Effects of poly aluminum chloride dosing positions on the performance of a pilot scale anoxic/oxic-membrane bioreactor (A/O-MBR)

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ABSTRACT

The effects of poly aluminum chloride (PACl) dosing positions on the performance of a pilot scale anoxic/oxic membrane bioreactor were investigated. PACl dosage was optimized at 19.5 mg Al₂O₃/L by jar test. Nutrients removal efficiencies and sludge properties were systematically investigated during periods with no PACl dosing (phase I), with PACl dosing in oxic tank (phase II) and then in anoxic tank (phase III). The results showed that total phosphorus removal efficiency increased from 18 to 88% in phase II and 85% in phase III with less than 0.5 mg P/L in effluent. Ammonia nitrogen removal efficiencies reached 99% in all phases and chemical oxygen demand removal efficiencies reached 92%, 91% and 90% in the three phases, respectively. Total nitrogen removal efficiency decreased from 59% in phase I to 49% in phases II and III. Dosing PACl in the oxic tank resulted in smaller sludge particle size, higher zeta potential, better sludge settleability and lower membrane fouling rate in comparison with dosing PACl in the anoxic tank.

INTRODUCTION

The membrane bioreactor (MBR), which combines a membrane separation process with standard activated sludge processes, can make effluent quality independent of biomass settling characteristics by physical interception. MBR has difficulty in removing phosphorus due to the relatively long sludge retention time (SRT) (Song et al. 2010). Excess phosphorus may result in eutrophication problems (Khan & Ansari 2005). In the biological nutrient removal process, the availability of usable carbon energy in wastewater governs the capability of nitrogen and phosphorus removal (Lee et al. 2005). In addition, large amounts of dissolved oxygen (DO; i.e., 6.0–7.0 mg/L) were brought into the anoxic zone by the internal backflow and mechanical mixing, which could hinder phosphorus release and denitrification. Therefore, a low organic loading rate and relatively high DO in the anoxic tank may result in poor phosphorus removal (Chuang et al. 1997). In China, the total phosphorus (TP) concentration of effluent from wastewater treatment plants (WWTPs) should be lower than 0.5 mg/L (GBt8918 2002). However, many WWTPs could not meet this standard. Consequently, coagulants such as aluminum salts, ferric salts, and their polymers were usually used to enhance the removal of phosphorus. In the last decade, many studies focused on methods for phosphorus removal and membrane fouling mitigation. It was reported that the addition of 30 mg/L alum was effective in removing 3 mg/L of phosphorus from the feed water, and the pH decreased from 7.6 to 5.5 with increasing dosage (0–500 mg/L) of alum without reducing the nitrogen removal efficiency (Song et al. 2008). However, Guo et al. found that inorganic floculants strongly affected nitrification because they could increase metal concentration in the mixed liquor and cause an adverse impact on nitrogen removal (Guo et al. 2010).

Coagulants can not only enhance phosphorus removal, but also change the sludge properties. Zahid and El-Shafai identified that alum addition significantly reduced the sludge volume index (SVI) and particle size distribution (PSD) range, and inhibited the growth of filamentous bacteria (Zahid & El-Shafai 2012). In an anoxic/oxic (A/O)-MBR, the main functions of bacteria in anoxic and oxic tanks are nearly opposite due to different levels of DO.
Although coagulant addition can impact the performance of A/O-MBR, the influence of coagulant dosing positions on nutrients removal have scarcely been discussed in previous studies, and only one study on the effect of ferrous salts dosing positions on nutrients removal has been reported (Wang et al. 2014).

Poly aluminum chloride (PACl) has become one of the most effective coagulant agents in wastewater treatment facilities with various applications, including removal of metal ions, phosphates, toxic metals and color. In addition, aluminum salts were effective in enhancing the filterability of mixed liquor and controlling membrane fouling (Song et al. 2008). In this study, the effects of PACl dosing positions on nutrients removal, sludge properties and membrane fouling in a pilot scale A/O-MBR were investigated. During the 3-month operation, nutrients removal such as total nitrogen (TN), TP, chemical oxygen demand (COD) and ammonia nitrogen (NH3-N) were systematically studied. In addition, the effects of PACl addition on sludge characteristics such as SVI, zeta potential and PSD were examined. The effects of extracellular polymeric substances (EPS) and soluble microbial products (SMP) on membrane fouling were also discussed.

MATERIALS AND METHODS

Pilot scale set-up

Figure 1 shows the schematic diagram of the pilot scale A/O MBR installation. The MBR was divided into an anoxic zone and an oxic zone, with a working volume of 6 m³ and 9 m³ respectively. The mixing was performed at a speed of 150 rpm using a mechanical mixer installed on top of the anoxic basin. A hollow fiber membrane module made of polyvinylidene fluoride (Litree Ultrafiltration Membrane Technology Co. Ltd, Suzhou, China) with a nominal pore size of 0.01 μm and a surface area of 144 m² was immersed in the oxic tank. The mixed liquor was aerated through six air diffusers located beneath the membrane module in order to supply 10 m³/h of air to provide oxygen for biomass growth, as well as to prevent membrane fouling by quasi cross-flow on the membrane surface. The membrane permeate flux was set at 14.5 LMH. The MBR was inoculated with activated sludge collected from the Zhen’an WWTP in Foshan, China.

The membrane module was operated intermittently with 11 min suction and 1 min backwashing to alleviate membrane fouling. The internal recycle from the oxic tank to the anoxic tank was enforced by a pump. SRT was controlled at 30 days by drawing sludge from the membrane basin at regular intervals.

Experimental design and operational conditions

The experimental period was divided into three stages (phase I, II and III), and each stage lasted for about a month. Phase I represented the period when no coagulant was dosed, while phases II and III represented the periods when the coagulant was dosed into anoxic and oxic tanks, respectively. In the three running phases, the operational parameters were kept constant except for some unavoidable changes, so that the results could be compared. Mixed liquor suspended solids (MLSS) was maintained at 4,000–5,500 mg/L. The internal recycle ratio was 100%. DO concentrations of oxic and anoxic tanks were maintained at 5.6–7.0 mg/L and 0.2–0.3 mg/L, respectively. Hydraulic retention times (HRTs) of anoxic and oxic tanks were 3.5 h and 5.3 h, respectively. To reduce the influence of the feed water quality and temperature as much as possible, a season with relatively stable feed water quality and temperature was selected to carry out the experiment.

Municipal wastewater and chemical coagulation

The effluent of the primary sedimentation basin in Zhen’an WWTP was used as the feed water for this pilot scale A/O MBR. PACl was chosen as the coagulant. The optimum PACl dosage was determined by the jar test, which could reduce TP from 2.4 mg/L (average concentration in the WWTP) to less than 0.5 mg/L.
The jar test was performed under both anoxic and oxic condition. Mixed liquor from the oxic tank of the WWTP was used as inoculated sludge. PACl was dosed at the levels of 0, 9.7, 19.5, 29.3 and 38.8 mg Al2O3/L. One liter of mixed liquor with 2.4 mg TP/L was poured into each beaker (12 beakers in total). DO concentrations in the first six beakers were maintained in the range of 0.2–0.4 mg/L by stirring, and DO concentrations in the other six beakers were kept at 6.0–7.0 mg/L. Different dosages of PACl were added to each beaker. After 40 min, around 200 mL mixed liquor from each beaker was used for the dead-end filtration test. Samples of filtrate were taken to analyze the TP concentration.

Water quality and sludge property monitoring

During the experimental period, COD, NH3-N, nitrate nitrogen (NO3-N), TN, TP and pH values of influent and effluent were monitored daily. COD and NH3-N contents of supernatants of the anoxic and oxic tanks were also measured daily. MLSS, mixed liquor volatile suspended solids (MLVSS) and SVI were assessed gravimetrically. The NH3-N, NO3-N, COD, TN and TP were measured by spectrophotometer (Hach DR 4000, Loveland, CO, USA) according to Standard Methods for the Examination of Water and Wastewater (APHA 2005). Among them, TP and TN samples were digested using a high pressure sterilization pot (LDZX-75KBS, Shanghai Shenan Medical Instruments, Shanghai, China) and COD samples were digested using a COD detector (5B-1(B), Lian-hua Tech Co., Lanzhou, Ltd).

PSD and zeta potential of activated sludge

The surface charge and zeta potential of the sludge in the oxic tank were measured daily using a Malvern Zetasizer Nano90 (Worcester, UK). The PSD of sludge was determined by laser particle analyzer (Ankersmid Eyetech-Comb, Ankersmid, The Netherlands).

SOUR monitoring

The DO was measured by a DO meter (WTW pH/Oxi 340i, Weinheim, Germany). The specific oxygen uptake rate (SOUR) of the activated sludge was calculated using Equation (1) (APHA 2005):

\[
\text{SOUR (mgO}_2/\text{(gMLVSS·h)}) = \frac{60G}{X}
\]

where \(G\) is the slope of the linear portion of the DO decline curve (mg/(L min)) and \(X\) is the MLVSS concentration (g/L).

SMP and EPS monitoring

Fifty milliliters of mixed liquid collected from the oxic tank was centrifuged at 4,000 r/min for 15 min, then the TOC of the supernatant was measured as the SMP using a Shimadzu TOC analyzer (TOC5000A, Kyoto, Japan). The remaining pellet was diluted to 50 mL with ultrapure water to extract EPS. EPS were determined by the sum of protein and carbohydrate (mg g\(^{-1}\)MLVSS) extracted from the sludge. Formaldehyde and NaOH were used to extract EPS (Liu & Fang 2002). The anthrone-sulfonic acid method (Dubois et al. 1956) was used to measure the content of carbohydrate with glucose as the standard reference. The rapid Lowry method (Shanghai Lida Biotech Co., Ltd, Shanghai, China) was used for protein determination, with bovine serum albumin (BSA) as the standard reference.

Membrane fouling monitoring

The membrane fouling was evaluated by trans-membrane pressure (TMP) using a pressure sensor to record. Equation (2) was used to calculate the membrane fouling rate (MFR):

\[
\text{MFR (kPa/d) = } \frac{\text{TMP}_d - \text{TMP}_0}{\Delta D}
\]

where MFR is the membrane fouling rate (kPa/d), \(\text{TMP}_d\) and \(\text{TMP}_0\) are the trans-membrane pressure of the first day and last day in the same phase of the system running, respectively, and \(\Delta D\) is the running time of the phase.

RESULTS AND DISCUSSION

Effects of PACl dosing positions on nutrients removals

The results of the jar test showed that phosphorous removal efficiency increased from 8 to 94% under oxic conditions and from 4 to 95% under anoxic conditions. The optimum dosages of PACl under oxic and anoxic conditions were both 19.5 mg Al2O3/L. Thus, this dosage was adopted in the pilot scale A/O-MBR system.

Figure 2(a)–2(d) shows the variations of nutrients (NH3-N, COD, TN, and TP) concentrations and their removal efficiencies. TN, NH3-N, and COD concentrations of the effluent reached the discharge standards of China (<15 mg/L, 5 mg/L, 50 mg/L, respectively; GB18918 2002). In the last two phases, the discharge of TP also met the requirement of the standard (TP < 0.5 mg/L).
The pH plays an important role in the process of microbial metabolism. The mean pH values of influent and effluent were 7.3 and 7.3 (phase I), 7.3 and 7.4 (phase II), 7.3 and 7.4 (phase III), respectively. Moreover, the pH values of the oxic and anoxic tanks were kept relatively stable during the experimental process. Although the removal of orthophosphate using PACI could release OH⁻/CO₃²⁻ ions into the solution, the effluent pH fluctuated in the range of 7.0–7.6, which indicated that pH was not impacted by PACI at the dosage of 19.5 mg Al₂O₃/L. This was different from the result obtained by Georgantas and Grigoropoulou, who used spent alum sludge to remove phosphorus under the initial pH of 6 (Georgantas & Grigoropoulou 2005).

The average removal efficiencies of NH₃-N (as shown in Figure 2(a)) reached 99% in all phases with all NH₃-N concentrations of effluent being consistently below 0.65 mg/L. In addition, the average amounts of removed NH₃-N reached 27.6 ± 3.5 mg N/l, 17.62 ± 2.9 mg N/l and 18.74 ± 2.6 mg N/l under the conditions of no PACI dose. When PACI was dosed in the oxic and anoxic tanks, respectively, NO₃-N concentrations in the effluent approached the TN concentrations shown in Figure 2(c). This result was consistent with that reported by Yang et al. (2011) who found that NH₃-N removal efficiency was over 98% in A/O MBR. Moreover, as shown in Figure 2(b), the average COD removal efficiencies in phases I, II and III were 92%, 91% and 90% respectively, with effluent concentrations all below 23 mg/L, which demonstrated that MBR could obtain high effluent quality with low variability, despite greatly fluctuating influent NH₃-N and COD concentrations. The removals of NH₃-N and COD were not influenced by PACI at 19.5 mg Al₂O₃/L. Owing to the high DO concentration and relatively long HRT in the oxic tank, nitrifying bacteria could grow and reproduce easily, which resulted in a good performance in NH₃-N removal. The high removal efficiencies of COD were attributed to metabolism by denitrifying bacteria, phosphorus release
bacteria and other heterotrophic bacteria, as well as an enhanced coagulation effect, which resulted from the PACI
dosed in phases II and III.

As shown in Figure 2(c), the mean removal efficiencies of
total nitrogen (TN) were 59%, 49% and 49%, with average removed
amounts of 19.6 ± 3.2 mg/L, 9.7 ± 3.0 mg/L and 9.8 ±
1.6 mg/L in phases I, II and III, respectively. The results
indicated that denitrification deteriorated to some extent
when PACI was dosed. As organic substances and phos-
phorus were necessary nutrients for denitrification, lack of
sufficient phosphate may inhibit denitrification (Liu et al.
2011). As COD and phosphate were extensively consumed,
no more nitrate could be eliminated by denitrifying bacteria.
In addition, PACI removed a portion of organic matters by
incorporating them into sludge, further reducing the organ-
ics for denitrifying bacteria.

The average TP removal efficiency was only 18% in phase
I (as shown Figure 2(d)). This revealed that phosphorus
removed by biomass incorporation was inefficient because it
was just corresponding to cell synthesis. According to the
data of phase I, phosphorus release in the anoxic tank was
not obvious. Kuba found that the transfer of nitrate into the
anaerobic phase inhibited phosphate release (Kuba et al.
1994). This phenomenon resulted in poor phosphorus accumu-
lation. In turn, the concentrations of phosphorus were nearly
the same in the anoxic and oxic tanks. In particular, TP con-
centrations of the supernatant from the oxic tank and
effluent were sometimes higher than that in the anoxic tank.
This could be attributed to the long SRT and cell lysis, which
would enable sludge to release some phosphorus into water.

The mean TP removal efficiencies reached 87% and
85% with residual TP less than 0.5 mg P/L by PACI coagu-
lation in the anoxic tank and oxic tank, respectively. The
experimental results highlighted that TP removal effects
were almost identical in phases II and III. During phase
II, the TP concentration of supernatant in the oxic tank
decreased sharply and was much lower than that in the
anoxic tank. In phase III, the TP concentration of supernatant
in the anoxic tank also decreased sharply, similar to that in
the oxic tank. The main reason was that the orthophosphate
rapidly reacted with the aluminum, forming some precipi-
tation (mainly aluminum phosphate) and other Al based
flocs, which could be retained by the membrane.

Effects of PACI dosing positions on sludge properties

As shown in Table 1, the SOUR decreased from 6.8 ± 0.4 mg
O2/(g MLVSS h) in phase I to 4.2 ± 0.5 and 4.4 ± 0.5 mg
O2/(g MLVSS h) in phases II and III respectively. The
results indicated that the metabolic activity of sludge might
be inhibited by PACI. As shown in Figure 3, the SVI and
MLVSS/MLSS values of sludge in the oxic tank were
reduced significantly by dosing PACI (19.5 mg Al2O3/L).
SVI values in phases II and III were much lower than in
phase I, which were consistent with the declining trend of
MLVSS/MLSS values because sludge particles aggregated
and thus exhibited better settleability after dosing PACI. In
addition, inorganic matters (mainly aluminum phosphate)
in activated sludge increased greatly. As presented in
Table 1, the mean particle sizes of sludge in the oxic tank
were 49.2 μm, 39.8 μm and 43.0 μm in phases I, II and III,
respectively. The corresponding particle size values of
sludge in the anoxic tank were 46.3, 43.8, and 36.5 μm
for phase I, II and III. The results implied that the sludge particle
size was reduced by dosing PACI. In particular, the
particle size of sludge in the tank where PACI was dosed
was smaller than that of the other tank.

The results were attributed to the reduction of filamen-
tous bacteria in phases II and III. Because the inorganic
constituent of MLSS was augmented, the growth of filamentous bacteria was controlled by inorganic coagulant (Paris
et al. 2005). Usually, sludge with a normal amount of filamen-
tous bacteria has a smaller floc size than the sludge
with abundant filamentous bacteria (Wang et al. 2010).
Jin also found that the flocs of activated sludge with high
quantities of filaments were relatively larger and had lower
density than small ones (Jin et al. 2003), which explains
why the sludge from phase I had higher SVI and larger

<table>
<thead>
<tr>
<th>Phase</th>
<th>Condition</th>
<th>SOUR/mg O2/(g MLVSS h)</th>
<th>MFR/kPa/d</th>
<th>SMP/mg DOC/L</th>
<th>EPS/mg/(g MLVSS)</th>
<th>Mean particle size/μm</th>
<th>Zeta potential/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Oxic</td>
<td>6.8 ± 0.4</td>
<td>0.65</td>
<td>20.0 ± 13.8</td>
<td>258.1 ± 35.5</td>
<td>49.2</td>
<td>−15.5 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>46.3</td>
<td>−</td>
</tr>
<tr>
<td>II</td>
<td>Oxic</td>
<td>4.2 ± 0.6</td>
<td>0.33</td>
<td>10.7 ± 5.4</td>
<td>218.2 ± 33.0</td>
<td>39.7</td>
<td>−11.0 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>43.8</td>
<td>−</td>
</tr>
<tr>
<td>III</td>
<td>Oxic</td>
<td>4.4 ± 0.5</td>
<td>0.37</td>
<td>14.4 ± 11.0</td>
<td>242.3 ± 34.5</td>
<td>43.0</td>
<td>−11.7 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>36.5</td>
<td>−</td>
</tr>
</tbody>
</table>
particle size. In phase II, the SVI and particle size of sludge in the oxic tank were smaller than those in phase III. Because the sludge reacted rapidly with PACI in the dosing tank, then flowed to the other tank where PACI had limited influence on sludge properties, the growth of filamentous bacteria was inhibited more significantly in phase II than in phase III.

**Effects of PACI dosing positions on membrane fouling**

As shown in Table 1, the MFRs and the concentrations of SMP and EPS increased in the following order: phase I > phase III > phase II. The results revealed that the MFR increased in accordance with the increase of SMP and EPS concentrations. It was reported that SMP and EPS played a very important role in membrane fouling and were the key membrane foulants (Lee et al. 2003). EPS, which are microbial products from metabolism and cell autolysis, mainly contain polysaccharide and protein. Protein concentrations in EPS were 102.4 ± 14.9 mg/(g MLVSS), 96.2 ± 17.7 mg/(g MLVSS) and 99.0 ± 18.4 mg/(g MLVSS) in phases I, II and III, respectively. Polysaccharide concentrations in EPS were 155.7 ± 27.6 mg/(g MLVSS), 122.0 ± 23.4 mg/(g MLVSS) and 143.3 ± 24.4 mg/(g MLVSS) in phases I, II and III, respectively. Polysaccharide concentrations were much higher than protein concentrations in this study. Bin found that polysaccharide was the most important foulant in comparison with protein and DNA, although protein's role was not negligible (Bin et al. 2008). The mean zeta potentials of sludge in the oxic tank increased from −15.6 mV in phase I to −11.0 and −11.7 mV in phases II and III (as shown in Table 1). The results showed that zeta potential increased slightly more in phase II than phase III, and the trend was in accordance with the EPS concentration. It was found that EPS concentration had a significant negative influence on the surface charge of sludge flocs by the excess growth of filamentous bacteria, which could result in a much greater release of EPS, lower zeta potential and aggravating membrane fouling (Meng et al. 2006). As discussed above, PACI inhibited the growth of filamentous bacteria more effectively in phase II. So, the MFR was smaller in phase II than in phase III.

**CONCLUSIONS**

In this study, high TP removal efficiencies were achieved by dosing PACI in oxic or anoxic tanks. The NH₃-N and COD removal efficiencies were not influenced by PACI. Although the TN removal efficiency decreased with dosing PACI, the content in the effluent still reached the Chinese standard. The SOUR of the mixed liquor was reduced by dosing PACI. Activated sludge, with lower SVI, zeta potential and PSD, could be expected by coagulation in the oxic tank. Membrane fouling was mitigated more effectively by dosing PACI in the oxic tank than in the anoxic tank.

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