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# Inhibition of chemical dose in biological phosphorus and nitrogen removal in simultaneous chemical precipitation for phosphorus removal

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## ABSTRACT

A study on the influence of chemical dosing on biological phosphorus and nitrogen removal was carried out through batch experimental tests by lab-scale and a full-scale wastewater treatment plant (employing a typical anaerobic–anoxic–oxic treatment). Results indicated that the inhibition of aluminum salt on biological phosphorus release and uptake processes is significant, as well as the inhibition of aluminum salt on Ammonia-Oxidizing Bacteria (AOB) is dominantly observed in the nitrification process and is recoverability. The inhibition of iron salt in biological phosphorus and nitrogen removal is weak, and only the inhibition of iron salt on phosphorus release at anaerobic periods emerge under large dosing. Evidence shows persistent inhibition from the accumulation of chemical doses in sludge mass. Intermittent chemical dosing proves recommendable for simultaneous chemical phosphorus removal.

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## 1. Introduction

The serious eutrophication of bodies of water in China has prompted the creation of regulations requiring total phosphorus (P) levels in wastewater treatment plant (WWTP) effluent to be lower than 0.5 mg P/L. In many regions of the world, 0.1 mg P/L is the required level. Many studies were proposed aim to enhance removal efficiency of nitrogen and phosphorus (Monclús et al., 2010; Maite and Yuan, 2010; Li et al., 2010). Simultaneous chemical precipitation, which serves as a supplement to biological methods, is a widely used technology for controlling P discharge in WWTP effluent. Chemical P removal is normally implemented by dosing of metal salts ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ ) (de Haas et al., 2000a). Many studies have investigated the operational conditions of chemical P removal and provided analyses of its reaction mechanism (de Haas et al., 2000b; Jeremy et al., 2009). The some issues have been addressed in previous bodies of research. The precipitation forms of iron (Fe) or aluminum (Al) and P in sludge and the relationship between the chemical and biological P removal was investigated (de Haas et al., 2000c,d; 2001a). The effects of the dosing method of metal salts (post-precipitation, simultaneous precipitation, pre-precipitation) on P removal and the influence of pH and turbidity on P removal was studied (Thistleton et al., 2001). The stoichiometric molar ratio of chemical dose and P concentration to best achievable P concentration and optimal dosing rate of metal salts was proposed (Thistleton et al., 2002). And the design and

operational variables required to limit P in effluents was proposed (Szabo et al., 2008). Moreover, a mechanism model of chemical P precipitation was proposed (Smith et al., 2008). To realize optimal biological and chemical removal of P in operational control processes, the precipitation function model of P removal and combined chemical–biological P removal model were developed (de Haas et al., 2001b,c; Takacs et al., 2006a,b). The process control technique for online adjustment of the ratio of biological P removal and control of aluminum salt participation has been employed (Ingildsen et al., 2006).

Previous study aims to achieve optimum orthophosphate concentration in effluents, but it remains poorly understood despite its wide application. Understanding the influence of chemical dosing on the biological reaction of nitrogen and P is particularly challenging and has not been thoroughly considered in practice. The various chemical and physico-chemical mechanisms involved in the removal of P by chemical and biological reactions are complex. Studies that consider the possible interaction between the mechanisms of biological and chemical P removal are rare. The inhibition of chemical doses on biological P removal and the competition between chemical and biological P removal have been discussed in a number of studies (de Haas et al., 2000c,d; 2001a). However, a comprehensive examination of the differences in influencing characteristics among different chemical doses in P release (main impact of biological P removal) is lacking. Analyses of the influence of different chemical doses on nitrification are especially deficient.

Therefore, this study aims to investigate the influence of typical chemical doses on biological P removal, particularly the influence on nitrification. We accomplish this by comparing batch experi-

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mental data to provide initial insight into the underlying mechanisms of this influence. The investigation was carried out through batch experiments on SBR and a full-scale WWTP [using anaerobic–anoxic–oxic (AAO) treatment]. The transfer of chemical doses between liquid and sludge, as well as the influence of chemical doses on nitrification was explored following the experiments. The influence of chemical doses on nitrification was examined by oxygen uptake rate (OUR) analysis. We anticipate that our findings will enhance the understanding of the mechanism behind the interaction between simultaneous chemical P removal and the biological reaction of activated sludge. The study likewise aims to improve the current optimal operational control strategy for the collaborative process of biological reaction and chemical P removal.

## 2. Methods

### 2.1. Test experiment

Batch test experiments on operational full-scale WWTP and lab-scale SBRs (parallel tests with different dosing amounts) were conducted. The full-scale WWTP employs a typical AAO treatment technique with simultaneous chemical P removal. It has a capacity of about  $20 \times 10^4 \text{ m}^3/\text{d}$ . The change of P concentration along the location of AAO reactors in long-term operation was investigated. The compare of P profile between before and after dosing was carried out by the internal investigation. In the parallel SBR tests, one system was used as a test system (to which Al was dosed), while the other served as control (no chemical addition). The change of P profile caused by chemical precipitation was measured as the difference in system P removal between the two systems. The lab-scale SBRs (9L) were operated with a cycle time of 8 h with 150 min non-aerated and 300 min aerated periods, followed by 30 min of settling and 10 min decantation. The oxygen concentration during the aerobic treatment was maintained at 2–3 mg/L (measured using YSI-58, USA). The synthetic wastewater containing glucose (organism cultures of activated sludge), ammonia, and P were pumped into the reactor in the first 7 min of the anaerobic treatment, resulting in the following concentrations in the reactor at the beginning of the cycle: 400–500 mg/L COD, 20–40 mg/L  $\text{NH}_4\text{-N}$ , and 10–20 mg/L  $\text{PO}_4\text{-P}$ , then the chemical doses was immediately added into the reactor. The effect of glucose on phosphorus removal was considered in the operation (Zengin et al., 2010). The solids retention time was maintained at about 20 d. The pH in the system, which fluctuated between 7.0 and 7.5, was recorded but not controlled. The samples were taken at the 0, 30, 90, 150, 210, 300, 360, and 420 min after start of the test of P profile. Effluent nitrogen and P, as well as P release at the end of the anaerobic treatment were monitored every 2–3 d. The samples of sludge and liquid were taken simultaneously.

### 2.2. OUR analysis

The evaluation of the inhibition of Fe and Al salt in nitrification was carried out by testing the OUR of the nitrifying biomass (Surmacz-Gorska et al., 1996). The experiments were performed on a

132 mL jar. The jar reactor received mixed liquid (MLSS about 3.5 g/L) from the reactor in the full-scale WWTP. Allylthiourea (NTU), a selective inhibitor of the *Nitrosomonas* group, was used to inhibit ammonia oxidation.  $\text{NaClO}_3$  is a selective inhibitor of  $\text{NO}_2\text{-N}$  oxidation by *Nitrobacter* at a concentration of 20 mM. The experimental procedure of inhibition of Fe and Al salt in nitrification was shown in Table 1. Each time, OUR was obtained by calculating the slope of the linear parts of the recorded DO profiles (measured using YSI-58, USA). The  $\text{NH}_4\text{-N}$  and  $\text{NO}_2\text{-N}$  oxidation rates of the mixed liquid in the activated sludge system were obtained by the addition of two selective nitrification inhibitors. The inhibition of Fe and Al salt on microorganisms of different categories was obtained by the addition of chemical dose and selective nitrification inhibitors.

### 2.3. Experimental analysis methods

Daily analyses of COD,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , MLSS, MLVSS, and sludge volume index (SVI) were conducted according to standard methods (APHA, 1995). Samples for the determination of soluble components were immediately filtered using 0.45- $\mu\text{m}$  filter paper and cooled to prevent further reaction after sampling. The sludge exhibited excellent settling throughout the entire operation, with the SVI between 100 and 200 mL/g. The MLVSS of the system was between 5–6 g/L. The TCOD removal efficiency, based on the incoming TCOD concentration of 400–500 mg/L, was between 85% and 93%. Sludge samples were immediately centrifuged at 5000 rpm for 10 min to remove microorganisms from the liquid medium, and subsequently tested. The chemical dose concentration in liquid was measured by inductively coupled plasma mass spectrometry (ICP-MS) after filtration treatment using 0.45- $\mu\text{m}$  filter paper. The chemical dose concentration in sludge was measured by ICP-MS after digestion (de Haas et al., 2000b) with nitric acid and hydrofluoric acid at 195 °C for 40 min using a microwave digestion system (Multiwave3000, American PE Company).

## 3. Results and discussion

### 3.1. Influence of different chemical doses on biological P removal

Fig. 1 shows the influence of Al,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  dosing on P removal during SBR operation. The chemical dose has an apparent inhibitory effect on P release during the anaerobic treatment in the comparison between parallel tests of different dosing. The biological P elimination by bacteria is substantially reduced; the rate of P release (to the supernatant) under anaerobic conditions is lower in systems with simultaneous addition of ferric or aluminum ions. Although it is unclear whether this stems from a purely biological or chemical effect, this result agrees with those obtained in previous studies (Röske and Schönborn, 1994a,b). A significant decrease in P concentration (15–4 mg/L) is observed with the increase in chemical dosing amount in the initial phase of the experiment, indicating that P removal is characterized by an initial quick removal upon the addition of metal salts. After the initial phase, the changes in P concentration profile vary under different chemical dosing amounts. This result indicates that the inhibition

**Table 1**  
The experimental procedure of inhibition experiment of Fe and Al salt in nitrification.

OUR Class	OUR(Total) $\text{mgO}_2/\text{L s}^{-1}$	OUR(AOB) $\text{mgO}_2/\text{L s}^{-1}$	OUR(NO <sub>2</sub> ) $\text{mgO}_2/\text{L s}^{-1}$	OUR(Heterotrophic) $\text{mgO}_2/\text{L s}^{-1}$
OUR of different categories	OUR(T) = OUR(Total)	OUR(A) = OUR(Total) – OUR(Dosing NTU)	OUR(N) = OUR(Total) – OUR(Dosing $\text{NaClO}_3$ )	OUR(H) = OUR(Total) – OUR(Dosing $\text{NaClO}_3$ ) – OUR(Dosing NTU)
OUR of Dosing chemical inhibition	OUR(TI) = OUR(Total) – OUR(Dosing chemical)	OUR(AI) = OUR(N) – OUR(Dosing chemical) – OUR(HI)	OUR(NI) = OUR(A) – OUR(Dosing chemical) – OUR(HI)	OUR(HI) = OUR(H) – OUR(Dosing chemical)

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