

Chemical stress from Fe salts dosing on biological phosphorus and potassium behavior

Jie Fan, Hang Zhang, Jiasong Ye and Bin Ji

ABSTRACT

In simultaneous precipitation, interaction between chemical and biological P removal could not be ignored. This work investigated effects of ferrous sulfate and Fe precipitates on metabolic behavior of bio-P and its counter cation of potassium. After dosing, mixed liquid suspended solids (MLSS) increased 9%, pH decreased from 7.35 to 7.00, sludge volume index (SVI) decreased, electrical conductivity increased. Chemical oxygen demand (COD) and NH_3 removal was not affected. Fe dosing initially showed synergistic effect, and then inhibition appeared at accumulative dose above 10 mgFe/gMLSS. Both precipitate FePO_4 and $\text{Fe}(\text{OH})_3$ deteriorated effluent P. FePO_4 dissolved 35% in anaerobic phase which failed to be totally reprecipitated in oxic phase, resulting in increased effluent P. FePO_4 inhibited K uptake rather than bio-P uptake. $\text{Fe}(\text{OH})_3$ caused reduction of bio-P release, meanwhile, its inhibition on K and bio-P uptake was greater than FePO_4 . Phosphorus metabolism was inhibited when sludge contained 0.15 mM FePO_4 or 0.10 mM $\text{Fe}(\text{OH})_3$. Increased K/P molar ratio and coefficient b could be indicators for Fe residual in sludge. Intermittent dosing was suggested for wastewater treatment plant (WWTP) operation.

Key words | activated sludge, biological phosphorus removal, ferric hydroxide, ferric phosphate, potassium

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INTRODUCTION

Biological phosphorus removal is economical and widely used in wastewater treatment plants (WWTP) to avoid eutrophication in receiving water body. biological phosphorus removal (BPR) is sensitive to many factors such as C/P ratio, environmental parameters and plant configuration, so effluent P is always not stable. Nowadays in China, effluent total phosphorus (TP) is required to be less than 0.5 mg/L. It is common to achieve this goal by chemical dosing such as Fe salts (ferric chloride, ferrous sulfate) or aluminum salts. Coagulate may be dosed on the primary settler (pre-precipitation), aeration tank (simultaneous precipitation), or behind the second settler (post-precipitation).

The interaction between activated sludge and chemicals in simultaneous precipitation is of the most concern. Previous studies had shown that activated sludge process was partially inhibited in the presence of Fe salts addition. pH dropped after the addition of ferrous ion into wastewater; overdose can even result in acidic pH unfavorable for nitrification (Banu *et al.* 2008). The activity of ammonium and nitrite oxidizing bacteria was affected by accumulation of Fe relating products into the sludge (Oikonomidis *et al.* 2010). Chemically dosed biomass had a

significant lower oxygen uptake rate, poor dewaterability and a reduction in volatile suspended solids (VSS).

Until now, a few researches were devoted to effect of chemical phosphorus removal on biological phosphorus removal. Under the condition of limited influent P, biological mechanism was clearly inhibited in the presence of FeCl_3 (De Haas *et al.* 2000). Fe(II) competed with the bio-P organisms and inhibited the biological phosphorus removal completely at doses exceeding 9 mg/L of Fe(II) (Valve *et al.* 2002). P release even disappeared after dosing for 6 months (Liu *et al.* 2011). Biological phosphorus removal could tolerate a maximum coagulant load, which once exceeded, led to a low reactor performance (Gregorio *et al.* 2011). However, it was unclear whether this derived from biological or chemical effect. Due to the complex constituent of precipitates, such as ferric phosphate, ferric hydroxide and ferric-oxo-hydroxo-phosphate (Caravelli *et al.* 2012), chemical P and biological P was not easy to distinguish, nevertheless potassium, which was an essential counter cation of polyphosphate, could help to reveal the biological P behavior in simultaneous precipitation. Potassium was co-transported with phosphorus into and out of

bacterial cells with a constant molar ratio of K/P (Schonborn *et al.* 2001).

The objective of this work is to (a) evaluate the performance of simultaneous precipitation with ferrous sulfate, (b) determine the transformation of ferric phosphate and ferric hydroxide in anaerobic/oxic phase, (c) effect of residual precipitates on biological phosphorus and potassium behavior.

MATERIALS AND METHODS

Reactors and operation

Activated sludge was inoculated from Huangjiahu WWTP. The reactors, 3 L of each, operated as A/O SBR consisting of anaerobic 1 h, oxic 4 h, settling 0.5 h. Wastewater was withdrawn from the sewers of campus. Influent wastewater quality was: chemical oxygen demand (COD)_{cr} 300–450 mg/L, 5-day biochemical oxygen demand (BOD₅) 120–220 mg/L, suspended solids (SS) 30–90 mg/L, NH₃-N 25–50 mg/L, total nitrogen (TN) 50–80 mg/L, total phosphorus (TP) 3–9 mg/L. Mixed liquid suspended solids (MLSS) was 3,000 mg/L. Sludge retention time (SRT) was maintained at 10 d.

After 2 weeks' acclimation, Fe dosing was implemented. The reactors labeled as control (undosed), SPR (simultaneous phosphorus removal), R1 (activated sludge with 0.075 mM FePO₄), R2 (activated sludge with 0.15 mM FePO₄), R3 (activated sludge with 0.05 mM Fe(OH)₃), and R4 (activated sludge with 0.10 mM Fe(OH)₃). FePO₄ or Fe(OH)₃ without activated sludge was dosed in wastewater to determine the transformation of precipitates. Samples were collected after first SRT FeSO₄·7H₂O dosing to compare the performance of control and SPR. Tests of R1–R4 were conducted three times and average values were used for analysis.

Dosing of chemicals

According to our previous jar test, SPR was achieved by dosing FeSO₄·7H₂O at the end of the oxic 3 h with Fe/P molar ratio of 1.5:1. Effluent P of the control was 2.3–3.7 mgP/L which need to be chemically removed with 0.11–0.18 mmolFe/L (6–10 mgFe/L). In the SPR system, besides the precipitation of FePO₄ and Fe(OH)₃, FeOOH, soluble mononuclear (Fe(OH)_n⁵⁻ⁿ, *n* = 1–4) or multinuclear hydrolysis species (Fe₂(OH)₂⁴⁺, Fe₃(OH)₄⁵⁺) were also formed (Caravelli *et al.* 2010). In view of the complex composition of the precipitates and impossible to separate,

chemically pure FePO₄·4H₂O and Fe(OH)₃ (purchased from Sinopharm Chemical Reagent Co. Ltd) were selected to simulate and represent the main precipitates FePO₄ and Fe(OH)₃.

Iron present in sludge was in the Fe³⁺ oxidation state regardless of ferrous or ferric iron was dosed (Wu *et al.* 2015). Considering the fraction of Fe³⁺ that formed FePO₄ and Fe(OH)₃ was 65% and 35% at pH 7 (Caravelli *et al.* 2010), and precipitates always accumulated in sludge, therefore the residual amount of FePO₄ in activated sludge was set as 0.075 mmol/L (usual dose, R1) and 0.15 mmol/L (overdose, R2). The residual amount of Fe(OH)₃ in activated sludge set as 0.05 mmol/L (usual dose, R3) and 0.10 mmol/L (overdose, R4).

Analytical methods

Samples from the supernatant were filtered through 0.45 μm cellulose acetate membrane. Orthophosphate (PO₄³⁻), soluble Fe²⁺ and MLSS were measured according to *Standard Methods* (APHA, 2005). Potassium was measured by potassium ion meter (PXS-270, Shanghai Leici Inc., China). Electrical conductivity (EC) was measured by EC meter (DDS-307, Shanghai Leici Inc., China).

RESULTS AND DISCUSSION

Performance of SPR

For the control test, effluent P was initially around 0.5 mg/L, influent P on day 7 increased from 2.8 to 4.6 mg/L, and then effluent P fluctuated to 1.0–1.5 mg/L. With dosing of ferrous sulfate, effluent P was below 0.5 mg/L and more stable. Average effluent P of the control and SPR was 0.98, 0.33 mg/L, demonstrating the effectiveness of chemical assisted biological phosphorus removal. After dosing, MLSS increased 9% (Figure 1(a)), pH decreased from 7.35 to 7.00, sludge volume index (SVI) decreased from 85 to 70 mL/g which indicated better settleability, EC increased from 790 to 831 μS/cm (Figure 1(b)). pH decrease was attributed to dose of ferrous sulfate (Banu *et al.* 2008) and competition between ferric phosphate and ferric oxidize (Zhang *et al.* 2013). The decrease of pH did not reach 6.5, which would inhibit P release and uptake (Oehmen *et al.* 2007).

Once ferrous sulfate was dosed at the end of oxic 3 h, uptake of potassium ceased and remained unchanged until the end of the aeration (Figure 1(c)); however, K uptake of control in last aeration hour was 0.43 mg/L. This result

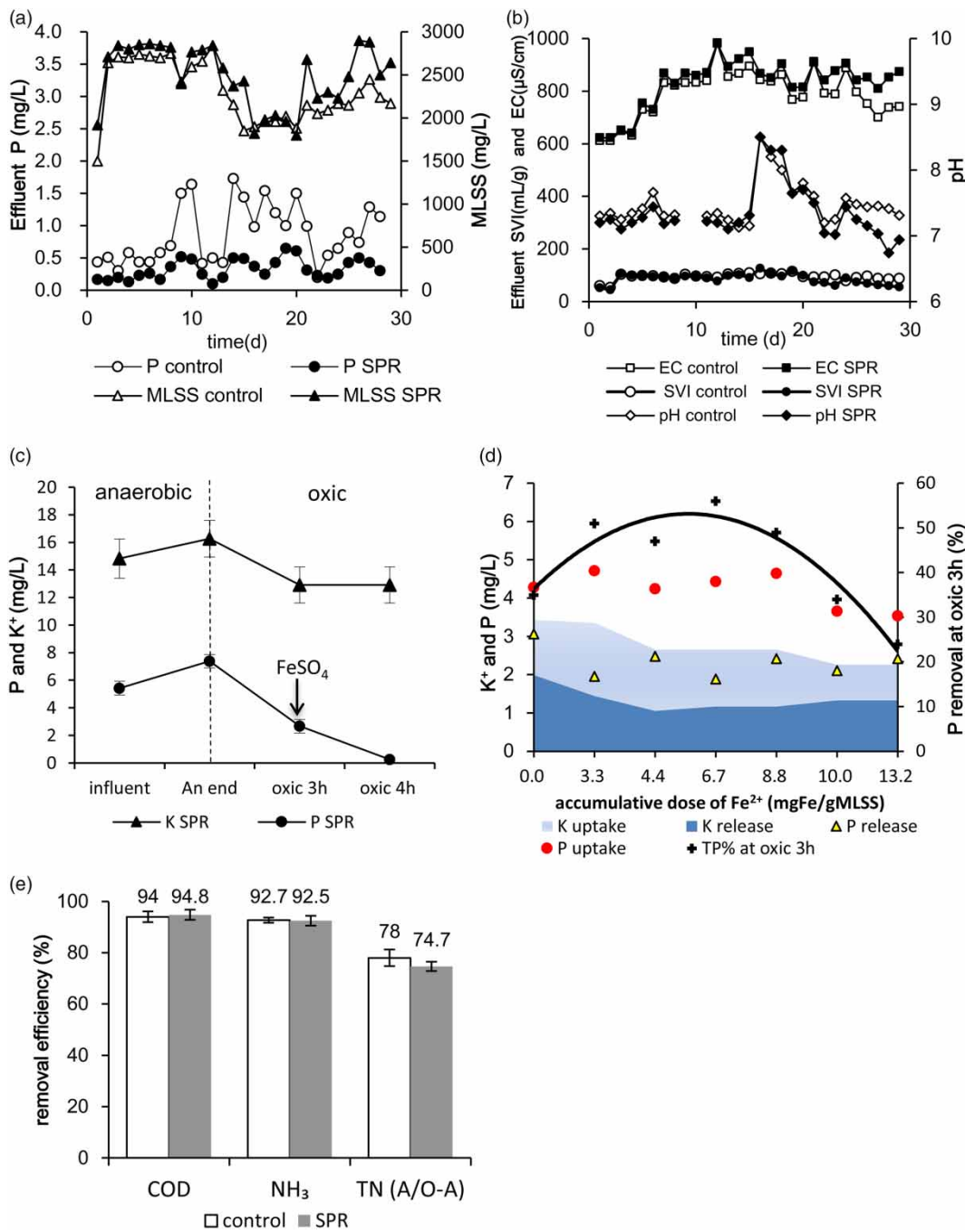


Figure 1 | Performance of the control and SPR system. (a) Effluent P and MLSS, (b) effluent SVI and EC, (c) K and P of SPR, (d) metabolism of K and P with accumulative dose, (e) COD, NH₃ and TN removal.

indicated inferior competition of phosphorus accumulating organisms (PAOs) compared with ferrous sulfate in the last aeration hour, and the reason could not be ascribed to lack of phosphorus (2.5 mgP/L at the end of oxic 3 h). After dosing for several days, accumulative effect was present (Figure 1(d)). P release immediately decreased by 28%, P uptake began to decrease when Fe dose was up to

10 mgFe/gMLSS. Release and uptake of potassium decreased by 47% and 23%, respectively, at accumulative dose of 4.4 mg Fe/gMLSS, and then kept stable. Furthermore, P removal at the end of oxic 3 h could explain combined effect of PAOs and Fe residuals. Accumulative dose of 6.7 mgFe/gMLSS showed a best synergetic P removal, while negative effect appeared at 10 mgFe/gMLSS, at which dose P uptake

began to decrease. From the results above, P release, K release and uptake was reduced immediately when dosing, but reduction of P uptake was delayed and appeared simultaneously with inhibition. Reduction of P uptake could be forewarning of depression of PAOs in WWTP operation.

With regard to the effect of Fe dosing on COD, $\text{NH}_3\text{-N}$, and TN removal (Figure 1(e)), COD removal was a little higher than the control. NH_3 removal was not impacted. Failed nitrification in literatures was due to low pHs (<6.0), which did not appear in this study. During anaerobic/oxic phase, TN removal had no difference with the control. In order to remove NO_x at the end of oxic, anoxic phase was introduced through N_2 stripping and addition of acetate, consequently TN removal with dosing was lower than the control. There was no consistent founding about TN removal with Fe dosing. Zhang *et al.* (2015b) found the addition of $\text{Fe(II):P} = 2$ in oxic phase did not interfere with TN reduction. Wang *et al.* (2015) dosed 20 mgFe/L in a pre-denitrification tank and TN removal was accelerated from 62% to 89%. The details about the mechanisms of TN removal with Fe dosing remain not fully understood and need further research.

Effect of FePO_4 on biological P and K metabolism

Due to reduction of redox potential in anaerobic phase, precipitate FePO_4 formed in aerobic phase could dissolve and release phosphorus to wastewater, so it was necessary to determine whether increased P release was related with PAOs or dissolution of FePO_4 . In order to confirm dissolution of FePO_4 , only ferric phosphate (without biomass) was dosed in wastewater (Figure 2(a)), in anaerobic phase P dissolved from 0.075 mM and 0.15 mM FePO_4 was 0.82 and 1.98 mg/L, respectively, accounted for 35% of the dosed FePO_4 . But ferrous iron dissolved from 0.075 mM, 0.15 mM FePO_4 was only 0.25, 0.60 mg/L, much less than dissolved P. The unbalanced dissolution of ferrous iron and phosphate was associated with capture of ferrous iron by S^{2-} (Gregorio *et al.* 2010) and OH^- , color of sludge with FePO_4 became dark in anaerobic phase. In aerobic phase, the dissolved P could not be totally precipitated and residual P was 0.40 and 0.75 mg/L, accounted for 17% of dosed FePO_4 . This phenomenon could be explained by deprivation of ferric or ferrous iron bounded as FeS and ferrous hydroxide in anaerobic phase and the reaction was irreversible (Gachter & Muller 2003). Thus, P dissolved from FePO_4 would release extra P to wastewater. This was one reason for deteriorated effluent P in WWTP.

In FePO_4 -biological systems R1 and R2, P release in anaerobic phase increased with increasing content of FePO_4

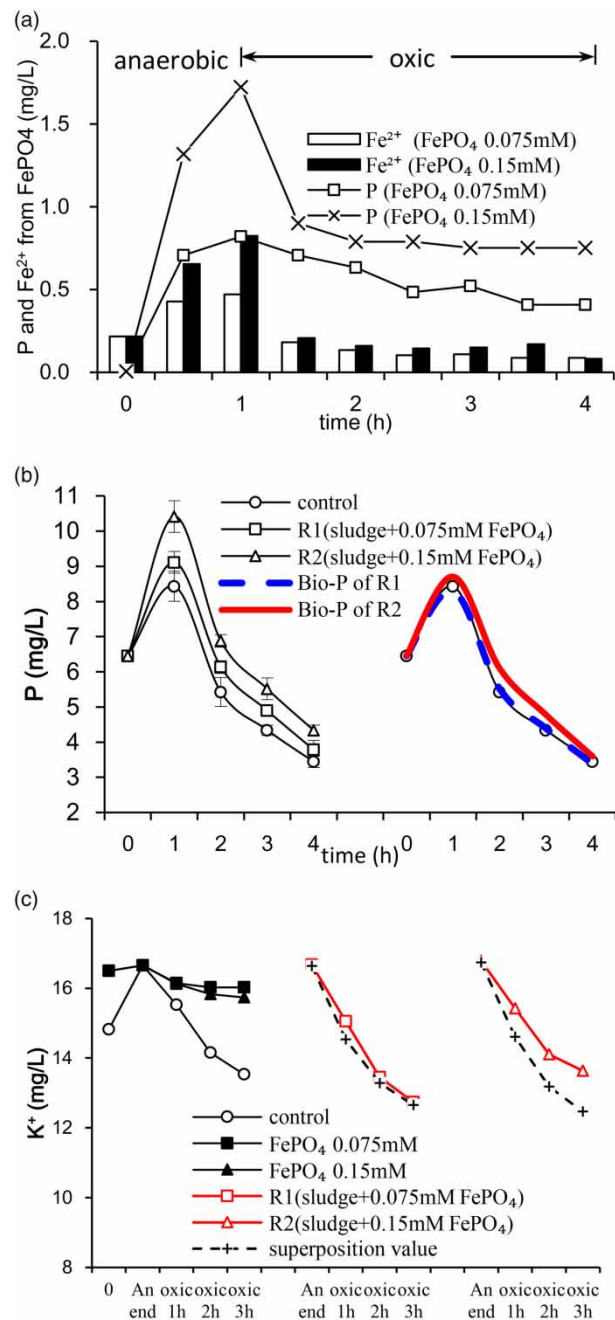


Figure 2 | Effect of FePO_4 on biological P and K. (a) Transformation of FePO_4 in wastewater, (b) combined P and bio-P of sludge with FePO_4 , (c) K adsorbed by sludge, FePO_4 , sludge with FePO_4 .

(Figure 2(b)). Effluent P of control, R1, R2 were 3.44, 3.78 and 4.34 mg/L. The increase in effluent P was coincidental with extra P from FePO_4 transformation (Figure 2(a)), extra P from FePO_4 was not be effectively utilized by PAOs. Based on finding (Caravelli *et al.* 2010) that presence of biomass did not affect the orthophosphate precipitation, orthophosphate precipitation was considered to be independent of biological

phosphorus removal in this work; bio-P could be calculated as difference between combined P (P in R1 or R2) and chemical P. Bio-P of R1 was the same as the control. In R2, a little more bio-P was released in anaerobic phase, but it failed to be absorbed in aerobic phase.

Potassium ion was absorbed not only by PAOs but also by FePO_4 as a result of charge neutralization, zeta potential of FePO_4 and activated sludge was -30 to -40 mV (Smoczyński *et al.* 2014), -10 to -20 mV (Zhang *et al.* 2015a), respectively. In Figure 2(c), K adsorption by sludge, 0.075 mM FePO_4 , 0.15 mM FePO_4 was 3.12 , 0.63 , 0.92 mg/L, respectively. K adsorption by FePO_4 could not be ignored since it accounted for 20–29% of that by activated sludge. When no interaction existed between FePO_4 and activated sludge for K adsorption, K uptake by FePO_4 and activated sludge could be superposed directly. If measured value was consistent with superposed value, there was no interaction. Otherwise, interaction appeared. K adsorption in R1 fit closely with the superposed value. 26% reduction of K adsorption in R2 reflected negative interaction between 0.15 mM FePO_4 and activated sludge. K inhibition in R2 was accompanied by increased bio-P release (Figure 2(b)), which was attributed to lack of potassium (Jiang 2011). Whether potassium adsorbed by FePO_4 could be available by PAO need further research.

Effect of $\text{Fe}(\text{OH})_3$ on biological P and K metabolism

It was expected that ferric hydroxide would adsorb phosphate, but in this work, ferric hydroxide prefers to adsorb potassium (13%) rather than phosphorus (5%) in wastewater (Figure 3(a)). In order to confirm the K adsorption by $\text{Fe}(\text{OH})_3$, potassium was dissolved in distilled water, and it was also adsorbed by $\text{Fe}(\text{OH})_3$. The possible reason for K adsorption in wastewater and distilled water was the negative charge of $\text{Fe}(\text{OH})_3$. Solubility of $\text{Fe}(\text{OH})_3$ and ferric hydrolysis can be described by Equations (1)–(5), in the pH range of wastewater, the main ferric specie was $\text{Fe}(\text{OH})_3$, meanwhile, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-$ coexisted (Duan & Gregory 2003). The reported point of zero charge (PZC) of synthetic $\text{Fe}(\text{OH})_3$ was 7.5 – 8.2 (Kosmulski 2009). When pH above PZC $\text{Fe}(\text{OH})_3$ surface was negatively charged, the amorphous $\text{Fe}(\text{OH})_3$ in the wastewater was able to be negatively charged and able to adsorb potassium.

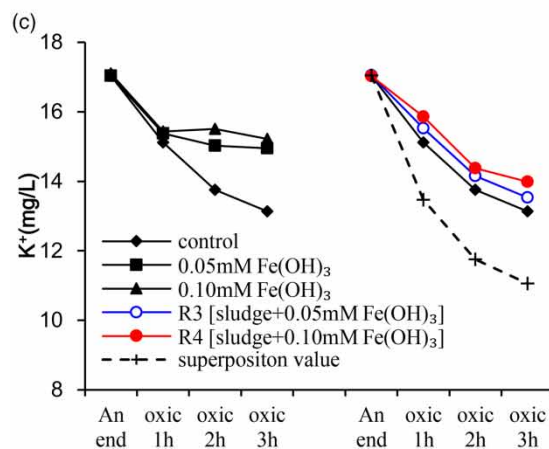
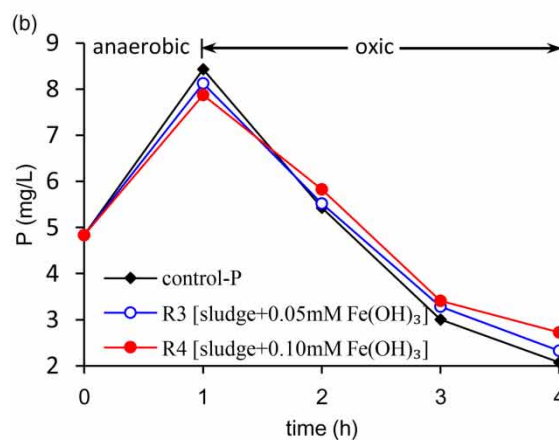
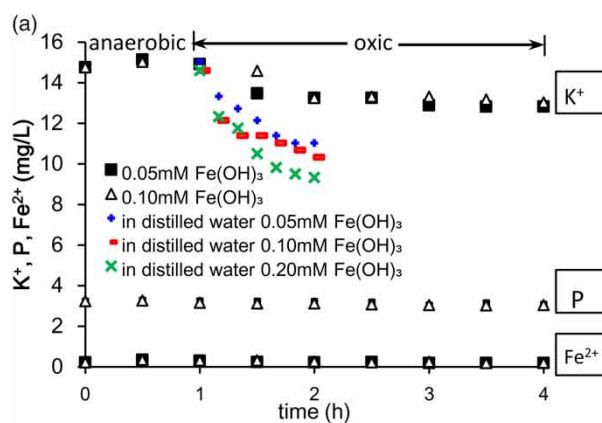
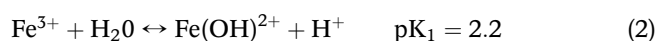
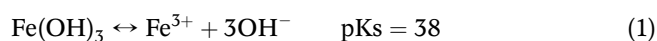
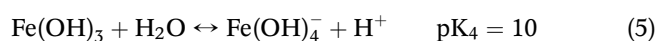
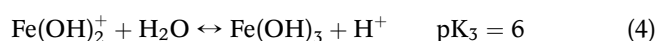
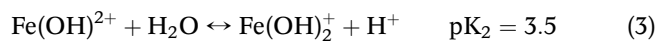


Figure 3 | Effect of $\text{Fe}(\text{OH})_3$ on biological P and K. (a) Adsorption of P and K by $\text{Fe}(\text{OH})_3$ in wastewater, (b) P profile of sludge, sludge with $\text{Fe}(\text{OH})_3$, (c) K adsorbed by sludge, $\text{Fe}(\text{OH})_3$, sludge with $\text{Fe}(\text{OH})_3$.



The P absorbed by $\text{Fe}(\text{OH})_3$ could be ignored compared with that by activated sludge, so P of R3 and R4 (Figure 3(b)) could be directly considered as bio-P. Bio-P release of R3 and R4 reduced 9% and 16%, respectively. Bio-P uptake in the first aerobic hour was the most different, and it reduced 13% and 32% for R3 and R4. It was obvious that bio-P uptake was more sensitive than bio-P release to inhibition caused by $\text{Fe}(\text{OH})_3$.

In Figure 3(c), K adsorption by $\text{Fe}(\text{OH})_3$ accounted for 48–53% of that by activated sludge. When activated sludge contained $\text{Fe}(\text{OH})_3$, negative interaction appeared as the measured values of R3 and R4 apparently deviated from the superposition value. Furthermore, K adsorption of R3 and R4 was even 10%, 22% less than the control, which clearly confirmed inhibition of PAOs by $\text{Fe}(\text{OH})_3$. Since there was no P competition between PAOs and $\text{Fe}(\text{OH})_3$, the reason for reduced P uptake was related with inhibition of K uptake.

Kinetics and inhibition analysis

The kinetic models for K adsorption and bio-P uptake were:

$$S = S_0 \exp(-kt) \quad (6)$$

where S_0 was the initial concentration, S was the concentration at time t , k was the reaction rate constant. In Table 1, K uptake was on behalf of both chemical and biological effect. Despite K adsorption by FePO_4 and $\text{Fe}(\text{OH})_3$ coincided with pseudo-second-order kinetic model, K uptake in R1–R4 still fit well with Equation 6 which usually describes the kinetics of biological process. The result demonstrated the dominance of biological effect. Negative interaction between Fe and activated sludge was determined as the reduction percentage of kinetic rate

constant (k). Bio-P uptake was not affected by FePO_4 . The inhibition of 0.075 mM, 0.15 mM FePO_4 on K uptake was 10% and 27%, respectively. With regard to $\text{Fe}(\text{OH})_3$, it inhibited both uptake of K and bio-P, and the inhibition degree was greater than FePO_4 . Decrease in ratio of bio-P uptake to release showed weak biological phosphorus metabolism when activated sludge contained 0.15 mM FePO_4 or 0.10 mM $\text{Fe}(\text{OH})_3$. Through analysis of the ratio of bio-P uptake to release and interaction on bio-P uptake, surplus bio-P release was induced by 0.15 mM FePO_4 , and this was in accord with results in Figure 2(b). $\text{Fe}(\text{OH})_3$ exerted a greater inhibition on bio-P uptake than bio-P release.

Indicators for chemical residuals

In biological phosphorus removal system, K showed a strong linear correlation with P in order to maintain electroneutrality of poly-P, K/P molar ratio always remained stable and can be considered a key factor. Measured K/P molar ratio in wastewater still maintained a linear relation when activated sludge contained FePO_4 or $\text{Fe}(\text{OH})_3$, but it cannot on behalf of constituents of intracellular poly-P because K and P was disturbed by FePO_4 or $\text{Fe}(\text{OH})_3$. In Figure 4, K/P molar ratio of the control was 0.48, a little higher than the reported value range from 0.21–0.40 (Macelino et al. 2009; Choi et al. 2011). This may be attributed to K concentration of the influent (Schonborn et al. 2001) and different a detection method adopted. Activated sludge with FePO_4 (R1 and R2) showed increased K/P molar ratio, while activated sludge with $\text{Fe}(\text{OH})_3$ (R3 and R4) showed an unchanged K/P molar ratio. Thus, the increase in K/P molar ratio could be used to estimate the existence of FePO_4 in sludge. K/P molar ratio measured in an SPR system was higher than the control, and demonstrated main chemical residual as FePO_4 . In WWTP operation,

Table 1 | Kinetics of potassium and bio-P uptake

		K uptake		Bio-P uptake		Bio-P uptake/release (mg/mg)	Interaction of Fe-sludge*	
		k (h^{-1})	R ²	k (h^{-1})	R ²		K uptake	Bio-P uptake
FePO_4	control	0.0714	0.98	0.2912	0.98	2.52		
	R1	0.0818	0.97	0.2923	0.94	2.66	–10%	0%
	R2	0.0663	0.95	0.2895	0.90	2.27	–27%	–1%
	superposition	0.0911	0.96					
$\text{Fe}(\text{OH})_3$	control	0.0875	0.97	0.4793	0.99	1.77		
	R3	0.0784	0.98	0.4271	0.99	1.76	–20%	–11%
	R4	0.0688	0.96	0.3716	0.98	1.69	–30%	–22%
	superposition	0.0985	0.95					

*Interaction of K uptake was calculated based on R1, R2 and superposition, interaction of bio-P uptake was based on R1, R2 and control.

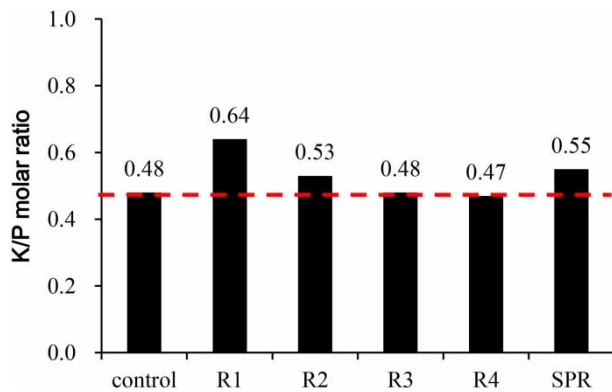


Figure 4 | K/P molar ratio in wastewater (R1:sludge + 0.075 mM FePO₄, R2:sludge + 0.15 mM FePO₄, R3:sludge + 0.05 mM Fe(OH)₃, R4:sludge + 0.10 mM Fe(OH)₃, SPR: simultaneous phosphorus removal).

K/P molar ratio could rise first then fall, because chemical residual changed from FePO₄ to mixture of FePO₄ and Fe(OH)₃ with the increase in dosage.

Another indicator to distinguish whether activated sludge contained chemicals was coefficient b. P uptake was proportional to P release, and could be assessed using Equation (7).

$$\Delta P_{\text{uptake}} = a \cdot \Delta P_{\text{release}} + b \quad (7)$$

Coefficient 'a' represented biological P removal and 'b' represented P removal not connected with biological mechanisms (Choi *et al.* 2011). In Figure 5, P uptake at the end of oxic 3 h and 4 h was distinguished (ferrous sulfate dosed at the end of oxic 3 h). Coefficient b of control, SPR-3 h and SPR-4 h was 1.16, 1.24, and 1.96, and increased coefficient b of SPR system indicated chemical residual effect on phosphorus removal. 'b' could be a simple indicator to monitor

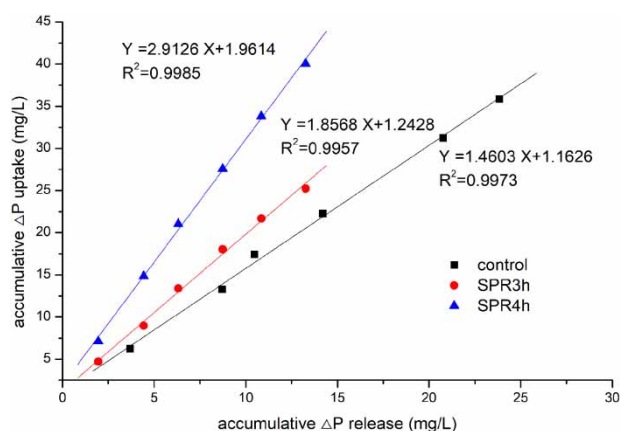


Figure 5 | Correlation of P uptake and release of control and SPR system.

the chemical residual in WWTP. On the other hand, it should be noted that 'a' of SPR-3 h and SPR-4 h higher than control did not associate with enhanced ability of biological phosphorus removal. 'a' of SPR-3 h did not reflect a dynamic change of ratio of P uptake to release decreased from 2.41 to 1.46, and 'a' of SPR-4 h sharply rose because of the dosing of ferrous sulfate.

CONCLUSION

With ferrous sulfate, MLSS increased 9%, pH decreased from 7.35 to 7.00, SVI decreased and electrical conductivity increased. Fe dosing caused immediate reduction of P release, K release and uptake; however, Fe and activated sludge had synergistic effect for P removal until accumulative dose reached 10 mgFe/mgMLSS, at which P uptake began to decrease and inhibition of residual Fe appeared. Precipitate FePO₄ actually releases surplus P to wastewater through A/O transformation, leading to increased effluent P. FePO₄ inhibited K uptake rather than bio-P uptake. Precipitate Fe(OH)₃ caused reduction of bio-P release and uptake, and its inhibition on K uptake was greater than FePO₄. Phosphorus metabolic capacity was weakened when Fe overdosed, so intermittent dose was suggested for WWTP operation. Indicators for Fe residual in sludge were proposed.

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