



Impacts of poly-aluminum chloride addition on activated sludge and the treatment efficiency of SBR

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ABSTRACT

Coagulants addition to a bioreactor is a widely used technology for improving phosphorus removal. As a common and low-cost coagulant, poly-aluminum chloride (PAC) may be widely used for wastewater treatment. In this article, the impacts of PAC on activated sludge and the treatment efficiency of sequencing batch reactor were investigated over 100 d for domestic wastewater treatment. Parameters of chemical oxygen demand (COD), nitrogen, phosphorus, MLSS, oxygen uptake rate (OUR), and dehydrogenase activity (DHA) were used to assess the activated sludge performance. The addition of 40 mg PAC/L (R2) enhanced phosphorus removal from 73.3% in control with zero PAC (R1) to 92.4% due to simultaneous chemical precipitation. PAC addition improved COD removal slightly and did not affect the removal efficiency of nitrogen. The average removal efficiency of COD of the reactor increased slightly from 86.2 to 89.6% by PAC addition. In R1, TN removal was in the range from 86.3 to 90.8%. Nitrogen removal efficiency remained unaffected (slightly dropped) during simultaneous precipitation in R2 and was in the range from 84.5 to 86.8%. The average inhibition rate of DHA and OUR was 32.1 and 55.3%, respectively. PAC addition gave proof to the increase of MLSS by some 40%. Results obtained from the present work confirmed that PAC addition, despite the toxicity and inhibition on micro-organisms, favored phosphorus removal in wastewater treatment.

Keywords: Wastewater treatment; Poly-aluminum chloride; Phosphorus removal; Oxygen uptake rate; Dehydrogenase activity

1. Introduction

Coagulants addition to a bioreactor, known as simultaneous chemical precipitation, is a widely used technology for controlling phosphorus discharge in wastewater treatment plant effluent [1]. Phosphorus removal is normally implemented by dosing metal salts (Fe^{2+} , Fe^{3+} , and Al^{3+}). Numerous substances have been used as simultaneous coagulants, including ferric

chloride, ferric sulfate, ferrous sulfate, and alum [2–5]. Fe salt is effective, but the wastewater should be supplemented with dicarbonate as a result of a drop of pH to values not compatible with the normal metabolic activity of activated sludge [6].

As a common coagulant widely used in drinking water treatment, poly-aluminum chloride (PAC) was reported in only few literatures for wastewater treatment. PAC addition to laboratory-scale mesophilic activated sludge processes treating diluted molasses

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wastewater was investigated [7]. Treatment of simulated dairy wastewater by PAC for high chemical oxygen demand (COD) removal was reported [8]. PAC was applied as a conditioner for waste activated sludge prior to its dewatering and drying [9].

Investigating the biological effects of aluminum has become a major focus of aquatic research [10]. Alum doses above 60 mg/L had toxic effect on the autotrophic bacteria with significant reduction in ammonia oxidation and total Kjeldahl nitrogen (TKN) removal in a cloth-media membrane bioreactor [5]. Alum caused inhibitory effects to the system at soluble concentrations of approximately 400 mg/L and above in a slaughterhouse wastewater treatment plant [11]. Techniques for the measurement of biomass activity, including oxygen uptake rate (OUR) and dehydrogenase activity (DHA) test [12], have been widely employed in biological water and wastewater treatment processes. Moreover, 2,3,5-triphenyl tetrazolium chloride (TTC)–DHA test is a very typical and sensitive methodology for quantification of biomass activity of activated sludge [13].

In the present paper, PAC addition was investigated for the treatment of synthetic domestic wastewater in a sequencing batch reactor (SBR) in terms of their COD, total nitrogen (TN), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), and total phosphorus (TP) removal efficiency. Parameters of OUR and DHA were used to assess the activated sludge performance on the other part. The effect of PAC on micro-organisms present in activated sludge was assessed by a respirometric technique (OUR) and by the 2,3,5-TTC–DHA test in the SBR.

2. Materials and methods

2.1. Batch experiment

The experiment extended for 100 d using two laboratory-scale SBRs (R1 and R2), with 10 L working volume and 8 L effective volume, with mixing and aeration equipment. R2 was used as a test system while the R1 served as control. Reactors were operated with a cycle time of 12 h with 180 min non-aerated and 500 min aerated periods, followed by 30 min of settling, and 10 min decantation. Two liter water was discharged during each cycle. The oxygen concentrations during the aerobic treatment were maintained at 2–3 mg/L. The synthetic wastewater containing sodium acetate, ammonium chloride, and potassium dihydrogen phosphate was pumped into the reactor in the first 5 min of the anaerobic treatment. In order to keep constant the wastewater quality and to favor the research on the characteristics of sludge, wastewater characteristics in the reactor at the beginning of the cycle were shown in Table 1.

The SBRs were inoculated with activated sludge, which had been taken from the secondary sedimentation tank of a domestic wastewater treatment plant and washed 4–6 times, with the initial sludge concentration (MLSS) of 2,000 mg/L. The reactors were operated in anaerobic–aerobic mode as mentioned. After 15 d or so, MLSS maintained at 5,000–6,000 mg/L, and the removal of COD and TN were stabilized. Then, PAC (28% Al_2O_3 , Zhongrun Water Industry Technology Development Co. Ltd., Shenzhen 518057, China) was added into R2 immediately after feeding. The dosage of PAC was determined as 40 mg/L according to jar tests. The solids' retention time was maintained at about 30 d. The pH in the system fluctuated between 6.8 and 7.5 without alkalis supplemented. The sludge and liquid samples were taken simultaneously and tested every 3 d.

2.2. Analytical methods

COD, TN, ammonia nitrogen ($\text{NH}_4^+\text{-N}$), TP, and MLSS of the samples were determined according to the Standard Methods [14]. Water pH was measured by an 828 Orion pH meter, while dissolved oxygen (DO) and water temperature were measured with YSI550A DO meter. OUR was measured as procedures [15]. TTC–DHA was determined as described by the method of Ryssovnielsen [16,17] using 2,3,5-TTC. One unit of activity is defined as 1 μmol of triphenylformazan produced per hour.

3. Results and discussion

3.1. Sludge concentration and OUR variation

As shown in Fig. 1(A), the average MLSS of R1 and R2 were 5.66 and 7.85 g/L, respectively, and PAC addition gave proof to the increase of MLSS by some 40%. It was suggested that the alumina hydroxide precipitates have properties which enmeshed colloidal organic material, and thus, contributing directly to an increase of sludge in the reactor. By adding PAC, sludge particles rapidly aggregated into large flocs due to bridging, charge neutralization, and hydrolysis products of Al^{3+} [18]. It has been shown that sludge settling rates increase with increasing floc size, and that sludge with a greater proportion of small particles tend to bind more water than sludge with a large proportion of large particles [19]. Therefore, PAC addition favors floc size increase, settling rate [8] as well as sludge produce.

Oxygen utilization rate gives an indication of microbial activity because micro-organisms convert O_2 to CO_2 during biodegradation of organic matter. The

Table 1
Characteristics of the wastewater

Parameters	COD (mg/L)	TN (mg/L)	TP (mg/L)	pH (-)
Value	283.1–320.9	26.8–31.6	4.8–5.2	6.8–7.2

average OUR of R1 was 10.8 mg O₂/(g MLSS h) while the average OUR of R2 was 4.8 mg O₂/(g MLSS h) (Fig. 1(B)). The PAC addition reduced OUR by 55.3%. A comparison of iron and aluminum ions shows that Al³⁺ has a bigger impact on OUR than Fe³⁺ [19]. PAC addition has a sharp impact on OUR decrease.

3.2. DHA variation

DHA variation of activated sludge in R1 and R2 is reflected in Fig. 1(C). It indicated that fluctuation of DHA was stable, and that DHA had a trend to continue growing. The average value of DHA was 34.1 and 23.2 units/(g MLSS) in R1 and R2, respectively. The PAC addition reduced DHA by 32.1%.

The drop of DHA can be result from the produce of inert complex of Al with ATP [20] and the energy-dependent efflux of Al [21]. The activity of micro-organisms is weakened because of the ATP consumptions. Al severely impedes the ability of the soil microbe *Pseudomonas fluorescens* to perform oxidative phosphorylation [22]. Moreover, aluminum addition favors flocs aggregation and sludge growth [18], preventing the absorption and degradation of nutrient for micro-organisms.

3.3. COD removal

Results of COD variations over the study period are presented in Fig. 2. The average removal efficiency of COD of the reactor increased slightly from 86.2 to 89.6% by PAC addition. Although Al leads to flocs aggregation and hinders the adsorption of organics, the hydrolysis of Al³⁺ can absorb organic matters. Hydrolyzing coagulants can be used to remove dissolved natural organic matter from water through adsorption of organic matter on amorphous hydroxide precipitate [23].

This result is compared with other work of PAC addition for wastewater treatment. A dosage of 500 mg/L PAC was used for the sole coagulation–flocculation method for the treatment of pulp and paper mill wastewater, which gives 91.3% of COD reduction [24]. Similarly, 300 mg/L PAC gives 69.2%

COD removal efficiency in 30 min for the treatment of dairy wastewater [8].

3.4. N removal

As depicted in Fig. 3, PAC addition showed no obvious effect in both TN (Fig. 3(A)) and NH₄⁺-N (Fig. 3(B)) removal. In R1, TN removal was in the range from 86.3 to 90.8%. Nitrogen removal efficiency remained unaffected (slightly dropped) during simultaneous precipitation in R2 and was in the range from 84.5 to 86.8%. The effluent concentrations of N constantly stayed at a low level. Under circumstances of adequate organic supply and DO, NH₄⁺-N could be transformed to nitrates or nitrites by nitrifying bacteria. Although inhibition of aluminum salt on ammonia-oxidizing bacteria (AOB) was dominantly observed in the nitrification process [1], 40 mg/L PAC addition to SBR over 100 d had no evident impact of N removal. This could be explained that more micro-organisms can compensate for slight inhibition, as R2 had more micro-organisms than R1.

A similar conclusion can be drawn out as for the ferric and ferrous iron salts addition to activated sludge for wastewater treatment. Although the activity of AOB was found to be affected by the accumulation of Fe relating products into the sludge, Fe²⁺ or Fe³⁺ addition (0.446 mM) did not affect the NH₄⁺-N removal efficiency in the laboratory reactors [25]. It was reported that the addition of FeSO₄·7H₂O to a laboratory scale anoxic/oxic reactor had no effect on the nitrogen removal efficiency, which varied from 78 to 85% [26].

3.5. P removal

Although inhibition of aluminum salt on biological phosphorus release and uptake processes was significant [1]; PAC addition significantly enhanced P removal. The average P removal efficiency of R2 was 92.4%, which was only 73.3% in the control (Fig. 4). This indicated that the effect of chemical precipitation was important. A dosage of 40 mg/L PAC (Al:P = 1.36:1, molar ratio) achieved effluent TP in the range of 0.15–0.56 mg/L.

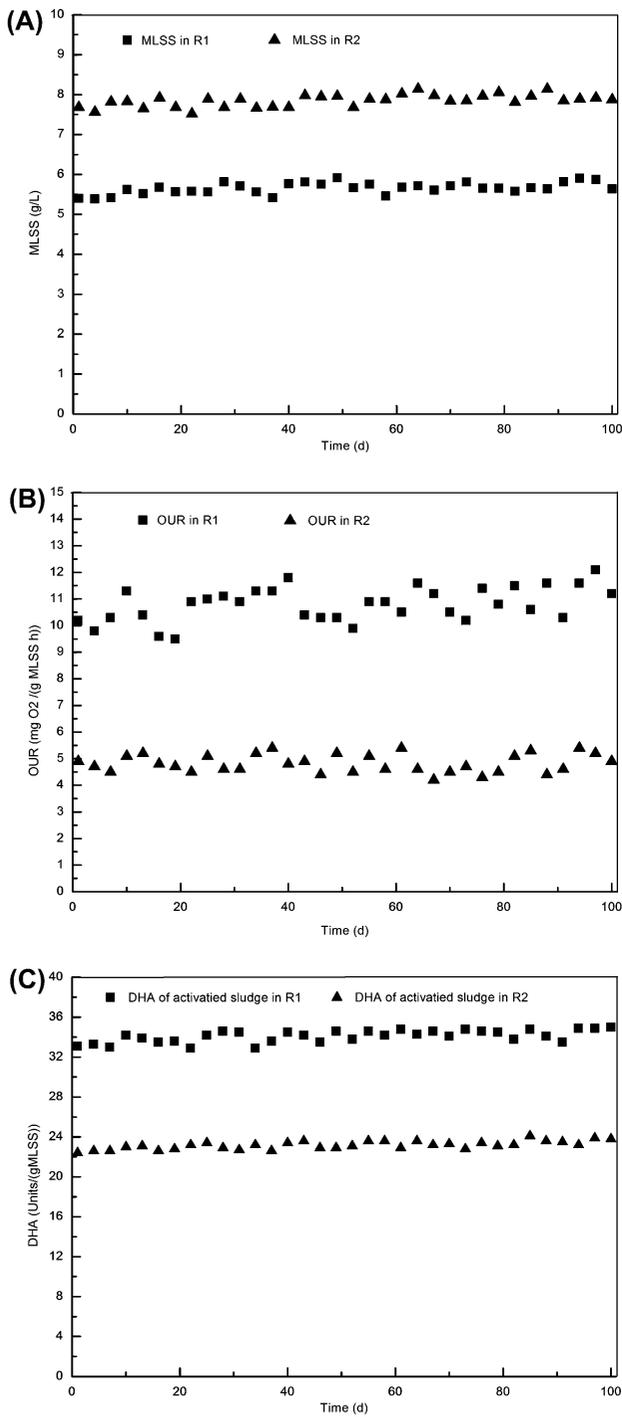


Fig. 1. Variations of sludge characteristics: (A) MLSS; (B) OUR; and (C) DHA.

Experiments of a higher molar ratio dosage of iron salts were conducted for simultaneous TP removal. Using ferrous sulfate (Fe:P=2.1:1, molar ratio) could achieve effluent TP in the range from 0.5 to 1.0 mg/L [26]. The application of different doses of ferric

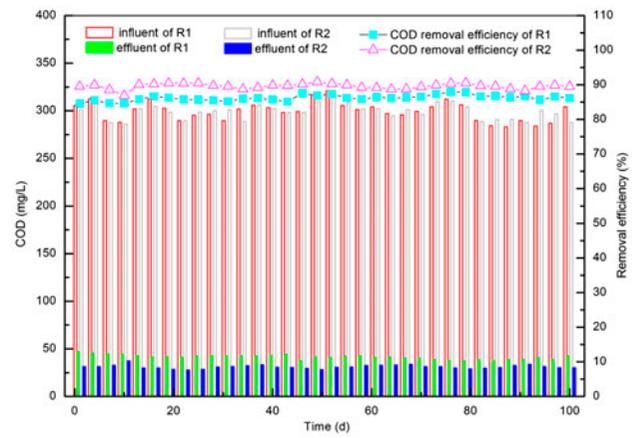


Fig. 2. Variations of COD.

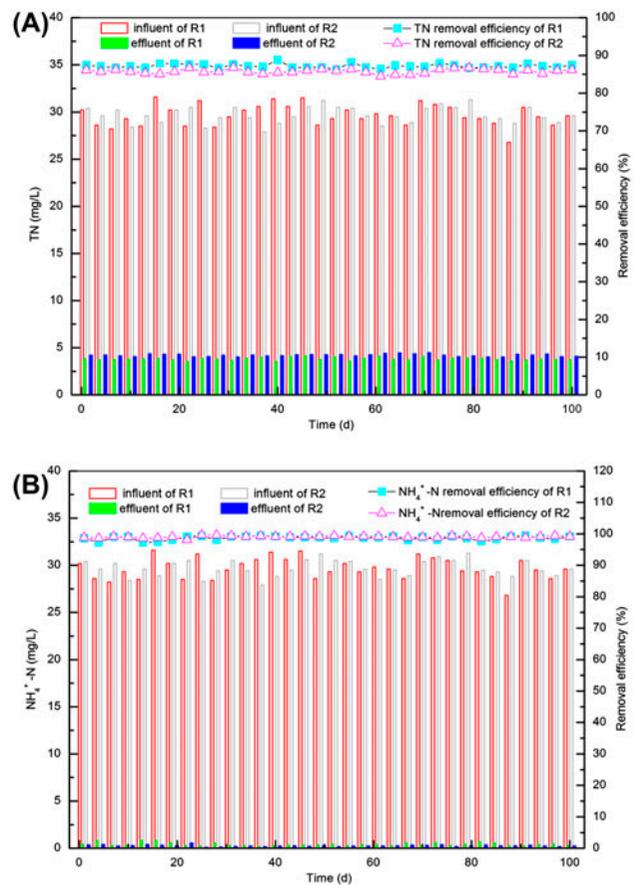


Fig. 3. Variations of nitrogen: (A) TN and (B) ammonia nitrogen.

chloride (Fe:P=1.5–2.3:1, molar ratio) to the aeration basin of an activated sludge reactor achieved total P removal higher than 90% [2]. This indicated PAC was better chemical in simultaneous chemical precipitation for phosphorus removal.



Fig. 4. Variations of TP.

3.6. Sludge disposal

The surplus sludge is usually buried as a waste material in landfills. As the domestic sludge contains no other toxic materials but high concentrations of aluminum, it may be buried in the area of aluminum mine. The sludge can also be used as a raw material to build concrete blocks using of stabilization/solidification process [27]. More methods need to be exploited to cope with the sludge containing aluminum and phosphorus.

4. Conclusion

In this article, PAC (28% Al_2O_3) was investigated for wastewater treatment in a SBR to treat domestic wastewater over 100 d. COD, nitrogen, phosphorus, MLSS, OUR, and DHA were tested to assess the activated sludge performance. PAC addition (40 mg/L, 0.22 mM Al^{3+}) to a SBR over 100 d showed permanent effluent quality. The addition of PAC enhanced MLSS growth by some 40%. While OUR and DHA were reduced by 55.3 and 32.1%, respectively. Despite the impact on activated sludge, the N removal efficiency was not affected. PAC addition slightly improved COD removal, and enhanced phosphorus removal largely by simultaneous chemical precipitation.

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