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

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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 $\leq$ 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

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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 $\leq$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 m^2. 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

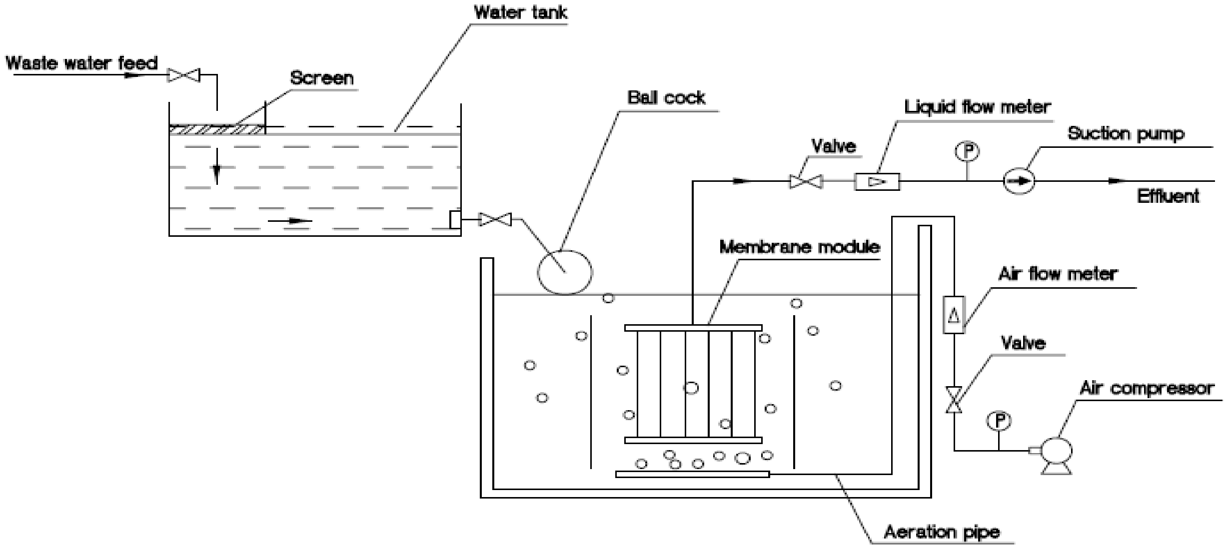

Fig. 1. Sketch of the pilot SMBR.

Table 1
Indexes of experimental wastewater

Indexes	Value range	Mean value
COD, mg/L	569–1420	902
NH_4^+-N, mg/L	9.6–40.7	21.6
TP, mg/L	3.2–17.1	7.6
NO_2^-, mg/L	0–0.04	0.01
pH	6.27–6.96	6.68
DO, mg/L	0.16–1.33	0.85
TN, mg/L	32.3–77.5	53.6
NO_3^-, mg/L	0–2.28	0.79

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 L·m^{-2}·h^{-1}, aeration (Q) = 6 m^3·h^{-1}, ratio of pumping time to break time (t_p/t_b) = 4 min/1 min, and ratio of up flow area to down flow area (A_r/A_d) = 1.7 m^2/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_{Cr}) was measured with a spectrophotometer (DR/2010, HACH, USA). MLSS, MLVSS in the reactor, total nitrogen (TN), total phosphorus (TP), ammonia nitrogen (NH_3-N), nitrite (NO_2^-), nitrate (NO_3^-) and total suspended solid (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

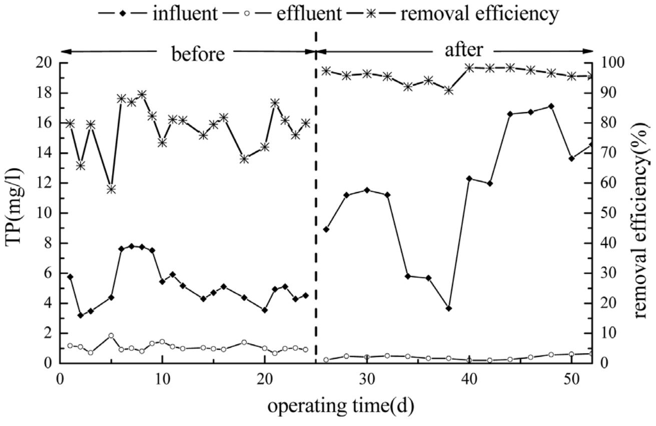

Fig. 2. The removal rates of TP before and after the addition of aluminum sulfate.

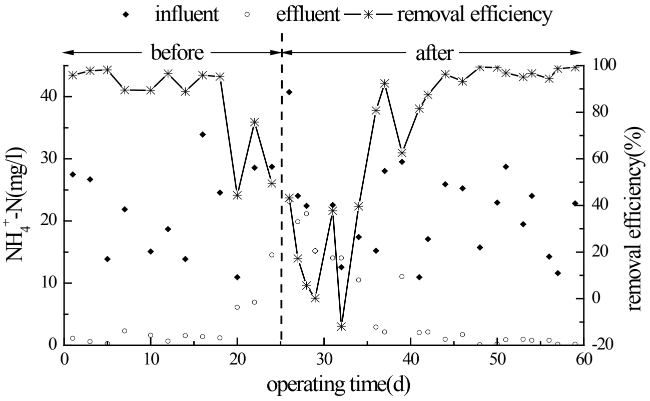

Fig. 3. The removal efficiency of ammonia before and after the addition of aluminum sulfate.

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 ($p > 0.05$).

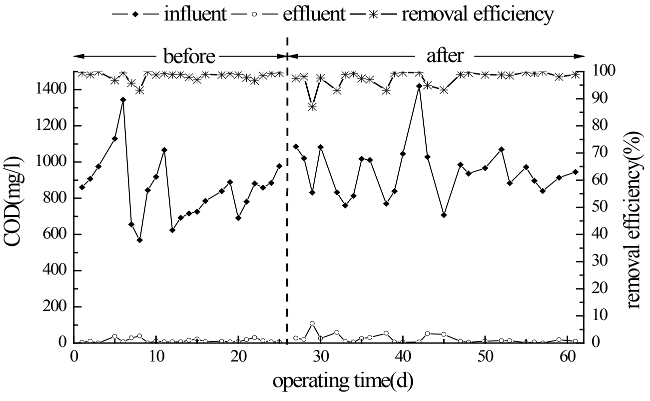

Fig. 4. The removal rates of COD before and after the addition of aluminum sulfate.

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.

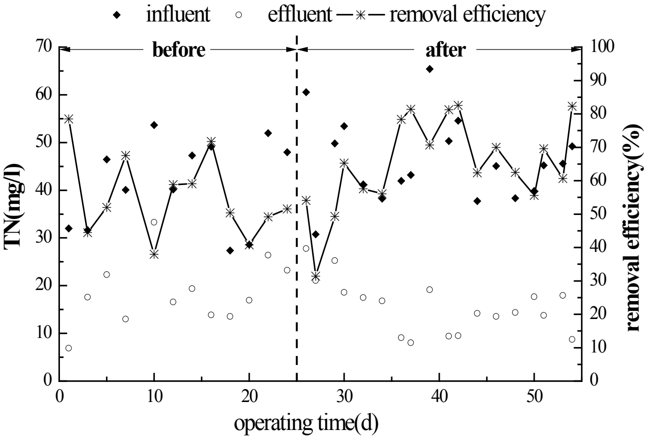

Fig. 5. The removal rates of TN before and after the addition of aluminum sulfate.

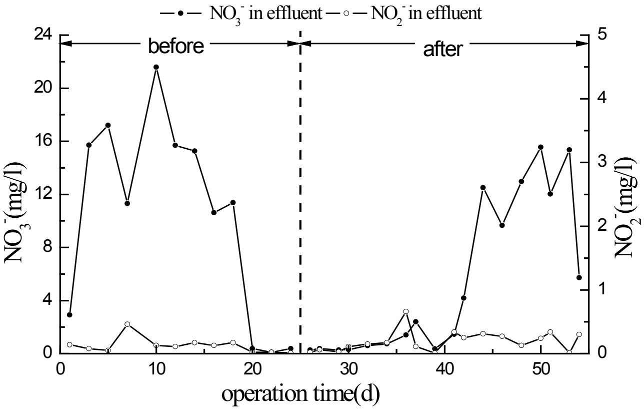

Fig. 6. The concentrations of NO_3^- and NO_2^- in the effluent before and after the addition of aluminum sulfate.

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 flocs 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 efficienciy 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.

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References

[1] D.L. Correll, The role of phosphorus in the eutrophication of receiving waters: A review, J. Environ. Qual., 27 (1988) 261–266.

[2] E. Oguz, A. Gurses and N. Canpolat, Removal of phosphate from wastewaters, Cem. Concr. Res., 33 (2003) 1109–1112.

[3] J.A. Howell, T.C. Arnot and W. Liu, Membrane bioreactors for treating waste streams, Ann. N.Y. Acad. Sci., 984 (2003) 411–419.

[4] W. Scholz and W. Fuchs, Treatment of oil contaminated wastewater in a membrane bioreactor, Wat. Res., 34 (2000) 3621–3629.

[5] S. Holler and W. Trosch, Treatment of urban wastewater in a membrane bioreactor at high organic loading rates, J. Biotechnol., 92 (2001) 95–101.

[6] H.H. Ngo, W. Guo and W. Xing, Evaluation of a novel sponge-submerged membrane bioreactor (SSMBR) for sustainable water reclamation, Bioresour. Technol., 99 (2008) 2429–2435.

[7] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf and T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination, 187 (2006) 271–282.

[8] P. Artiga, G. García-Toriello, R. Méndez and J.M. Garrido, Use of a hybrid membrane bioreactor for the treatment of saline wastewater from a fish canning factory, Desalination, 221 (2008) 518–525.

[9] T.A. Mohammed, A.H. Birima, M.J.M.M. Noor, S.A. Muyibi and A. Idris, Evaluation of using membrane bioreactor for treating municipal wastewater at different operating conditions, Desalination, 221 (2008) 502–510.

[10] K.H. Ahn, K.G. Song, E. Cho, J.W. Cho, H.J. Yun, S.H. Lee and J.Y. Kim, Enhanced biological phosphorus and nitrogen removal using a sequencing anoxic/anaerobic membrane bioreactor (SAM)

process, Desalination, 157 (2003) 345–352.

[11] C. Abegglen, M. Ospelt and H. Siegrist, Biological nutrient removal in a small-scale MBR treating household wastewater, Wat. Res., 42 (2008) 338–346.

[12] B. Lesjean, R. Gnirss, H. Buisson, S. Keller, A. Tazi-Pain and F. Luck, Outcomes of a 2-year investigation on enhanced biological nutrients removal and trace organics in membrane bioreactor (MBR), Wat. Sci. Technol., 52 (2005) 453–460.

[13] B. Farizoglu, B. Keskinler, E. Yildiz and A. Nuhoglu, Simultaneous removal of C,N,P from cheese whey by jet loop membrane bioreactor (JLMBR), J. Hazard. Mater., 146 (2007) 399–407.

[14] S.R. Chae and H.S. Shin, Effect of condensate of food waste (CFW) on nutrient removal and behaviours of intercellular materials in a vertical submerged membrane bioreactor (VSMBR), Bioresour. Technol., 98 (2007) 373–379.

[15] I. Katz and C.G. Dosoretz, Desalination of domestic wastewater effluents: phosphate removal as pretreatment, Desalination, 222 (2008) 230–242.

[16] USEPA (US Environmental Protection Agency), Process Design Manual for Phosphorus Removal, EPA/625/1-87/001, USEPA, Cincinnati, Ohio, 1987.

[17] R.Y. Surampalli, R.D. Tyagi, O.K. Scheible and J.A. Heidman, Nitrification, denitrification and phosphorus removal in sequential batch reactors, Bioresour. Technol., 61 (1997) 151–157.

[18] L.M. Yuan, C.Y. Zhang, Y.Q. Zhang, Y. Ding and D.L. Xi, Biological nutrient removal using an alternating of anoxic and anaerobic membrane bioreactor (AAAM) process, Desalination, 221 (2008) 566–575.

[19] Y.L. Wang, S.L. Yu, W.X. Shi, R.L. Bao, Q. Zhao and X.T. Zuo, Comparative performance between intermittently cyclic activated sludge-membrane bioreactor and anoxic/aerobic-membrane bioreactor, Bioresour. Technol., 100 (2009) 3877–3881.

[20] C.B. Ersu, S.K. Ong, E. Arslankaya and P. Brown, Comparison of recirculation configurations for biological nutrient removal in a membrane bioreactor, Wat. Res., 42 (2008) 1651–1663.

[21] Z. Ahmed, B.R. Lim, J. Cho, K.G. Song, K.P. Kim and K.H. Ahn, Biological nitrogen and phosphorus removal and changes in microbial community structure in a membrane bioreactor: Effect of different carbon sources, Wat. Res., 42 (2008) 198–210.

[22] B. Lesjean, R. Gnirss and C. Adam, Process configurations adapted to membrane bioreactors for enhanced biological phosphorous and nitrogen removal, Desalination, 149 (2002) 217–224.

[23] A.I. Omoike and G.W. Vanloon, Removal of phosphorus and organic matter removal by alum during wastewater treatment, Wat. Res., 33 (1999) 3617–3627.

[24] O. Jenkins, J.F. Fergusson and A.B. Menar, Chemical processes for phosphate removal, Wat. Res., 5 (1971) 369–387.

[25] L.E. de-Bashan and Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Wat. Res., 38 (2004) 4222–4246.

[26] M. Polanska, K. Huysman and C.V. Keer, Investigation of microbially available phosphorus (MAP) in flemish drinking water, Wat. Res., 39 (2005) 2267–2272.

[27] J. Tian, H. Liang, X. Li, S.J. You, S. Tian and G.B. Li, Membrane coagulation bioreactor (MCBR) for drinking water treatment, Wat. Res., 42 (2008) 3910–3920.

[28] J. Zhang, Y.X. Sun, Q.B. Chang, X.Q. Liu and G.Y. Meng, Improvement of crossflow microfiltration performances for treatment of phosphorus-containing wastewater, Desalination, 194 (2006) 182–191.

[29] J. Citulski, K. Farahbakhsh and F. Kent, Optimization of phosphorus removal in secondary effluent using immersed ultrafiltration membranes with in-line coagulant pretreatment — Implications for advanced water treatment and reuse applications, Can. J. Chem. Eng., 36 (2009) 1272–1283.

[30] K.G. Song, Y. Kim and K.H. Ahn, Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor, Desalination, 221 (2008) 467–474.

[31] M. Maurer and M. Boller, Modelling of phosphorus precipitation in wastewater treatment plants with enhanced biological phosphorus removal, Wat. Sci. Technol., 39 (1999) 147–163.

[32] J.Q. Jiang and N.J.D. Graham, Pre-polymerised inorganic coagulants and phosphorus removal by coagulation — a review, Water S.A., 24 (1998) 237–244.

[33] D.W. de Haas, M.C. Wentzel and G.A. Ekama, The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal. Part 1: Literature review, Water S.A., 26 (2000) 439–452.

[34] K.S. Narasiah, C. Morasse and J. Lemay, Nutrient removal from aerated lagoons using alum and ferric chloride.A case study, Wat. Sci. Technol., 23 (1991) 1563–1572.

[35] Y. Zhang, D. Bu, C.G. Liu, X. Luo and P. Gu, Study on retarding membrane fouling by ferric salts dosing in membrane bioreactors, Water and Environment Membrane Technology (WEMT) Conference, Seoul, Korea, 2004.

[36] Z. Wu, E. Xiao, W. Liang, S.P. Cheng and F. He, Optimization of operational conditions in a submerged membrane bioreactor, Fresenius Environ. Bull., 16 (2007) 654–659.

[37] APHA–AWWA–WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed, APHA, AWWA and WEF, Washington, DC, 1998.

[38] S. Yeoman, T. Stephenson, J.N. Lester and R. Perry, The removal of phosphorus during wastewater treatment: A review, Environ. Pollut., 49 (1988) 183–233.

[39] O.S. Amuda and I.A. Amoo, Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment, J. Hazard. Mater., 141 (2007) 778–783.

[40] Y. Miura, M.N. Hiraiwa, T. Ito, T. Itonaga, Y. Watanabe and S. Okabe, Bacterial community structures in MBRs treating municipal wastewater: Relationship between community stability and reactor performance, Wat. Res., 41 (2007) 627–637.

[41] J. Citulski, K. Farahbakhsh, F. Kent and H.D, Zhou, The impact of in-line coagulant addition on fouling potential of secondary effluent at a pilot-scale immersed ultrafiltration plant, J. Mater. Sci., 325 (2008) 311–318.

[42] H.F. Zhang, B.S. Sun, X.H. Zhao and Z.H. Gao, Effect of ferric chloride on fouling in membrane bioreactor, Separ. Purif. Technol., 63 (2008) 341–347.

[43] K. Pochanna, J. Keller and P. Lant, Model development for simultaneous nitrication and denitrification. Wat. Sci. Technol., 39 (1999) 235–243.

[44] T. Clark, T. Stephenson and A.K. Arnold-Smith, The impact of aluminium-based co-precipitants on the activated sludge process, Process Saf. Environ. Prot., 77 (1999) 31–36.