Clarification of phosphorus fractions and phosphorus release enhancement mechanism related to pH during waste activated sludge treatment

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Abstract

This study aimed to clarify phosphorus (P) fractions in waste activated sludge

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(WAS) and explore release performance and enhancement mechanism of different P species related to pH. Results showed that inorganic P (IP) was the major P fraction in raw sludge (87.86% of total solid P), and non-apatite inorganic P (NAIP), the most labile P forms, occupied 81.30% of IP, suggesting that WAS could be selected as potential substitution of phosphate rock. The optimized acid and alkaline conditions were pH=4 and pH=12 for molybdate reactive P accumulation, increased by 311.20 mg/L and 479.18 mg/L compared to raw sludge, which were 3.80 and 5.84 times higher than that of control, respectively. The mechanism study demonstrated that high pH promoted NAIP release, and apatite P was sensitive to low pH. Moreover, the releasable and recoverable P depended on both fractions of different P species in sludge and pH adjustment for sludge treatment.

Keywords: Waste activated sludge; Phosphorus species; Enhancement mechanism; pH; molybdate reactive P accumulation.

1. Introduction

Phosphorus (P) is an indispensable and irreplaceable element for all living creatures (e.g., animal, plant and bacteria), and a critical factor to agriculture production, which is directly linked to increasing food demand due to the growing world population (Cordell et al., 2009; Zhang et al., 2013). However, phosphate rock, as the word's main P resource, is non-renewable, and its demand will outstrip supply after the year 2035 (Cordell et al., 2009; Xu et al., 2015). This makes the new strategy for P recovery from an alternative and renewable resource be one of the greatest challenges in the world.

Waste activated sludge (WAS), is one of the most important municipal wastes. More than 11.2 million tons of dry sludge is generated every year in China, and over 80% is disposed eco-unfriendly (Suanon et al., 2016). It is reported that more than 90% P in wastewater (WW) is transferred into the sludge (Balmer, 2004; Blöcher et al., 2012), thus WAS may be one potential substitution for phosphate rock. P contents in sludge depend on the WW treatment process. It is around 2% for traditional activated sludge process, and 4-10% for enhanced biological phosphorus removal (EBPR) process. Even though WAS has a high P content, it cannot be directly reused in agriculture production or for land application because of the heavy metals or other pollutants (Babel and Del Mundo Dacera, 2006; Kim et al., 2015; Suanon et al., 2016). Considering that P in WAS either distributes in organisms or exists as phosphate sedimentation, P is often recovered with hydroxyapatite or struvite after P releasing with sludge hydrolysis (Doyle and Parsons, 2002; Kim et al., 2015; Zhang et al., 2014), thus, to find an efficient way to release P from solid to liquid phase is the first step for P recovery from WAS.

Recently, various methods for WAS disintegration have been developed, such as chemical (Bi et al., 2014; He et al., 2016a; He et al., 2016b; Zhou et al, 2015), mechanical (Yang et al., 2015a), biological (Yang et al., 2015a; Yang et al., 2015b) and combined treatments (He et al., 2016a; Yang et al., 2015a). However, most treatment methods have been intensively investigated for enhanced either short-chain fatty acids (SCFAs) or methane production through anaerobic digestion process (He et al., 2016a; Wang et al., 2013; Yang et al., 2015a; Zhang et al., 2014), few studies have been

diverted attention to P release and further recovery. In comparison with other approaches, acid/alkaline methods may be an attractive and effective way to release P from WAS. Latif et al. (2015) have reported that the highest soluble P from sludge was observed at pH 5.25 (75% of the total P). Nevertheless, higher alkaline hydrolysis pH was beneficial to the release of P in the studies of Bi et al. (2014) and Kim et al. (2015), and the maximal total P (TP) release efficiencies reached 90% when the sodium hydroxide addition was 1.0 N (Kim et al., 2015). It is thus clear that present studies on the effects of pH on P release from WAS are not consistent, and need further clarification. Moreover, the aforementioned studies usually focused on the P release performance, and seldom attentions have been paid to the mechanism that how pH facilitates P release from WAS.

As well known that the forms of P in sludge exhibit enormous differences in different P removal systems, detailed identification of P species in WAS is essential to understand the characteristics and distributions of different P species and thus disclose the P release mechanisms. Presently, some researches have studied the P species and release properties of lake, river and land sediments, and declared that the P release properties attributed to the fractions of different P species in sediments (Dittrich et al., 2013; Jin et al., 2006; Zhu et al., 2012). To date, Huang et al. (2015) and Xie et al. (2011) have reported that the distributions of P species in sludge greatly depended on influent characteristics and operation conditions. However, the transformations of different P species, and the potential releasable and recoverable P fractions closely related with pH,

is poorly understood.

This study aimed to identify the fractions of different P species in sludge and to evaluate the releasable and recoverable P through anaerobic fermentation process at different pH. In addition, the mechanism that how pH facilitates the release of different P species from solid to liquid phase was investigated. It is expected that this work would not only be meaningful for the exploration of P-release methods from WAS but also provide insights into the role of pH in enhancement of P release, which will be benefit to develop applicable technologies for P recovery from WAS.

2. Materials and Methods

2.1 Source of WAS

The WAS was taken from the secondary sedimentation tank of a local WW treatment plant (WWTP), running with anaerobic-anoxic-aerobic (A^2/O) system, Harbin, China. The WAS firstly was thickened by gravitational sedimentation for 24 h at 4°C, then screened with a 1 mm sieve to remove impurities, finally stored at 4°C prior for later test. The main characteristics were: soluble chemical oxygen demand (SCOD) 57±5 mg/L, total chemical oxygen demand (TCOD) 32.40±1.14 g/L, short-chain fatty acids (SCFAs) 55±3 mg COD/L, total suspended solid (TSS) 32.84±0.59 g/L, volatile suspended solid (VSS) 17.28±0.50 g/L, NH_4^+ 18.10±3.01 mg/L, PO_4^{3-} 77.80±7.34 mg/L, total dissolved P (TDP) 78.84±0.00 mg/L and TP 31.54±0.47 mg/g TSS and pH 6.63±0.01.

2.2 Batch experiment

Batch laboratory-scale anaerobic fermentation experiments were conducted in 500 mL serum bottles filled with 350 mL of WAS. The effects of constant pH on P release from solid to liquid phase, and the transformations of different P species in both liquid and solid phase were investigated in 11 groups of tests. The pH of group 1 was not adjusted, serving as the control test, while the pH of groups 2-10 was controlled at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, and 12.0, respectively, by adding 4 M NaOH or 4 M HCl during the whole fermentation period. Before fermentation, nitrogen gas was introduced to the reactors for 10 min to remove oxygen, then the reactors were capped, sealed, and stirred in an air-bath shaker (100 rpm) at 35±1°C for 12 days. All the fermentation experiments were carried out in triplicate.

2.3 P fractionations in liquid and solid phase

The P in liquid phase was divided into three types: TDP, molybdate reactive P (MRP) and organic P (OP), and MRP is defined as the free ortho-phosphate ion (PO_4^{3-}). The concentrations of OP were calculated as the difference between TDP and MRP, and the measurement methods of TDP and MRP were the same as the previous studies (He et al., 2016b; Xie et al., 2011).

The P species in solid phase were analyzed according to the Standards in Measurements and Testing (SMT) Programme extraction protocol, which has been widely applied in sediments and soils (Huang et al., 2015; Pardo et al., 2003; Xie et al., 2011). Based on the SMT extraction method, P in WAS can be divided into five fractions: (1) total solid P (TSP), extracted by 3.5 M HCl, (2) inorganic P (IP), extracted

by 1 M HCl, (3) OP, the residual after IP extraction was treated at 450°C, then extracted by 1 M HCl, (4) non-apatite inorganic P (NAIP, the P associated with oxides and hydroxides of Al, Fe, Mg and Mn), and (5) apatite P (AP, the P specie associated with Ca). Note that TSP=IP+OP, and IP=NAIP+AP. The detailed extraction procedures and the analysis methods for different P species were consistent with the previous publications (Huang et al., 2015; Pardo et al., 2003; Xie et al., 2011).

2.4 Analytical methods

Sludge samples collected from the reactors were centrifuged at 10,000 rpm for 10 min. Then supernatant samples were filtered by 0.45 um cellulose nitrate membrane filters, and filtrated samples were finally stored at 4°C prior to analysis. The measurements of SCOD, TCOD, SCFAs, NH_4^+, TSS, VSS and pH were conducted in the same methods mentioned in previous publications (He et al., 2016a; He et al., 2016b). The metal ions of the filtrated samples were pre-treated by concentrated nitric acid, and measured by inductively coupled plasma optical emission spectrometry (Perkin Elmer Optima 5300DV ICP-OES Spectrometer, USA) (He et al., 2016b). The experimental data were analyzed by Excel 2013, Origin8.0 and SPSS17.0.

2.5 Kinetic modeling of MRP accumulation in liquid phase

For the purpose to understand MRP accumulation mechanisms in liquid phase at different pH, two kinetic models, pseudo-first-order (equation 1, Eq.1) and pseudo-second-order (Eq. 2) models, are built to interpret the dynamics of MRP

accumulation process (Rahmani-Sani et al., 2015; Yang and Al-Duri, 2005).

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \quad (1)$$

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (2)$$

The pseudo-first-order (Eq. 1) and pseudo-second-order (Eq. 2) models can be re-arranged to the following linear equations, (Eq. 3) and (Eq. 4), respectively (He et al., 2016b; Rahmani-Sani et al., 2015).

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t (mg/L) are the increased MRP concentration at equilibrium and any time t (h), respectively. k_1 (h^{-1}) is the first-order rate constant, and k_2 ((L/mg)/h) is the second-order rate constant.

The correlation coefficient (R^2), average relative error ($ARE(\%)$) and normalized standard deviation (NSD, $\Delta q(\%)$) are employed to evaluate the model comparison. The ARE and NSD are determined by the following equations (He et al., 2016b; He et al., 2016a; Rahmani-Sani et al., 2015):

$$ARE(\%) = \frac{100}{N-1}\sum_{i=1}^{N}\left(\frac{q_{t,exp}-q_{t,cal}}{q_{t,exp}}\right)_i^2 \quad (5)$$

$$\Delta q(\%) = 100\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(\frac{q_{t,exp}-q_{t,cal}}{q_{t,exp}}\right)_i^2} \quad (6)$$

Where $q_{t,exp}$ and $q_{t,cal}$ (mg/L) are the experimental and theoretical MRP concentrations at any time t (h), respectively.

3. Results and discussion

3.1 P fractions in solid phase

It was clear that IP was the major P fraction in the raw sludge (87.86% of TSP), and IP was mainly distributed in NAIP, accounting for 81.30% of IP and 71.43% of TSP, respectively (Fig. 1). The AP, the species associated with Ca, accounted for 18.70% of IP, which was 4.35 times less than NAIP. The percentage of OP was 10.27% of TSP. According to the SMT protocol, in the solid phase, TSP = IP +OP (Li et al., 2014; Xie et al., 2011), but the sum of IP and OP in present sludge sample was lower than measured TSP, 1.87% of which was named as other P (Fig.1), this might be attributed to the limitation of SMT protocol (Li et al., 2014). The similar distributions of different P species in sludge fed with domestic WW have been reported (Xie et al., 2011), which is significantly different from lake, river and soil sediments (Kim et al., 2004; Pardo et al., 2003; Zehetner et al., 2008; Zhu et al., 2012).

It is significant that most of P in WAS could be potentially released due to the high contents of NAIP, which is considered as the most labile P formation (Pardo et al., 2003; Xie et al., 2011). In addition, both NAIP and OP are regarded as potentially releasable and bio-available P (Huang et al., 2015; Pardo et al., 2003; Xie et al., 2011). In this work, the percentage of NAIP + OP was more than 80% of TSP. This suggested that WAS could be selected as the potential substitution of phosphate rock to recover P in the near future.

3.2 P release performance and kinetics at different pH

3.2.1 P release performance

The effects of pH on the P release performance and rate are shown in Fig. S1. It

was obvious that the MRP concentrations increased at any pH under anaerobic fermentation condition, compared to the MRP in raw sludge. In all cases, the concentration of MRP rose rapidly during the initial 2 days, especially under acid conditions, amounting to greater than 93% of the total release capacity. Yet under alkaline conditions, the released MRP still gradually increased after the first 2 days. From section 3.1, IP was the major fraction in the sludge, meanwhile, the P-precipitants closely related to pH and amount and type of cations (such as Mg, Ca, Al and Fe) contained in the system (Latif et al., 2015), thus, the physical and chemical reactions (such as sorption-adsorption and precipitation-solubilization) were all active for solid-P transformation by either acid or alkaline treatment (Jin et al., 2006; Kim et al., 2003; Kim et al., 2004; Wang et al., 2006; Wang et al., 2005; Xu et al., 2015). Compared to acid treatment, the sludge disintegration and consequent biological process more feasibly contribute to MRP accumulation under alkaline condition, because the OP released from extracellular polymeric substances (EPSs) or microorganism cells may be converted to MRP by microorganism (Bi et al., 2014; He et al., 2016b; Xie et al., 2010; Xie et al., 2011). The detailed release mechanisms of different P species would be discussed in the following section. The favorable conditions for MRP accumulation were pH=4 and pH=12, respectively, under acid and alkaline conditions, and the corresponding concentrations of increased MRP were 311.20 mg/L and 479.18 mg/L, which were 3.80 and 5.84 times higher than that of control, respectively.

3.2.2 Kinetic modeling

The kinetic study is of great significance to gain insight into the physical-chemical process of MRP accumulation at different pH. The plots of the experiment data in the form of $ln\ (q_e - q_t)$ versus t or t/q_t against t (h) would be a straight line if the given model (pseudo-first-order or pseudo-second-order model) is the optimal expression (Feng et al., 2015). The linear regressions of the two models are presented in Fig. 2(A and B) and the parameters are given in Table 1. For all the constant pH tests, the linear regression coefficients obtained by the first-order kinetic model were lower than that obtained by the second-order kinetic model, suggesting that pseudo-second-order model was predominant for the MRP accumulation. This is different from the previous study (He et al., 2016b), in which, the first-order kinetic is predominant. The difference may be caused by different physical-chemical process happened with different treatment methods. By contrast, for the control test, the first-order kinetic model was relatively better fit than the second-order kinetic model, similar with the result reported by He et al. (2016b). The matched curves between measured and modeled values by pseudo-second-order model are illustrated in Fig. 2(C) and Table 1. It can be seen that the calculated values of pseudo-second-order well agreed experimental values at any time. The overall rate of MRP release from solid to liquid phase was controlled by a pseudo-chemical reaction when the sludge was treated by acid or alkaline (Feng et al., 2015; Rahmani-Sani et al., 2015).

3.3 Effects of pH on the re-distribution of different P fractions in solid phase

3.3.1 Release efficiency of various P fractions

For IP, the release efficiency increased linearly with the decreasing pH under acid condition (pH=3-7). Similarly, the IP release efficiency also increased rapidly with the increasing pH under alkaline condition (pH=8-12) (Fig. 3(A) & Fig. S2 (A3)). The maximal IP release efficiency was 69.85%, obtained at pH=12, which was 10.46 times higher than that of control, and the minimal one was 3.04%, obtained at pH=8, which was 2.19 times less than that in control. The IP release efficiency was closely related to the changes of NAIP and AP in the solid phase. For AP, when pH decreased from 6 to 3, the maximal release efficiency was 93.69%, achieved at pH=3, but decreased linearly with pH increasing from 7 to 12 (Fig. 3A & Fig. S2 (A2)). And NAIP was more likely to be released under alkaline condition (Fig. 3A & Fig. S2 (A1)), and the maximal release efficiency was 89.84%, achieved at pH=12.

When pH was less than 5, little OP (4.77-6.11%) was released, but the OP release efficiencies slightly increased from 45.88% to 56.09% when pH ranged from 5 to 8 (Fig. 3A & Fig. S2 (A4)). It is mainly due to the biological P release process happened during WAS anaerobic fermentation process under neutral condition (Liu et al., 1996; Acevedo et al., 2015; He et al., 2016a). Also, the OP release efficiencies still showed an increased trend with pH increasing from 9 to 12 (Fig. 3A & Fig. S2 (A4)). Although the biological P release process would be inhibited under high alkaline condition (Liu et al., 1996), the OP release is predominantly caused by sludge disintegration under alkaline conditions (He et al., 2016; Kim et al., 2015; Xu et al., 2015), the particulate COD release rates were 14.31%-37.77% when pH increased from 9 to 12, which positively correlated to

the release efficiencies of OP (Fig. S3).

The aforementioned results suggested that P release from the solid to liquid phase occurred under both acid and alkaline conditions (Fig. 3A and Fig. S2 (A5)), and the influences of pH on P release was mainly reflected through the predominant P species in sludge. While NAIP was the main fraction, extreme alkaline treatment was more favorable for P release, on the contrary, AP was more sensitive to low pH (Jin et al., 2006; Kim et al., 2003). In this work, the maximal release efficiency of TSP, 66.10%, obtained at pH=12. Similar with the findings of this work, Bi et al. (2014) reported that the optimal MRP release efficiencies obtained at initial pH13, 41.96%, the difference may be caused by the different ingredients in the sludge used. In contrast, Latif et al. (2015) reported that the increased solubility of P in WAS related to the dissolution of Ca-P and Mg-P compounds under acidic conditions, and 75% of the TP was observed to be soluble at pH 5.25. The above discussions illustrated that P release from sludge occurred under both acid and alkaline conditions, whether the released P binded or not with cations (such as Fe, Al, Mg, and Ca) depended upon pH, and amount and type of cations presented in system. Therefore, the selection of pH for the enhanced P release was depended on the predominant P fraction in WAS.

3.3.2 Clarification of different solid-P to liquid-P

In order to clarify the contributions of different solid-P fractions to the increased TDP, a release contribution equation is conducted, Eq. (7).

$$Release\ contribution\ (\%) = \frac{P^{x}_{(solid,\ Raw)} - P^{x}_{(solid,\ experiment)}}{TDP_{(liquid,\ expriment)} - TDP_{(liquid,\ raw)}} * 100 \qquad (7)$$

Where $P^{x}_{(solid,\ Raw)}$ and $P^{x}_{(solid,\ experiment)}$(mg P/ gTSS) are the contents of given P species ($x = NAIP, AP, IP\ and\ OP$, respectively.) in solid phase of the raw and treated sludge, respectively. $TDP_{(liquid,\ expriment)}$ and $TDP_{(liquid,\ raw)}$ (mg P/ gTSS) are the contents of TDP in solid phase of the treated and raw sludge, respectively.

It was evident that IP was the main source of TDP under both acid and alkaline conditions (Fig. 3(B)), the release contributions were 82.10%-98.13% when pH decreased from 5 to 3 and 77.82%-88.59% when pH increased from 9 to12, respectively. In addition, the released NAIP was the most notable contributions to TDP (Fig. 3(B)). The analysis of P fractions in solid phase of raw sludge showed that IP (NAIP and AP) was the major P fraction (Fig. 1), and NAIP was 4.35 times more than AP. Though high pH promoted the release of NAIP, NAIP could be also released under acid condition due to metal ions leaching (Latif et al., 2015; Qian and Jiang, 2014; Wang et al., 2015). By contrast, the release contributions of OP was 45.88-56.09% while pH ranging from 6 to 8. It can be concluded that the release contributions of given solid-P species to TDP depended on both the fractions of different P species in sludge and pH applied to treat sludge.

3.4 P mass balance analysis

To understand the migration and transformation mechanisms of different solid-P to liquid-P, P mass balances in TSP, TDP and TP are analyzed. Compared to the raw sludge, the content of TSP decreased under any pH conditions (Fig. 4 (A)). Though IP could be released under both acid and alkaline conditions, the NAIP and AP had different release

characteristics. The percentage of AP exhibited decrease trend with pH decreasing under acid condition, but showed increase trend with pH increasing under alkaline condition. And for NAIP, the proportion decreased under both acid and alkaline conditions, but the latter caused a more significant decrease (Fig. 4 (A) &Fig. 3A). It was obvious that the alkaline condition caused more reduction of TSP, on one hand, NAIP was the major fraction, which was more easily dissolved at higher pH. On the other hand, higher pH caused more notable sludge disintegration, and then OP was released from either EPSs or microorganism cells (Bi et al., 2014; He et al., 2016b; Kim et al., 2015; Xu et al., 2015).

In all case, MRP was the main form in liquid phase (Fig. 4 (B)), in the range of 81.13%-100%. The reason was that MRP was the main form of released IP (Dittrich et al., 2013; Jin et al., 2006; Latif et al., 2015; Zhu et al., 2012), also, released OP might be converted to MRP by microbial metabolism process (He et al., 2016b; Xie et al., 2011; Xie et al., 2010). The higher percentages of OP observed at higher pH due to remarkable sludge disintegration (Bi et al., 2014; He et al., 2016b; Kim et al., 2015; Xu et al., 2015). In contrast with TSP, TDP in liquid phase all increased (Fig. 4 (B) and (C)).

3.5 An overall mechanism for P release from WAS at different pH

Based on the results obtained in this work, an overall pathway related to pH for P release from WAS is proposed (Fig. 5). In raw TSP, P exists as OP and IP (NAIP and AP), OP represents the P fraction bond to organic matters, and can be released by sludge disintegration (path (1)) or microbial metabolism (path (2)). In addition, the released OP

may be converted to MRP by phosphatase (path (3)). High pH promotes NAIP release (path (6)) but causes AP formation (path (9)), and low pH enhances AP release (path (7)), also, some NAIP is released or formed at low pH (path (8)). The MRP in liquid phase mainly comes from paths (5), (6) and (7), and OP mainly comes from path (4). And the two parts mentioned above contribute to TDP. The release of OP increased with pH increasing under both acid and alkaline condition (Fig. 3(A) and Fig. S2 (A4)). However, the mechanisms were not consistent. When pH ranged from 5 to 8, the OP release might mainly due to the microbial metabolism during anaerobic fermentation period (Liu et al, 1996), (path (2)). And when pH increased from 9 to 12, sludge disintegration caused by the alkaline treatment might be the predominant contribution for OP release (Bi et al., 2014; He et al., 2016b; Kim et al., 2015; Pardo et al., 2003) (path (1)). The details for IP release mechanisms are discussed as follows.

At low pH (3-6), a remarkable amount of AP was dissolved, and lower pH applied, more AP released (Fig. 3 (A) and Fig. S2 (A5)). This is because H^+ has a positive effect on Ca-P dissolution, and lower pH provides more H^+ leading to more Ca-P dissolve (Jin et al., 2006; Latif et al., 2015; Qian and Jiang, 2014; Wang et al., 2015), an increase of 27.73%-260.49% (i.e., 20.37-191.29 mg/L) has been observed on Ca^{2+} release compared to the raw sludge while pH decreasing from 6 to 3. In addition, the carbon dioxide produced during the microbial metabolic process also contributes to the dissolution of Ca-P under acid condition (Gao et al., 2015; Jiang and Wu, 2008). It was noteworthy that NAIP was also dissolved under acid condition (Fig. 3 (A) and Fig. S2 (A1). The

possible reason is that metal ions (such as Fe and Mg) leaching caused by H^+ led to the P-precipitants be soluble (Latif et al., 2015; Qian and Jiang, 2014; Wang et al., 2015). And when pH decreased from 6 to 3, the concentrations of Fe and Mg in liquid phase increased by 12.83%-511.67% and 67.42%-186.55%, respectively, compared to the raw sludge, which were positively correlated with the released NAIP, a further investigation is needed to identify the relationship between released P and leached cations in the coming study (path (8)).

At high pH (8-12), a considerable amount of NAIP was dissolved, and higher pH applied, more NAIP released (Fig. 3 (A) and Fig. S2 (A1)). This is because under alkaline condition, on one hand, OH^- can dissolve Al-P and unite with Fe^{3+}, which has been bounded to phosphate anion, and then phosphate anion is released from solid to liquid phase by precipitation-dissolution and ion-exchange reactions (Jin et al., 2006; Gao et al., 2015; Jiang and Wu, 2008), on the other hand, OH^- can lead to sludge colloids carry negative electricity, which will enhance the desorption between phosphate anion and sludge colloids (Jiang and Wu, 2008). It was notable that the AP in solid phase presented positive growth with pH increasing from 8 to 12 (Fig. 3(A) and Fig. S2 (A2)), which was adverse to P release. The reason is that the hydroxyapatite has been formed under alkaline condition (path (9)).

3.6 Implications of the findings for WW and WAS treatments.

The findings obtained in this work revealed that P release from WAS occurred under both acid and alkaline condition, and the recoverable P from sludge depended on

the predominant P fraction in sludge and pH applied to treat sludge. Until now, P is mainly recovered with crystallization as hydroxyapatite or struvite (Bi et al., 2014; Kim et al., 2015). In present study, the concentrations of NH_4^+ gradually increased at any pH (Fig. S4 (A)) during the fermentation period, and the highest NH_4^+ accumulation obtained under alkaline condition (514.15 mg/L at pH 10.0 and 518 mg/L at 11.0). In view of NH_4^+ accumulated in the liquid phase and the fermentation liquid presented alkaline property, struvite was attractive to simultaneously recover P and nitrogen (N) (Bi et al., 2014; Warmadewanthi, 2009). And high NH_4^+ would enhance formation of the ammonia precipitates struvite (Fig. S4 (B)) (Zhang et al., 2016). In addition, the SCFAs were also produced during WAS anaerobic fermentation, and it was obvious that alkaline condition was more favorable for SCFAs production compared to acid condition (e.g., 351mg COD/ gVSS at pH 11, Fig. S5 (A)), and the two highest individual SCFAs were acetate and propionate, with a total percentage of 45.59-76.51% (Fig. S5 (B)). As well known, the available biodegradable COD in influent, cannot meet the carbon source (CS) demand for nutrients removal in biological WW treatment process, especially EBPR process (He et al., 2016a). Considering that chemically synthesized CS (e.g., acetate, propionate and glucose) is neither cost-effective nor sustainable (He et al., 2016a), it is of great significance if the SCFAs produced during P release process can be recovered as the external CS in situ in full scale WWTPs.

Based on the findings obtained in this work and referenced the previous study (He et al., 2016a), a new door may be opened for WAS and WW treatments. As

shown in Fig.6, an alternative and potential outline for both resource recovery from WAS and CS supplementation for WW treatment in situ in WWTPs is proposed. The alkaline anaerobic fermentation is applied to treat WAS for releasing carbon and nutrients. After settling, a fermentation liquid (rich in C, N and P elements) is achieved. As the fermentation liquid presents alkaline, the magnesium salts is added to the C, N, and P separation system to recover P and N simultaneously by struvite with coagulation/sedimentation process, and then the supernatant, rich in SCFAs, can be used as the external CS for the WW treatment process. Based on the performance of WAS anaerobic fermentation at pH11 obtained in this study and the results reported by Warmadewanthi (2009), who reported that 92.1% P from WW could be recovered as struvite, 47.43% TP (calculated by soluble MRP) and 18.67% TCOD (calculated by Total SCFAs produced) could be recovered. Therefore, the outline for WW and WAS treatments proposed in this work may be potential and practical for the sustainable operation of WWTPs in the future.

4. Conclusions

This work was developed to identify P fractions in sludge and investigate P release enhancement mechanism related to pH from WAS. The following major conclusions could be presented. (1) WAS could be selected as potential substitution of phosphate rock to recover P. (2) The overall rate of MRP accumulation process was controlled by a pseudo-chemical reaction. (3) The releasable and recoverable P depended on both the fraction of different P species in sludge and pH adjustment for sludge treatment. (4)

Based on the findings of this work, a potential and practical concept was proposed for WW and WAS treatments.

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Table 1 Kinetic parameters for MRP accumulation in liquid phase.

pH	$q_{e,exp}$ (mg/L)	Pseudo-first-order kinetic			Pseudo-second-order kinetic model				
		k_1 (h^{-1})	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2	*ARE*	Δq
Control	159.75	0.0156	138.21	0.892	1.10E-04	191.44	0.863	0.86	9.29
pH=3	369.29	0.0177	184.02	0.888	6.96E-04	371.92	0.999	2.93	17.12
pH=4	389.00	0.0159	215.00	0.893	5.45E-04	390.30	0.999	1.85	13.59
pH=5	340.25	0.0094	179.09	0.610	6.39E-04	340.96	0.997	0.75	8.68
pH=6	199.17	0.0107	163.36	0.951	4.33E-04	204.38	0.989	0.65	8.05
pH=7	169.09	0.0069	123.37	0.625	9.90E-04	169.54	0.983	0.73	8.54
pH=8	189.83	0.0051	126.74	0.361	1.14E-03	188.91	0.980	0.51	7.16
pH=9	213.69	0.0146	141.08	0.736	8.16E-04	214.79	0.993	1.92	13.84
pH=10	372.71	0.0147	301.63	0.913	1.97E-04	380.83	0.986	3.37	18.34
pH=11	533.46	0.0125	500.73	0.846	7.10E-05	529.80	0.962	5.53	23.52
pH=12	556.98	0.0198	346.48	0.941	2.55E-04	577.80	0.999	2.50	15.82

Figure captions

Fig. 1 P fractions in solid phase of raw sludge.

Fig. 2 Kinetic modeling of MRP accumulations in liquid phase. (A) the fitting line of pseudo-first-order, (B) the fitting line of pseudo-second-order, (C) the matched curves between measured and modeled values by pseudo-second-order model.

Fig. 3 Release efficiencies (A) and contributions (B) of P from solid to liquid phase at different pH.

Fig. 4 P mass balance at different pH. (A) TSP, (B) TDP, and (C) TP.

Fig. 5 Pathway for the migration and transformation of the TSP to TDP.

Fig.6 Schematic diagram of a potential outline of WW and WAS treatments in WWTPs.

Fig. 1

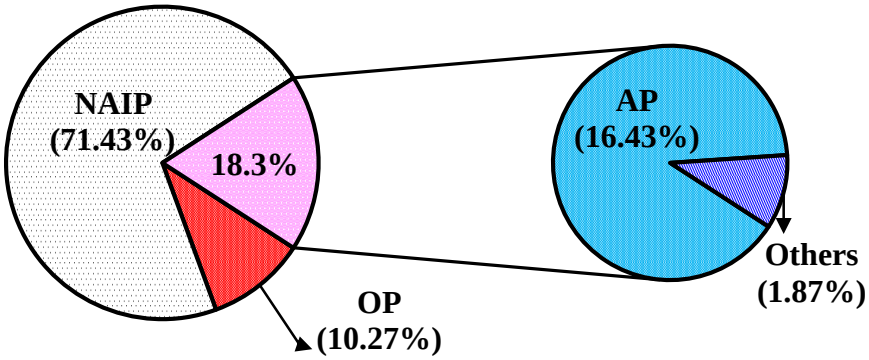


Fig. 2

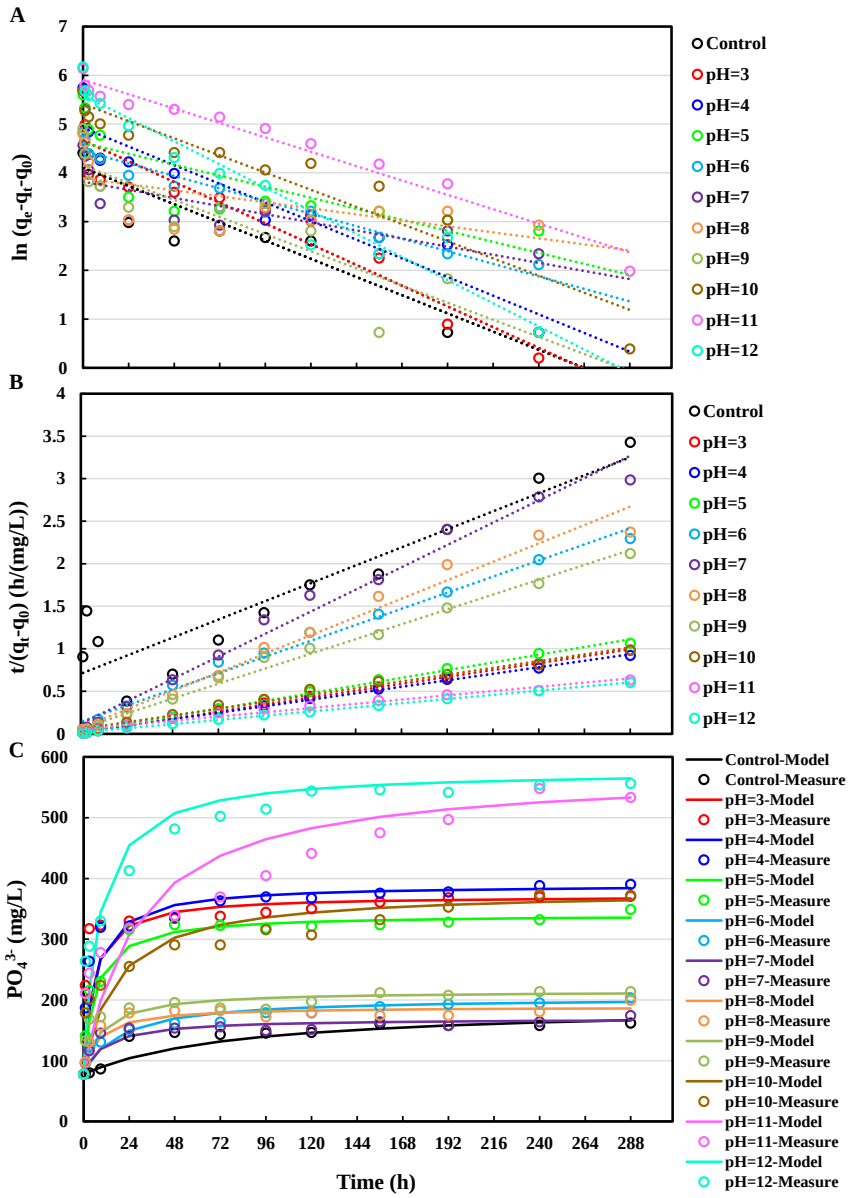

A
ln (qe-qt-q0)
Control
pH=3
pH=4
pH=5
pH=6
pH=7
pH=8
pH=9
pH=10
pH=11
pH=12
B
t/(qt-q0) (h/(mg/L))
C
PO4 3- (mg/L)
Control-Model
Control-Measure
pH=3-Model
pH=3-Measure
pH=4-Model
pH=4-Measure
pH=5-Model
pH=5-Measure
pH=6-Model
pH=6-Measure
pH=7-Model
pH=7-Measure
pH=8-Model
pH=8-Measure
pH=9-Model
pH=9-Measure
pH=10-Model
pH=10-Measure
pH=11-Model
pH=11-Measure
pH=12-Model
pH=12-Measure
Time (h)

Fig. 3

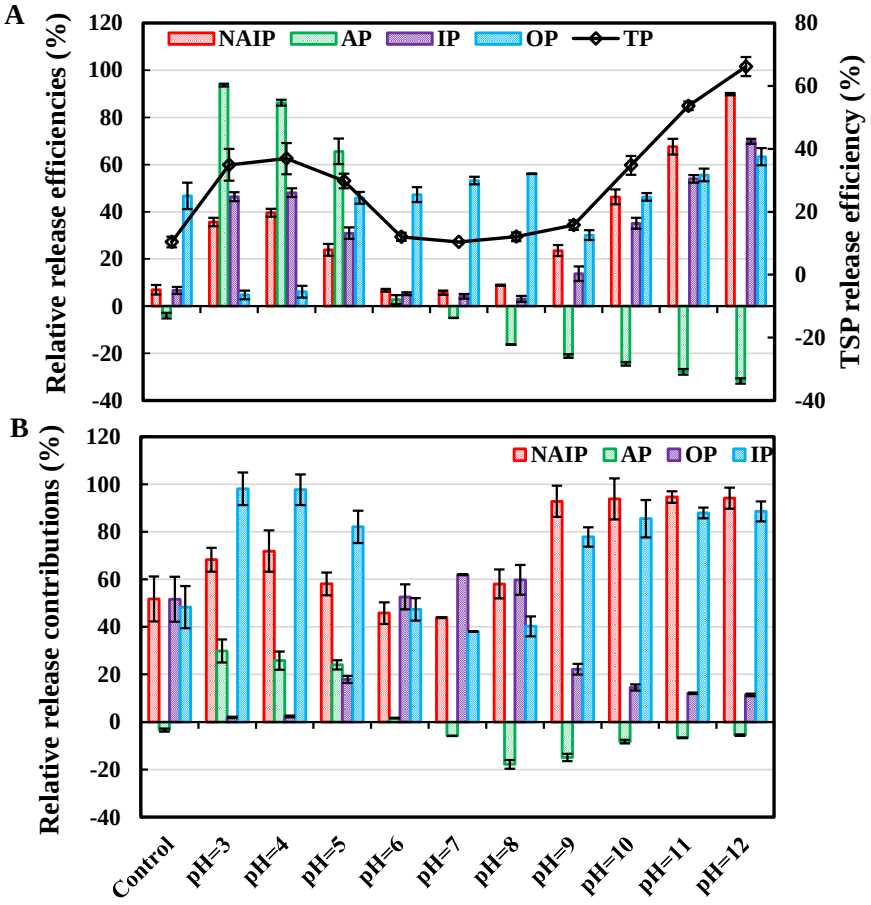

A
Relative release efficiencies (%)
TSP release efficiency (%)
NAIP
AP
IP
OP
TP
B
Relative release contributions (%)
NAIP
AP
OP
IP
Control
pH=3
pH=4
pH=5
pH=6
pH=7
pH=8
pH=9
pH=10
pH=11
pH=12

Fig. 4

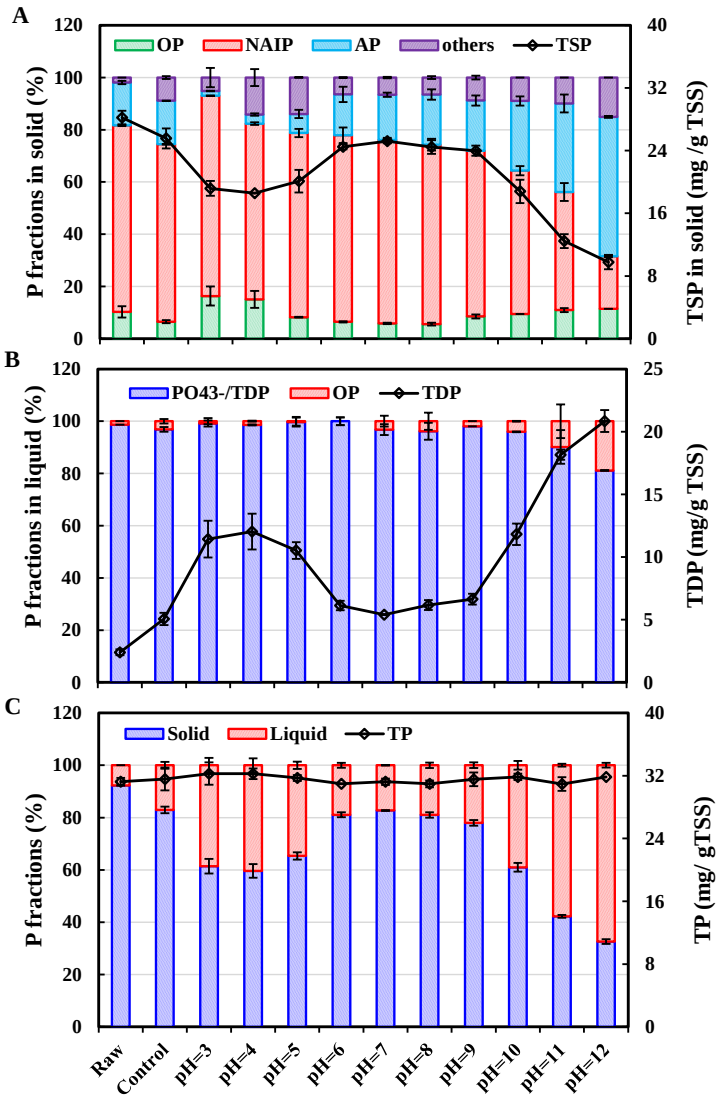

A
OP
NAIP
AP
others
TSP
P fractions in solid (%)
TSP in solid (mg /g TSS)
B
PO43-/TDP
OP
TDP
P fractions in liquid (%)
TDP (mg/g TSS)
C
Solid
Liquid
TP
P fractions (%)
TP (mg/ gTSS)
Raw
Control
pH=3
pH=4
pH=5
pH=6
pH=7
pH=8
pH=9
pH=10
pH=11
pH=12

Fig. 5

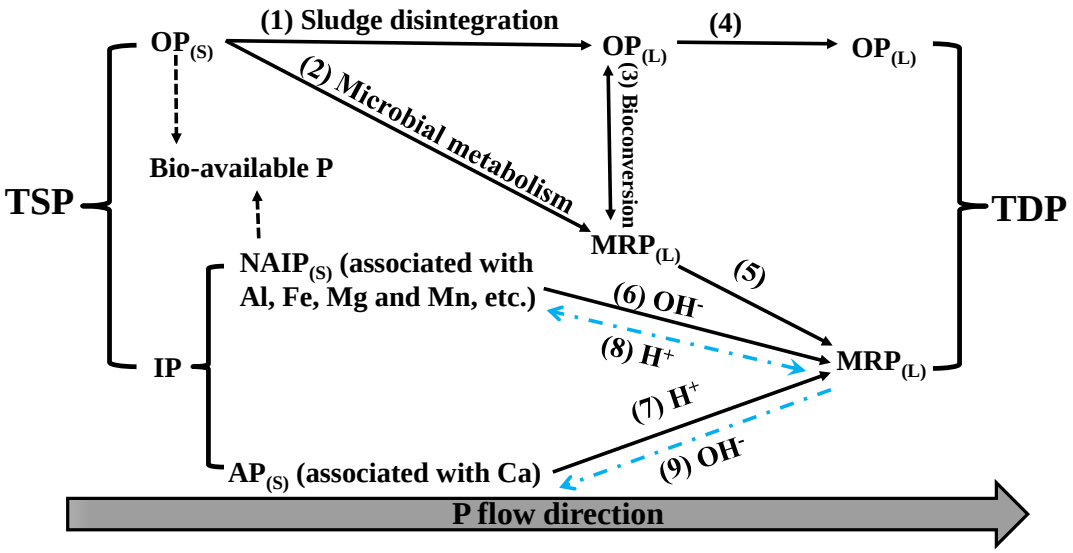
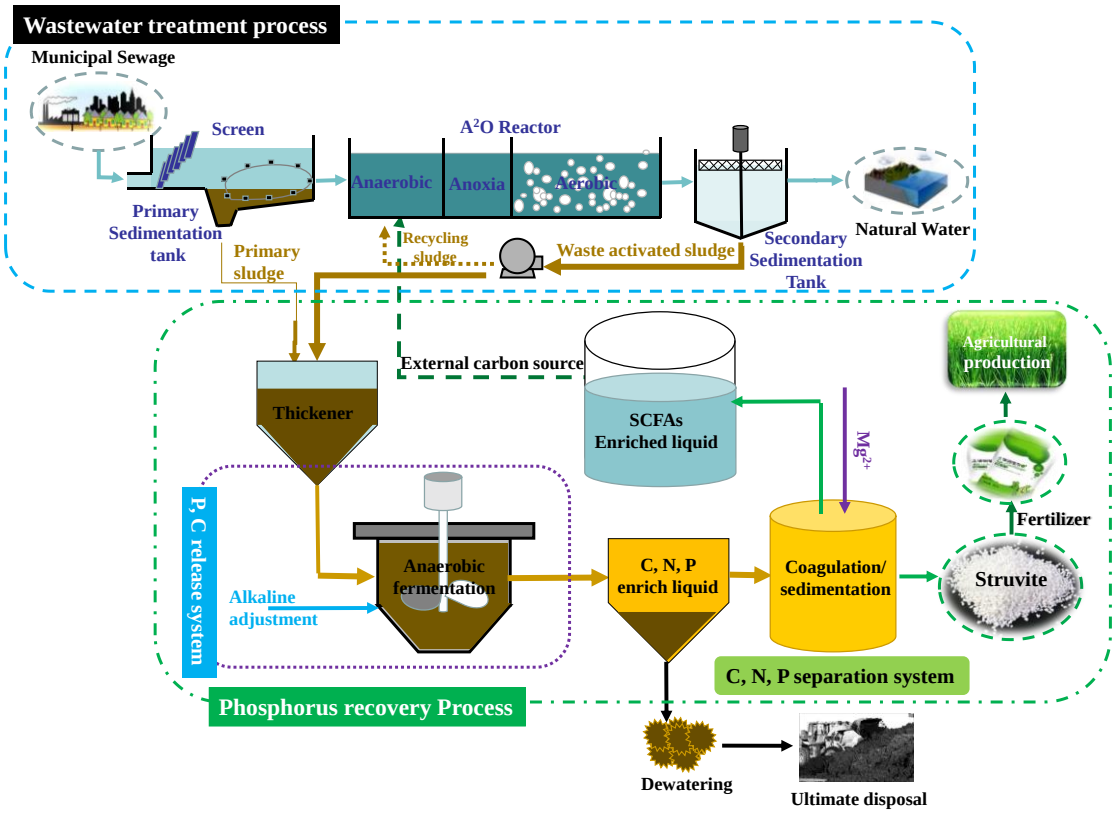
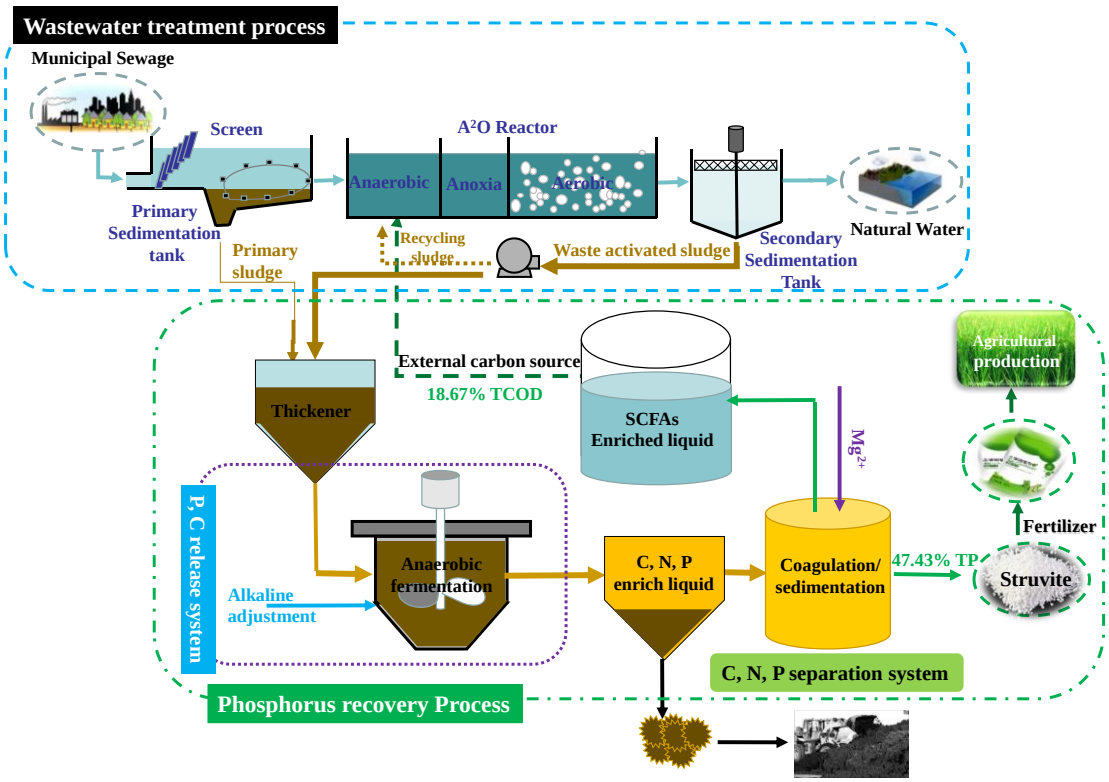

(1) Sludge disintegration
OP(S)
OP(L)
(4)
OP(L)
(2) Microbial metabolism
(3) Bioconversion
Bio-available P
TSP
TDP
MRP(L)
NAIP(S) (associated with Al, Fe, Mg and Mn, etc.)
(5)
(6) OH-
(8) H+
MRP(L)
IP
(7) H+
(9) OH-
AP(S) (associated with Ca)
P flow direction

Fig. 6


Wastewater treatment process
Municipal Sewage
Screen
A²O Reactor
Anaerobic
Anoxia
Aerobic
Primary Sedimentation tank
Primary sludge
Recycling sludge
Waste activated sludge
Secondary Sedimentation Tank
Natural Water
External carbon source
Thickener
SCFAs Enriched liquid
Agricultural production
Mg²⁺
Fertilizer
P, C release system
Alkaline adjustment
Anaerobic fermentation
C, N, P enrich liquid
Coagulation/ sedimentation
Struvite
C, N, P separation system
Phosphorus recovery Process
Dewatering
Ultimate disposal

Graphic abstract