Experimental Study on Deep Chemical Phosphorus Removal Based on High Discharge Standard

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Abstract. For controlling water eutrophication and decreasing total phosphorus (TP) in effluent of wastewater treatment plants, chemical phosphorus removal was studied. Results showed that the optimal FeCl₃·6H₂O and polyaluminium chloride (PAC) dosage were 20 and 10 mg L⁻¹, respectively, and the reaction time was 15 minutes. Under this condition, the TP concentration was 0.24 and 0.23 mg L⁻¹, respectively. No matter adding PAC or FeCl₃·6H₂O, their suspended (SS) and residual metal salts were 2 and 0.15 mg L⁻¹. The effect of chemical phosphorus removal process on the concentration of COD and NO₃--N showed that the removal efficiency of COD was 45.5% and NO₃--N was only 3.1% when PAC was phosphorus removal agent. However, the efficiency of COD was 34.8% with FeCl₃·6H₂O adding.

1. Introduction
Water eutrophication caused by nitrogen and phosphorus threatens water safety. In order to slow down the occurrence of this phenomenon, wastewater discharge standards in China have been continuously improved to decrease the effluent of total nitrogen (TN) and total phosphorus (TP). On October 1, 2015, Tianjin has established new requirements that discharge standard was raised from the national first-class A standard to the local A standard for urban wastewater treatment plants with a design scale of more than 10 000 m³ d⁻¹. Meanwhile, more and more wastewater treatment plants raised the first-class A discharge standard (TN< 15 mg L⁻¹ and TP< 0.5 mg L⁻¹) to higher local standards (TN< 10 mg L⁻¹ and TP< 0.3 mg L⁻¹). However, the requirement for TP was hard to reach the standard.

In the last decade, for meeting the first-class A discharge standard, Anaerobic/ Anoxic/ Aerobic (AAO) process and sequencing batch reactor (SBR) process were widely applied in China [1]. However, these processes often have common disadvantage of low removal efficiency of phosphorus, which makes it difficult to meet the higher requirements of phosphorus (TP< 0.3 mg L⁻¹) in wastewater discharge.

Chemical phosphorus removal is an effective means of phosphorus removal [2]. Aluminum and iron salts could precipitate with phosphorus to remove phosphorus. In recent years, the application of two kinds of salts has been extensively studied [3]. However, with the continuous improvement of discharge standard, there is no report on conditions optimization of phosphorus removal agents for higher requirements. Meanwhile, many wastewater treatment plants add filter unit after chemical phosphorus removal, so it is very meaningful to study the residual metal salts to control the solidification of the filter.

Therefore, in this study, optimization of phosphorus removal reagents and operation parameters
were conducted. Besides, the influence of phosphorus removal on SS and aluminum and iron salts were discussed. The last, the simultaneous removal effect of other pollutants in the process of chemical phosphorus removal was studied.

2. Materials and Methods

2.1. Experimental system and operational conditions

Based on the premise that biological phosphorus removal meets the first-class A discharge standard (TP≤0.5), the effect of different agents on TP removal was investigated to determine the optimum agent type, agent dosage and reaction time. During the experiment, the influent pH was 6.72, initial SS was 6 mg L⁻¹, TP concentration was 0.5 mg L⁻¹. FeCl₃·6H₂O and PAC were selected as phosphorus removal agents.

KH₂PO₄ was added to raw wastewater (secondary effluents) to adjust the influent TP for chemical phosphorus removal. The relevant indexes of raw wastewater were shown in Table 1. The coagulation process was conducted as following: fast stirring for 1 min (200 rpm min⁻¹), then slowly stirring (50 rpm min⁻¹), and finally settling for 30 min.

Table 1. Raw wastewater quality of chemical phosphorus process

| Parameters | COD | TP | TN | NO₃⁻N | pH | SS |
|------------|-----|----|----|-------|----|----|
| Concentration | 15~35 | 0.3~1.0 | 10~15 | 7~11 | 6.5~7.1 | 6~18 |

2.2. Analytical methods

Samples were collected from the influent tank and secondary settler once three days. Besides, samples in anaerobic, first-anoxic, first-oxic, second-anoxic and second-oxic zones were collected once a week. COD, NO₃⁻N soluble phosphorus (SP) and TP were analyzed according to Standard Methods (APHA, 2005). DO, pH, temperature were monitored online by using WTW pH/Oxi 340i meter with DO and pH probes (WTW, Germany). Total iron and total aluminium were determined by inductive coupled plasma emission spectrometer (ICP-OES, optima8000).

3. Results and discussion

3.1. Effect of agent on TP removal

3.1.1. Optimization on TP removal by FeCl₃·6H₂O

The influent TP was 0.5 mg L⁻¹, in which the average concentration of SP was 0.36 mg L⁻¹, and the average PO₄³⁻-P concentration was 0.31 mg L⁻¹. The effect of dosage and reaction time on TP removal was shown in Figure 1 when FeCl₃·6H₂O was selected as coagulant.

As can be seen from Figure 1, for all experience groups, TP concentration in effluent decreased gradually with the increase of reaction time, and the amplitude turned to slow after 15 min. Meanwhile, with the dosage increase of FeCl₃·6H₂O, the TP removal efficiency increased gradually, and the TP concentration in effluent decreased gradually. The optimum FeCl₃·6H₂O dosage was 20 mg L⁻¹ with 0.24 mg L⁻¹ TP concentration in effluent within 15 minutes, which could meet the requirement of discharge. Therefore, when the influent TP was 0.5 mg L⁻¹, the optimum dosage of FeCl₃·6H₂O dosage and reaction time was 20 mg L⁻¹ and 15 min, respectively.

Si-Min et al. used FeCl₃·6H₂O as flocculant and achieved good TP removal efficiency with a dosage of 80 mg L⁻¹[4]. Bian et al.added 22 mg L⁻¹ FeCl₃·6H₂O into phosphorus removal process, which could decreased TP from 3-5 mg L⁻¹ to reach the discharge standard of pollutants for municipal
wastewater treatment plant(GB18918 -2002) [5].

3.1.2. Optimization on TP removal by PAC

The removal of TP was shown in Figure 2 when PAC was used as coagulant. Similar to FeCl₃·6H₂O, TP concentration in effluent decreased with the increase of reaction time, and the highest TP removal efficiency appeared at first 5 min and decreased rapidly 5 minutes later. Similarly, the increase of PAC concentration led to the increase of TP removal efficiency. The effluent TP concentration was 0.23 mg L⁻¹ with the addition of 10 mg L⁻¹ PAC and 15 min reaction time. The result met the high discharge standard of phosphorus (surface water environment quality IV standard). Hence, the optimum dosage and reaction time were 10 mg L⁻¹ and 15 min, respectively.

PAC was a kind of effect phosphorus removal agent, Sun and Yang concluded that the optimal condition for TP removal by PAC was 40 mg L⁻¹, and the removal efficiency was higher than 80% [6]. Kim and Chung discussed the effect of chemical phosphorus removal as a pretreatment from raw wastewater on MBR-based municipal wastewater and found that TP removal by ferric salt was more effective compared with PAC [7].

3.2. Removal of SS and residual of metal salts
As the chemical phosphorus effluent will enter into subsequent denitrifying deep bed filter, the concentration of SS and total iron in the water will impact on the operation of the denitrifying deep bed filter. Therefore, the changes of SS and total metal (total iron and total aluminum) concentration in effluent under different dosage were also investigated. The fruit is shown in Figure 3.

It can be seen from Figure 3(A) that when the reaction time was 15 minutes, with the increase of FeCl₃·6H₂O dosage, the SS in effluent decreases gradually. Meanwhile, the concentration of total iron increased. When the concentration of FeCl₃·6H₂O were 20 mg L⁻¹, the effluent SS was 2 mg L⁻¹ and the total iron was 0.15 mg L⁻¹.

The change of SS and total aluminum in effluent at 15 min reaction time were also examined, and shown in Figure 3(B). It can be seen that the increase of PAC concentration resulted to the decreases of SS in effluent gradually and increase of total aluminum concentration. The effluent SS was 2 mg L⁻¹ and the total aluminum was 0.15 mg L⁻¹ at the optimum PAC dosage (the concentration of PAC was 10 mg L⁻¹).

3.3. Effect of chemical phosphorus removal process on COD and NO₃⁻N removal
In following denitrifying deep bed filter experiment, NO$_3^-$-N was reacted with COD in this denitrification process. So, the effect of chemical phosphorus removal process on the concentration of COD and NO$_3^-$-N was necessary to be studied.

The experimental conditions were as follows: influent TP was 0.5 mg L$^{-1}$, SS was 6 mg L$^{-1}$, reaction time was 15 min. Meanwhile, FeCl$_3$·6H$_2$O and PAC was added 20 mg L$^{-1}$ and 10 mg L$^{-1}$, respectively. The effects of chemical phosphorus removal on COD and NO$_3^-$-N removal were shown in Figure 4 and Figure 5.

Figure 4 showed that FeCl$_3$·6H$_2$O owned obviously removal effect on COD, but little removal effect on NO$_3^-$-N. The removal efficiency of COD was 45.5%, however, that of NO$_3^-$-N was only 3.1%. When PAC was used as chemical phosphorus removal agent, as shown in Fig. 5, the results were close to that by FeCl$_3$·6H$_2$O. The removal efficiency of COD was 34.8%, which was less than that by FeCl$_3$·6H$_2$O. Meanwhile, the removal efficiency of NO$_3^-$-N was not obvious different with FeCl$_3$·6H$_2$O.

Normally, some tiny sludge flocs and some insoluble organic particles are existed in the effluent of
secondary biological treatment. These substances that constitute part of the effluent COD, are difficult to be used by microorganisms in biological section. In the process of chemical phosphorus removal, the combination of phosphorus removal agents with phosphate produced other chemicals, such as FePO₄ and AlPO₄, which depended on micro flocs or insoluble particulate matter as the nucleation to have the polymerization, and then part of COD from the secondary effluent was removed from the solution by sedimentation. Soluble inorganic salts such as NO₃⁻-N hardly participate in the polymerization reaction, so the effect of chemical phosphorus removal on NO₃⁻-N could be neglected.

4. Conclusion
The optimal FeCl₃·6H₂O and PAC dosage was 20 and 10 mg L⁻¹, respectively, and the reaction time was 15 min for TP removal. Under this optimal condition, the effluent TP concentration met discharge standard. Investigating SS and residual metal salts, no matter adding PAC or FeCl₃·6H₂O, their effluent concentrations were identical. Chemical phosphorus removal process had more impacts on COD removal than NO₃⁻-N when PAC and FeCl₃·6H₂O were as phosphorus removal agents.

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