Effect of a low concentration of aluminum sulfate on the treatment performance of a submerged membrane bioreactor

Jun-jun Chang\textsuperscript{a,b}, Li-ying Yuan\textsuperscript{a}, En-rong Xiao\textsuperscript{a}, Zhen Liang\textsuperscript{a}, Wei Liang\textsuperscript{a,*}, Zhen-bin Wu\textsuperscript{a}

\textsuperscript{a}State Key Laboratory of Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, 430072, China

Tel. +86 (27) 68780065; Fax +86 (27) 68780675; email: liangwei02@sinihua.org.cn

\textsuperscript{b}Graduate University of the Chinese Academy of Sciences, Beijing, 100049, China

Received 17 November 2009; Accepted in revised form 5 December 2010

ABSTRACT

Phosphorus is a crucial element in the eutrophication process. According to China’s water pollutant discharge Class 1A standard, treated wastewater must meet 0.5 mg/L of phosphorus prior to discharge to a sensitive water body. In recent years, wastewater treatment technologies such as membrane bioreactors have been demonstrated to achieve high-quality effluent and present the potential for wastewater reuse applications. However, an efficient and cost-effective phosphorus removal process is still not warranted. In this study, a submerged membrane bioreactor (SMBR) with addition of a low concentration of aluminum sulfate ([mol Al : mol P ≤ 1] was used to evaluate its treatment performance. The results showed that significant phosphorus removal could be achieved with addition of a low aluminum sulfate dosage to meet national phosphorus discharge standard; however, no significant effect was observed on the removal of COD and ammonia. The addition of a low concentration of aluminum sulfate could offer as an economical solution to increase the phosphorus removal efficiency of a SMBR, and thereby improve the water quality of the water bodies.

Keywords: Membrane bioreactor; Low concentration; Aluminum sulfate; Treatment performance

1. Introduction

One of the crucial factors responsible for eutrophication is high level of nutrients, especially phosphorus [1,2]. Nutrients from point sources including municipal wastewater and industrial wastewater can be reduced through wastewater treatment technologies; however, achieving high treatment performance on a consistent basis could present a challenge. In recent years, membrane bioreactors (MBR) have been widely used in many wastewater treatments and reuse applications due to its high treatment performance for chemical oxygen demand (COD), ammonia and total suspended solid (TSS) as well as its low sludge yield, compact installation, high loading rate capability, and so on [3–9]. Many recent studies focused on the phosphorus removal using MBRs [10–15].

In general, phosphorus removal can be partially accomplished by its uptake for biomass synthesis during biological oxygen demand (BOD) removal. A typical phosphorus content of microbial solids is 1.5–2% based on dry weight and a total phosphorus removal of 10–30% can be attained by wasting excess microbial solids [13,16]. Biological phosphorus removal also occurs while subjecting the sludge to alternating anaerobic and aerobic conditions as phosphorus accumulating organisms (PAO) assimilate the products from the BOD fermentation under anaerobic
condition [17]. Then during the aerobic phase, a greater quantity of phosphorus than needed for growth is taken up by the PAO, and phosphorus removal is achieved by removing excess sludge [10,18–22]. However, there is a limitation on the total phosphorus (TP) removal capacity of the biological process, and sometimes the treatment objective can not be met, especially for wastewater with high TP concentration.

Chemical phosphorous removal, including using aluminum sulfate as a coagulant [23], has also been utilized widely due to its effectiveness [24,25]. Phosphorous can be effectively removed by precipitating as insoluble Al-phosphates [26]. Furthermore, phosphate may be adsorbed onto the positively charged Al(OH)₃ colloids formed through hydrolyzation. Many studies have demonstrated that good phosphorous removal efficiency could be achieved with aluminum salt addition [27–30]. Although the stoichiometric molar ratio of Al:P in AlPO₄ is 1:1, the actual dose ratio could vary between 2:1 and 3:1, especially when phosphate is lower than 10 mg/L [31–33]. It was observed that in order to achieve 90% TP removal in an aerated lagoon with an average influent TP concentration of 4.8 mg/L, aluminum sulfate must be added at a dose ratio of 3.2:1 (molar ratio Al:P) [34]. Zhang et al. [35] also reported that a higher coagulant dosage was required for mixed liquor in an MBR system than that for normal water and wastewater treatment. However, a high coagulant dose could bring some negative effects such as decreased microbial activities of activated sludge [35], increased operational costs, resulted in a rapid increase of mixed liquor suspended solid (MLSS), and a low mixed liquor volatile suspended solid (MLVSS)/MLSS.

The aims of this study were to: 1) evaluate the feasibility of using a low concentration of aluminum sulfate [mol Al: mol P ≤1] to improve the treatment performance for phosphorus removal in a SMBR; and 2) evaluate the effects of a low concentration of aluminum sulfate addition on removal rates for COD, TN and ammonia.

2. Materials and methods

2.1. Experimental system

A 320L pilot-scale SMBR (Fig. 1) with a hollow fiber membrane module made of polyvinylidene fluoride (PVDF) was used in this study [36]. The nominal pore size of the membrane was 0.2 µm and the inner/outer diameter was 0.6 mm/1.0 mm. The membrane surface was 0.2 m². The water level in the reactor was controlled by a ball cock. Aeration was provided through perforated plastic pipes located below the submerged membrane module. In order to enhance the cross flow of the mixed liquor, two baffles were installed to form the upflow and downflow sections of the reactor. Treated effluent was continuously withdrawn by a suction pump. Aeration rate and effluent flow rate were monitored using flow measuring devices. The trans-membrane pressure was measured using a pressure gauge.

2.2. Wastewater and sludge characteristics

The wastewater used in the study was a mixture of septic tank effluent and synthetic wastewater (Table 1). Activated sludge used in the reactor was taken from the aeration basin of a municipal wastewater treatment plant in Wuhan, China. The sludge was acclimated in the SMBR for about 20 d, and the experiment began when stable and high removal efficiencies for COD and ammonia were achieved, indicating steady state had been reached. No sludge was removed from the reactor intentionally except...
about 500 ml mixed liquor was taken out for analysis of MLSS and MLVSS.

2.3. Operational conditions of the reactor

The SMBR was operated under the optimal operating condition reported in an earlier study [36]. The operation parameters were set at membrane flux \((J_V) = 10 \text{ L·m}^{-2}·\text{h}^{-1}\), aeration \((Q) = 6 \text{ m}^3·\text{h}^{-1}\), ratio of pumping time to break time \((t_p/t_b) = 4 \text{ min/1 min}\), and ratio of up flow area to down flow area \((A_r/A_d) = 1.7 \text{ m}^2/\text{m}^2\).

The pH in the reactor was maintained between 7.5–8.1 by adding NaHCO\(_3\) into the influent tank. The hydraulic retention time (HRT) of the system was 8 h. The temperature was kept at 24–30°C.

2.4. Addition of aluminum sulfate

Based on the mean concentration of TP (7.6 mg/L) in the influent, 4.5 mg/L of Al\(^{3+}\) [as Al\(_2\)(SO\(_4\))\(_3\)] was added into the influent feeding tank. Although during days 26–52, the mean influent concentration of TP reached 11.3 mg/L, the Al\(^{3+}\) dosage was not adjusted.

2.5. Analytical methods

pH and DO values were measured using a portable electrode device (ORION 5 STAR, Thermo Electron Corporation, USA). Chemical oxygen demand (COD\(_c\)) was measured with a spectrophotometer (DR/2010, HACH, USA). MLSS, MLVSS in the reactor, total nitrogen (TN), total phosphorus (TP), ammonia nitrogen (NH\(_4\)-N), nitrite (NO\(_2\)) and Total Suspended Solids (TSS) of the influent and effluent were determined in accordance with Standard Methods [37].

2.6. Statistics analysis

Statistics analysis was performed with SPSS 17.0 software package for windows. The differences of removal efficiencies and the concentrations of pollutants before and after the addition of aluminum sulfate were tested for significance by independent-sample t test. Significance was defined by \(p < 0.05\).

3. Results

3.1. Effect of aluminum sulfate on the TP removal rates

The removal rates for TP before and after the addition of aluminum sulfate were determined (Fig. 2).

Prior to the addition of aluminum sulfate, the phosphorus removal rates varied significantly, ranging from 57.9% to 89.5%, with a mean removal rate of 78.3%. The concentrations in the effluent ranged between 0.66 and 1.85 mg/L, with a mean value of 1.07 mg/L.

After the addition of aluminum sulfate, the removal rates of TP remained relatively stable with a mean value of as high as 95.8%, and a significant improvement for TP removal efficiency was detected \((p < 0.05)\). Although the concentrations of TP in the influent in the late experimental period increased, even as high as 17.1 mg/L, most of the time TP concentrations in the effluent remained within 0.5 mg/L, which is within Class A1 discharge standard in China. The concentration of TP in the effluent was lowered significantly \((p < 0.05)\) after the addition of aluminum sulfate, although the TP concentration in the influent was significantly higher \((p < 0.05)\).

3.2. Effect of aluminum sulfate on the removal rates of ammonia

The removal rates for ammonia before and after the addition of aluminum sulfate were determined (Fig. 3).

A mean 94.2% ammonia removal rate was achieved during days 1–18 with a mean effluent concentration of 1.18 mg/L.

During days 19–35, a decrease and fluctuation of removal efficiency was observed, and filamentous bacteria were identified in the sludge under microscope.

During days 36–60, the filamentous bacteria in the

---

**Table 1**

<table>
<thead>
<tr>
<th>Indexes</th>
<th>Value range</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg/L</td>
<td>569–1420</td>
<td>902</td>
</tr>
<tr>
<td>NH(_4)-N, mg/L</td>
<td>9.6–40.7</td>
<td>21.6</td>
</tr>
<tr>
<td>TP, mg/L</td>
<td>3.2–17.1</td>
<td>7.6</td>
</tr>
<tr>
<td>NO(_2), mg/L</td>
<td>0–0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>pH</td>
<td>6.27–6.96</td>
<td>6.68</td>
</tr>
<tr>
<td>DO, mg/L</td>
<td>0.16–1.33</td>
<td>0.85</td>
</tr>
<tr>
<td>TN, mg/L</td>
<td>32.3–77.5</td>
<td>53.6</td>
</tr>
<tr>
<td>NO(_3), mg/L</td>
<td>0–2.28</td>
<td>0.79</td>
</tr>
</tbody>
</table>

---

Fig. 2. The removal rates of TP before and after the addition of aluminum sulfate.
reactor almost disappeared, and high ammonia removal rate previously observed returned. Overall, a mean removal rate of 94.8% was achieved and the mean concentration of ammonia in the effluent was 0.91 mg/L. No significant difference was noted for ammonia removal efficiencies ($p > 0.05$) before and after the addition of aluminum sulfate.

3.3. Effect of aluminum sulfate on the removal rates of COD

The removal rates for COD before and after the addition of aluminum sulfate were determined (Fig. 4).

Relatively stable removal rates for COD were achieved during the entire experiment although the influent COD concentration fluctuated greatly with a mean value of 902 mg/L. The mean removal rates for COD before and after the addition of aluminum sulfate were 98.3% and 97.2%, respectively. No significant difference was found ($p > 0.05$).

3.4. Effect of aluminum sulfate on the removal rates of TN

The removal rates for TN, together with the concentrations of NO$_3^-$ and NO$_2^-$ in the effluent, before and after the addition of aluminum sulfate were determined (Figs. 5, 6).

The removal rates for TN varied between 38.0% and 78.5%, with a mean of 55.2%, before the addition of aluminum sulfate (Fig. 5). Since the reactor was not designed for denitrification, the TN removal rate, as expected, was relatively low and the rates varied depending on influent concentrations.

After the addition of aluminum sulfate, the removal rates for TN varied between 31.4% and 82.6%, with a mean of 65.1%. Significant difference for TN removal efficiency was found ($p < 0.05$), although the TN concentration in the influent had no significant difference ($p > 0.05$). The mean removal rate for TN just decreased a little during days 19–35 despite of the present of filamentous bacteria.

Fig. 3. The removal efficiency of ammonia before and after the addition of aluminum sulfate.

Fig. 4. The removal rates of COD before and after the addition of aluminum sulfate.

Fig. 5. The removal rates of TN before and after the addition of aluminum sulfate.

Fig. 6. The concentrations of NO$_3^-$ and NO$_2^-$ in the effluent before and after the addition of aluminum sulfate.
The mean concentration of NO$_3^-$ in the effluent reached 13.5 mg/L during days 1–18 (Fig. 6). During days 19–35, nitrification was inhibited by sludge bulking as indicated by low concentrations of NO$_3^-$ in the effluent and low ammonia removal. After the system was restored to normal operating condition, the mean concentration of NO$_3^-$ in the effluent increased to 9.9 mg/L, which was lower than that before the addition of aluminum sulfate, although no significant difference was detected ($p > 0.05$).

4. Discussion and conclusions

It is common to use chemical reagents to remove phosphorus in wastewater treatment due to their high reliability, ease of operation and low energy consumption [24,38]. However, there are at least a number of factors that could affect and determine the actual quantity of chemical reagents needed to achieve a desirable TP concentration in the effluent including:

1. wastewater characteristics (i.e. concentrations of chemicals, alkalinity, pH, etc);
2. quantity and nature of mixed liquor suspended solids, microorganisms;
3. mixing intensity for coagulation and flocculation;
4. biological processes (i.e. aerobic, anaerobic/anoxic).

In general, within a certain TP concentration range, phosphorus removal efficiency increases with increasing flocculant dosage [28,30,39]. However, a high concentration of flocculant not only could add additional costs, but also could change the microorganism community in the reactor due to pH change [40]. In addition, high dosage could exert a negative effect on sludge activities [35], and it could result in high excess sludge production and make sludge disposal more difficult.

Our study results showed that a significant improvement (17.5%) for TP removal was achieved with a low dose of Al$^{3+}$ as Al$_2$(SO$_4$)$_3$. Also, the system was able to maintain high TP removal rates even when the mean concentration of TP in the influent was increased by nearly 50% (from 7.6 mg/L to 11.3 mg/L). The aluminum sulfate dosage used in this reactor was lower than that reported by Citulski et al. [29,41].

Meanwhile, the MLSS in the reactor increased slowly during the entire experiment, which was from 2.4 g/L to 4.5 g/L before the addition of aluminum and from 4.5 g/L to 5.6 g/L after the addition, respectively. The phosphorus assimilated by activated sludge after the addition of aluminum probably was not the main removal mechanism for TP. High and stable TP removal efficiency was maintained after the addition of aluminum in the SMBR with long sludge retention time (SRT), which might be due to that a mount of coagulant floc was retained in the feeding tank and phosphate was removed by adsorption.

In addition to enhancing phosphorus removal rate, the mean removal rate for TN was also improved from 55.2% to 65.1% after the addition of aluminum. Song et al. [30] also reported that an improvement in TN removal was achieved after the addition of alum. The possible reason for the observed improvement was that the adsorption of Al(OH)$_3$ could remove nitrogen pollutants in big granule state, and addition of coagulant could increase the mean sludge floc size [30,42], which was beneficial to simultaneous nitrification and denitrification [43]. The decrease of the mean NO$_3^-$ concentration after the addition of aluminum sulfate indicated that denitrification was enhanced. Although the addition of aluminum sulfate could affect the growth and metabolism of nitrifying bacteria [44], the dosage used in the study was small. Therefore, the effect of aluminum sulfate on the removal efficiency of ammonia was minimum, which was consistent with the result observed by Song et al. [30].

Based on the results of this study, a low concentration of aluminum sulfate addition could be utilized to improve the treatment performance in a SMBR.

Acknowledgement

This work was supported by grants from the Key Science Research Project of Eleventh Five-Year Plan (2009ZX07106-003, 2008ZX07316-004), Tianjin Project of CAS (TJZX2-YW-07), and Agricultural Science and Technology Achievement Transformation Project (No. 2009GB2A100015). Many thanks are given to the anonymous reviewers and Mr. James Wang of EPA in USA for suggestions on the manuscript.

References


