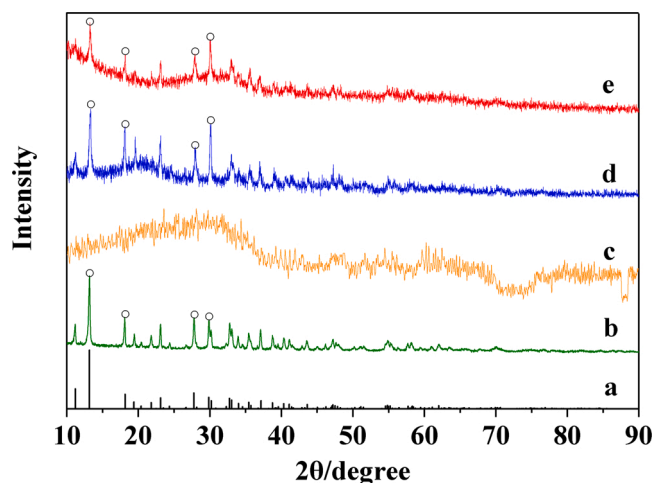


Fig. 7. XRD patterns of the precipitates with a pH of 5.0: (a) standard spectra; (b) synthetic vivianite; (c) precipitate without  $\text{N}_2$  and ascorbic acid; (d) precipitate after  $\text{N}_2$  treatment; (e) precipitate after treatment with ascorbic acid.

peaks that are consistent with that of the standard vivianite pattern, indicating that the precipitates are vivianite; no other peaks observed. However, more and sharper peaks appeared in the pattern of the precipitate after  $\text{N}_2$  treatment compared with that treated with ascorbic acid. This might have occurred because the antioxidant capacity of ascorbic acid was inhibited under neutral conditions. Some  $\text{Fe}^{2+}$  was oxidized to  $\text{Fe}^{3+}$  and formed an amorphous product, which caused the broad XRD peaks. This indicates that  $\text{N}_2$  is better at preventing  $\text{Fe}^{2+}$  oxidation than ascorbic acid, and that higher vivianite purity can be achieved by using  $\text{N}_2$  compared with ascorbic acid.

#### 3.6.2. Co-precipitation of metal ions

Fig. 6d shows that the synthetic vivianite mainly consists of large transparent flower-like crystals with high uniformity. Compared with

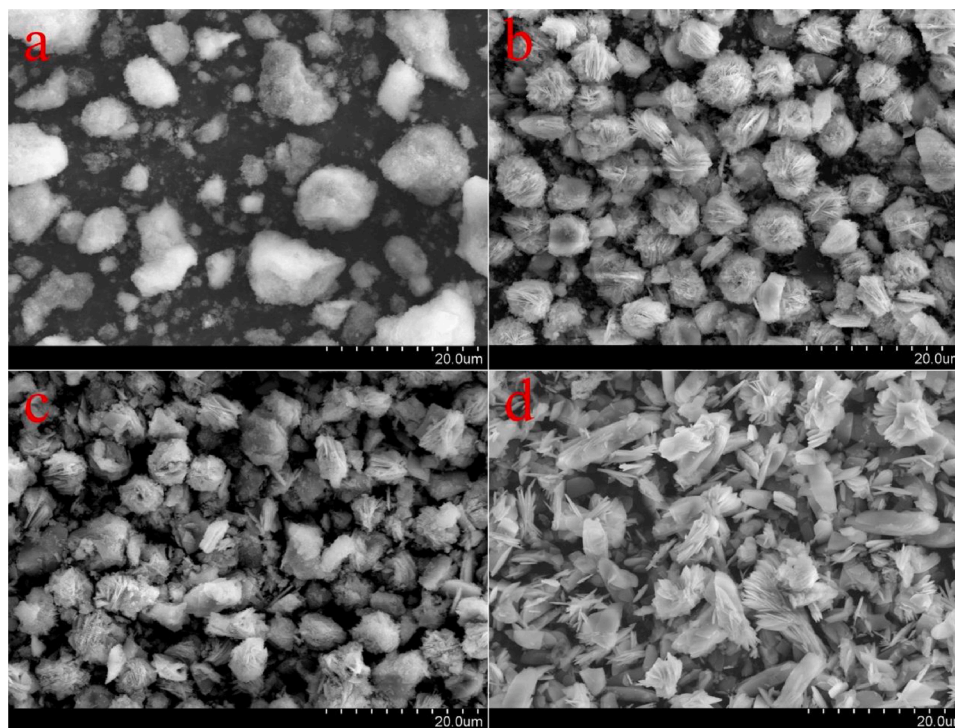


Fig. 6. SEM diagram of the precipitation products of the supernatant with pH of 5.0 under different conditions: (a) control; (b)  $\text{N}_2$ ; (c) ascorbic acid; and (d) synthetic vivianite.

synthetic vivianite, the P recovery products are globular-like crystals containing several amorphous impurities. This demonstrates that a small amount of Fe or other metal compounds may be present in the product, apart from vivianite. According to the EDS analysis, the calculated purities of the recovered vivianite were 85.44 % (pH 5.0, N<sub>2</sub>), 81.21 % (pH 5.0, ascorbic acid), 91.39 % (pH 11.0, N<sub>2</sub>), and 91.01 % (pH 11.0, ascorbic acid), respectively. The EDS analysis indicates that the products obtained from the supernatant with pH of 5.0 contain Ca and Mg (Table S2). In contrast, the products from the pH 11.0 supernatant contain a small amount of Ca or Mg and the vivianite crystals are purer. This demonstrates that co-precipitation of Ca<sup>2+</sup> and Mg<sup>2+</sup> occurred during the precipitation of the pH 5.0 supernatant, which reduced the purity of the product. This is consistent with the results reported in section 3.2. Furthermore, to explore the heavy metal safety of the vivianite products, the heavy metal content after precipitation was analyzed (Table S3). The main standard requirement for products used as fertilizers in China is that the Cr, Cd, and Pb levels are lower than 300, 3, and 100 mg/kg, respectively [40]. In this work, the concentrations of Cr (48.66 mg/kg), Cd (0.44 mg/kg), and Pb (6.90 mg/kg) in vivianite were much lower than the corresponding standards. The results confirmed that the vivianite recovered from WAS could potentially be used as a P fertilizer.

### 3.6.3. Assessment of the P recovery

Compared with control, the pH adjustment accelerated the P release and shortened the P release balancing time to 4–5 d (Fig. 1). This means that the P release can be completed in the normal fermentation period (10–20 d). Generally, acid or alkali treatment is simple and requires little energy [41]. Compared with the results of adjusting the AF pH to 11.0, less acid/alkaline were consumed and more P was released by adjusting the AF pH to 5.0. In addition, the release of heavy metals does not pose a risk to subsequent recovery. Taken together, AF at pH 5.0 was more suitable for higher P release. However, pH adjustment may affect the production of volatile fatty acids, hydrogen, and methane [12,42]. Therefore, the elimination of possible negative effects of pH adjustment on the AF process must be further studied.

Generally, the products of P recovery by the crystallization process are struvite or hydroxyapatite. The recovery rates of total P from WAS using these two methods were in the range of 30–40 % and 30–50 %, respectively [43–45]. In this study, the recovery rate of total P reached approximately 60 %. Considering the difference between initial P releases, both vivianite and struvite had similarly high recovery ability (above 90 %) for dissolved PO<sub>4</sub><sup>3-</sup>-P. This demonstrates that P recovery in the form of vivianite is a competitive practice. Although the vivianite can be generated by in situ-induced crystallization in sludge [26,29], it is difficult to separate the fine vivianite particles from the sludge. Even if magnetic separation is applied; the vivianite purity will be lower than 60 % and further purification needed [46]. In this study, P dissolution was combined with recrystallization. The formed vivianite could be separated by simple centrifugation, with a high recovery rate and purity (>80 %). This confirms the potential of this method for the recovery of high-purity products under complex interferences.

## 4. Conclusions

The adjustment of the AF pH markedly accelerates the P release from WAS and is conducive to the P recovery from the supernatant. A higher P release efficiency was obtained at pH 5.0 compared with pH 11.0. However, Ca<sup>2+</sup> and Mg<sup>2+</sup> are released with P under acid conditions, and the co-precipitation of Ca<sup>2+</sup> and Mg<sup>2+</sup> decreases the vivianite purity. The P release could not be notably enhanced by further reducing the ORP of AF. The released P can be effectively recovered by vivianite crystallization after Fe<sup>2+</sup> protection using N<sub>2</sub> or ascorbic acid. The total P recovery rate mainly depends on the P release from WAS. After AF at pH 5.0, 64.0 % of solid P could be recovered by subsequent vivianite crystallization and vivianite purity over 80 %. Furthermore, the heavy

metal concentration of the products is below the risk thresholds. This study provides new insights into P recovery based on the combination of P dissolution and recrystallization.

## CRedit authorship contribution statement

**Changyu Li:** Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Visualization. **Yanqing Sheng:** Conceptualization, Writing - review & editing, Supervision. **Hengduo Xu:** Investigation.

## Declaration of Competing Interest

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

## Acknowledgements

This research was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences [Grant No. XDA23050203] and the National Nature Science Foundation of China [Grant No. 41373100]. Additional support was provided by the Key Project of the Research and Development Plan of Yantai [Grant Nos 2018ZHG080 and 2018ZHG083] and the Key Research and Development Program of Shandong Province [Grant No. 2019GSF109002].

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2020.104663>.

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