

# Effect of chemical dose on phosphorus removal and membrane fouling control in a UCT-MBR

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## HIGHLIGHTS

- Phosphorus removal was enhanced effectively by dosing aluminum sulfate and effluent phosphorus concentration was lower than 0.5 mg/L.
- Sludge activity was not inhibited but improved slightly with addition of aluminum sulfate.
- EPS concentrations both in mixed liquid and on membrane surface were decreased, contributing to the effective mitigation of membrane fouling.

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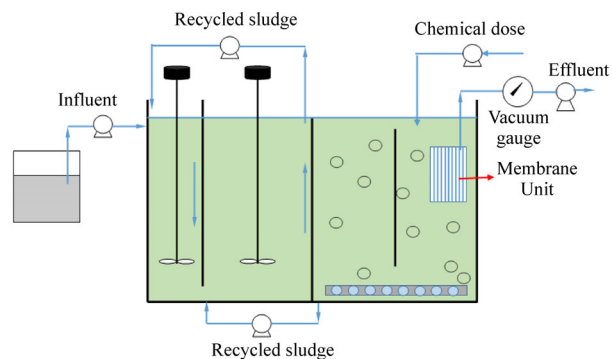
Enhanced nutrients removal

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## GRAPHIC ABSTRACT



## ABSTRACT

To enhance phosphorus removal and make the effluent meet the strict discharge level of total phosphorus (TP, 0.5 mg/L), flocculant dosing is frequently applied. In this study, the performance of aluminum sulfate dosing in a University of Cape Town Membrane Bioreactor (UCT-MBR) was investigated, in terms of the nutrients removal performance, sludge characteristics and membrane fouling. The results indicated that the addition of aluminum sulfate into the aerobic reactor continuously had significantly enhanced phosphorus removal. Moreover, COD,  $\text{NH}_4^+-\text{N}$  and TN removal were not affected and effluent all met the first level A criteria of GB18918-2002. In addition, the addition of aluminum sulfate had improved the sludge activity slightly and reduced trans-membrane pressure (TMP) increase rate from 1.13 KPa/d to 0.57 KPa/d effectively. The alleviation of membrane fouling was attributed to the increased average particle sizes and the decreased accumulation of the small sludge particles on membrane surface. Furthermore, the decline of extracellular polymeric substance (EPS) concentration in mixed sludge liquid decreased its accumulation on membrane surface, resulting in the mitigation of membrane fouling directly.

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## 1 Introduction

With the rapid development of industry and agriculture, wastewater with high levels of nitrogen and phosphorus was discharged in sensitive areas, hence the eutrophication phenomenon had become a worldwide environmental issue (Li et al., 2017a). Indeed, the serious eutrophication of water bodies in China has motivated the creation of

standards requiring total phosphorus (TP) levels in wastewater treatment plant (WWTP) to be lower than 0.5 mg/L (Liu et al., 2011), avoiding the increased algae growth in the receiving water bodies. Moreover, the demand for the recycle and reuse of wastewater was increasing gradually (Monclús et al., 2010).

A possible solution to deal with such issues is presented by membrane bioreactor (MBR) technology, in which solid and liquid separation is performed by membranes. In recent years, MBR has gained increasing popularity and presented a superior way in wastewater reuse and recycle. Compared with conventional activated sludge processes, MBR exhibits several advantages like high quality of

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effluent, a small footprint and lower sludge production (Dalmau et al., 2013), as well as a near complete rejection of pathogenic bacteria (Arrojo et al., 2005).

However, in terms of biological phosphorus removal capability, the single MBR system shows the weakness because of the longer sludge retention time (SRT), hence MBR is usually adopted with conventional nutrient removal process for effective nitrogen and phosphorus removal. Based on the traditional nitrogen and phosphorus removal theories, some biological nutrient removal processes related to MBRs (BNR-MBR), such as A<sup>2</sup>/O-MBR (Banu et al., 2009), UCT-MBR (Trapani et al., 2011), MUCT-MBR (Zhang et al., 2009) have been proposed for municipal wastewater treatment, and the results showed that all of processes mentioned above exhibited a favorable performance on both nutrients removal and solid-liquid separation.

Compared with A<sup>2</sup>/O-MBR, UCT-MBR process showed perfect nitrogen and phosphorus removal performance, which might be explained by the eliminated influence of nitrate in return sludge. Thus, UCT-MBR process has received considerable scientific interest in recent years as an alternative pathway for effective biological nitrogen and phosphorus removal. It was reported that the removal efficiency was significantly affected by the influent COD/N ratios in UCT-MBR process. Ge et al. (2010) found an increasing removal efficiency when influent COD/N was ranging from 4.5 to 7.5. Besides, Wang et al. (2014b) also has investigated the impact of influent COD/N on nutrients removal and found that when influent COD/N ratio was 5.3–7.3, the process showed excellent performance on nitrogen and phosphorus removal. Whereas, the effluent TP could not meet the stricter discharge level A criteria of GB18918-2002 (0.5 mg/L) even under optimal influent COD/N (Mannina et al., 2016).

In addition, membrane fouling was considered as one of the major obstacles for wide-spread applications of MBR and it was mainly caused by the deposition of small particle and adsorption of EPS on membrane surface. Membrane fouling resulted in the rapid increase of TMP, reduced permeability, which directly led to the increase of energy consumption. With respect to fouling factors, EPS, which are extracted from bacteria in bioreactor and composed of a variety of organic substances, are usually regarded as the major controlling factor in MBR system (Drews et al., 2006; Satyawali and Balakrishnan, 2009).

Chemically enhanced phosphorus removal process, as a supplementary means of biological phosphorus removal, has been concerned recently, and iron salt, aluminum salt and ferric salt are currently the most widely used flocculant in wastewater treatment. Such additives could result in a favorable removal of TP, as well as high molecular weight organics removal by adsorption (Wu et al., 2015; Wu et al., 2016), and make effluent of TP and COD below 0.5 mg/L and 50 mg/L, respectively. Wu (2016) investigated two sets of BAF-ozonation systems, with and without Fe<sup>2+</sup>, the

result showed that the dosage of Fe<sup>2+</sup> into BAF can significantly enhance the COD and TP removal. Buisson H (1998) added Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> into MBR and found that the effluent TP concentration decreased from 9.4 mg/L to 1.0 mg/L. Li (2017b) used a membrane bioreactor to treat biological aerated filter effluent in a municipal wastewater plant, and chemical phosphorus removal was accomplished in the MBR. The results showed that ferric chloride of 20 mg/L and aluminum sulfate of 30 mg/L were the optimal dosages for total phosphorus (TP) removal, and the TP removal efficiency was over 80%.

In addition, it could also decrease the compressibility of sludge flocs, increase the porosity of the cake layer, reduce the concentration of EPS and change the particle size distribution of activated sludge, which would have a positive impact on membrane fouling control. Based on the results obtained, chemical addition could increase the critical flux and extend the duration between mesh cleaning. However, it was also observed that the increasing addition of chemical flocculant had a slight adverse effect on sludge activity (Wu et al., 2016). Al-based salts are the most commonly used coagulants in water and wastewater treatment due to their low cost and abundant availability (Hussain et al., 2014). Furthermore, Fe-based salts could result in the color in the effluent. So, we choose aluminum sulfate as the tested chemical reagent.

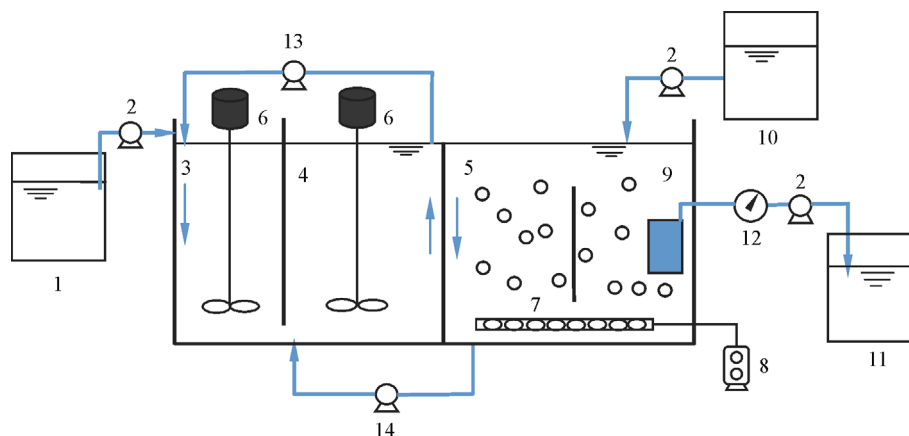
In this study, a bench-scale UCT-MBR system was operated under two conditions of different influent COD concentrations (COD/N ratios were 7.3 and 5.3, respectively) and chemical dose (aluminum sulfate) was applied to further reduce the effluent TP concentration to be below 0.5 mg/L. The objective of the study is to examine the feasibility and suitability of using aluminum sulfate as chemical dose. In particular, the comparisons of the removal efficiency of different nutrients, the sludge characteristics and membrane fouling with and without aluminum sulfate were conducted to provide the theoretical basis for the practical application of chemical dose in wastewater treatment. To the best of our knowledge, no published studies on the effect of aluminum sulfate addition based on UCT-MBR process were found currently.

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## 2 Materials and methods

### 2.1 Setup and operation

As shown in Fig. 1, the experimental laboratory-scale reactor studied is an adaptation of the UCT process. It comprises a MBR with a UCT configuration able to biologically remove nitrogen and phosphorus, as well as organic matters. The bioreactor has a total volume of 12 L, consisting of three reactors in series, an anaerobic tank (17% of the total volume), an anoxic tank (33%) and an aerobic (50%) compartment in which the polyvinylidene



**Fig. 1** Schematic overview of the UCT-MBR setup: 1. Influent tank; 2. Pump; 3. Anaerobic reactor; 4. Anoxic reactor; 5. Aerobic reactor; 6. Mixer; 7. Air diffuser; 8. Blower; 9. Membrane unit; 10. Chemical dosing tank; 11. Wastewater tank; 12. Vacuum gauge; 13. Recycled pump (r); 14. Recycled pump (R).

difluoride (PVDF) membrane unit is submerged. The membrane unit used with a total area of 0.05 m<sup>2</sup> is characterized with a nominal pore size of 0.1 μm. Moreover, the permeate was extracted by an extraction pump imposing an average flux of 16 L/(m<sup>2</sup>·h) and a suction cycle of 10 min followed by 2 min relaxation was applied. To maintain the high biomass concentration in every reactor, the anaerobic recirculation (r) and anoxic recirculation (R) were controlled around 200% and 300%, respectively. In addition, the hydraulic retention time (HRT) is around 18 h and the sludge has been regularly withdrawn, in order to maintain the SRT about 25 d.

## 2.2 Seeding sludge and influent characteristics

The initial activated sludge used in the reactor was collected from the A<sup>2</sup>/O process of Xuzhou Tongshan Sewage Treatment Plant (China), in which biological nutrient removal was successfully adopted. The experimental campaign was divided into 4 phases and the influent COD/N was chosen according to previous studies (Ge et al., 2010; Wang et al., 2014b), each phase was characterized by different COD/N ratios. A synthetic domestic wastewater was used as the experimental influent, containing the following (per liter) substances: CH<sub>3</sub>COONa (0.269–0.346 g); NH<sub>4</sub>Cl (0.134 g); KH<sub>2</sub>PO<sub>4</sub> (0.022 g); MgSO<sub>4</sub> (0.032 g); KHCO<sub>3</sub> (0.1 g); KCl (0.015

g); CaCl<sub>2</sub> (0.010 g). Additionally, 1 mL trace element liquid was added per liter which was composed of H<sub>3</sub>BO<sub>3</sub> (0.17 g); FeCl<sub>3</sub>·6H<sub>2</sub>O (1.52 g); KI (1.80 g); ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.15 g); EDTA (10.00 g); CuSO<sub>4</sub>·5H<sub>2</sub>O (0.03 g); MnCl<sub>2</sub>·4H<sub>2</sub>O (0.12 g); CoCl<sub>2</sub>·6H<sub>2</sub>O (0.15 g). The experiments were carried out continuously for about 100 days and the concentrations of influent wastewater and aluminum sulfate were shown in Table 1.

## 2.3 Analytical methods

### 2.3.1 Liquid and sludge samples

Liquid samples were filtered immediately through Millipore filter units (0.45 μm pore size) for analysis. COD, NH<sub>4</sub><sup>+</sup>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, total nitrogen (TN), TP, mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) were analyzed in accordance with Standard Method of American Public Health Association (APHA, 2012). In addition, the concentrations of proteins (PN) were analyzed by the Lowery method (Lowry et al., 1951) with bovine serum albumin (BSA) as standard, and polysaccharide (PS) concentrations were measured by the phenol-sulfuric method (Dubois et al., 1956) with glucose as the standard. Moreover, the sum of PN and PS was considered as the total EPS. A vacuum gauge was mounted between the membrane unit and

**Table 1** Characteristics of influent wastewater and aluminum sulfate dose in different phases

Phase	1	2	3	4
Aluminum sulfate dose (mg/L)	0	10	0	50
COD (mg/L)	261.2–274.9	251.7.2–270.5	196.5–217.9	204.8–216.4
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	34.4–42.8	36.2–41.3	36.9–39.4	37.2–39.4
TP (mg/L)	4.72–5.22	4.63–5.02	4.88–5.16	4.89–5.05
TN (mg/L)	36.9–43.8	38.6–45.3	37.4–41.6	38.2–42.6

wastewater pump to measure the TMP. Furthermore, sludge particle size was measured using laser particle size analyzer (Microtrac S3500).

### 2.3.2 Batch experiment

(1) Phosphorus release rate: 1 L mixed activated sludge sample from anaerobic reactor was collected, washed and aeration for 2 h, then fed with 100 mg COD (128.2 mg CH<sub>3</sub>COONa) and mixing the liquor for anaerobic reaction, the samples were collected in different time and TP concentrations were measured.

(2) Anoxic denitrification rate: 1 L mixed activated sludge sample from anoxic reactor was obtained and washed for 3 times, fed with 100 mg COD (128.2 mg CH<sub>3</sub>COONa) and 20 mg NO<sub>3</sub><sup>-</sup> (32.58 mg KNO<sub>3</sub>), the samples were collected in different time and the NO<sub>3</sub><sup>-</sup> concentrations were measured.

(3) Aerobic nitrification rate: 1 L mixed activated sludge sample from aerobic reactor was achieved then washed for 3 times, 10 mg NH<sub>4</sub><sup>+</sup>-N (38.2 mg NH<sub>4</sub>Cl) was added for 2.5 h nitrification and the NH<sub>4</sub><sup>+</sup> concentrations were measured.

### 2.3.3 Extraction of EPS

The extraction of EPS from the mixed activated sludge was according to thermal treatment method (Morgan et al., 1990). The mixed activated sludge samples collected from different reactors were centrifuged (3200 rpm, 30 min) and the supernatant was filtered through Millipore filter units (0.45 μm pore size) to analyze the loosely bound EPS (LB-EPS). After discarding the supernatant, the pellet remained was washed and suspended with saline water (0.9% NaCl solution). Then, the mixed liquor was subject to heat treatment (100°C, 60 min) and centrifuged again (3200 rpm, 30 min), the supernatant was filtered through Millipore filter units (0.45 μm pore size) to analyze the tightly bound EPS (TB-EPS). Moreover, the EPS analysis was conducted in triplicate and the average concentration was calculated.

## 3 Results and discussion

### 3.1 Overall performance

Variation curves of different nutrients removal efficiency and concentrations during the entire experimental phase were shown in Fig. 2. According to Fig. 2, most of COD was removed after the anaerobic and anoxic process. In the subsequent aerobic reactor, COD concentrations were 27.2 mg/L and 26.3 mg/L, respectively in phase 1 and 3. Furthermore, a part of residual COD (31.6%–39.5%) in supernatant was removed again by membrane separation

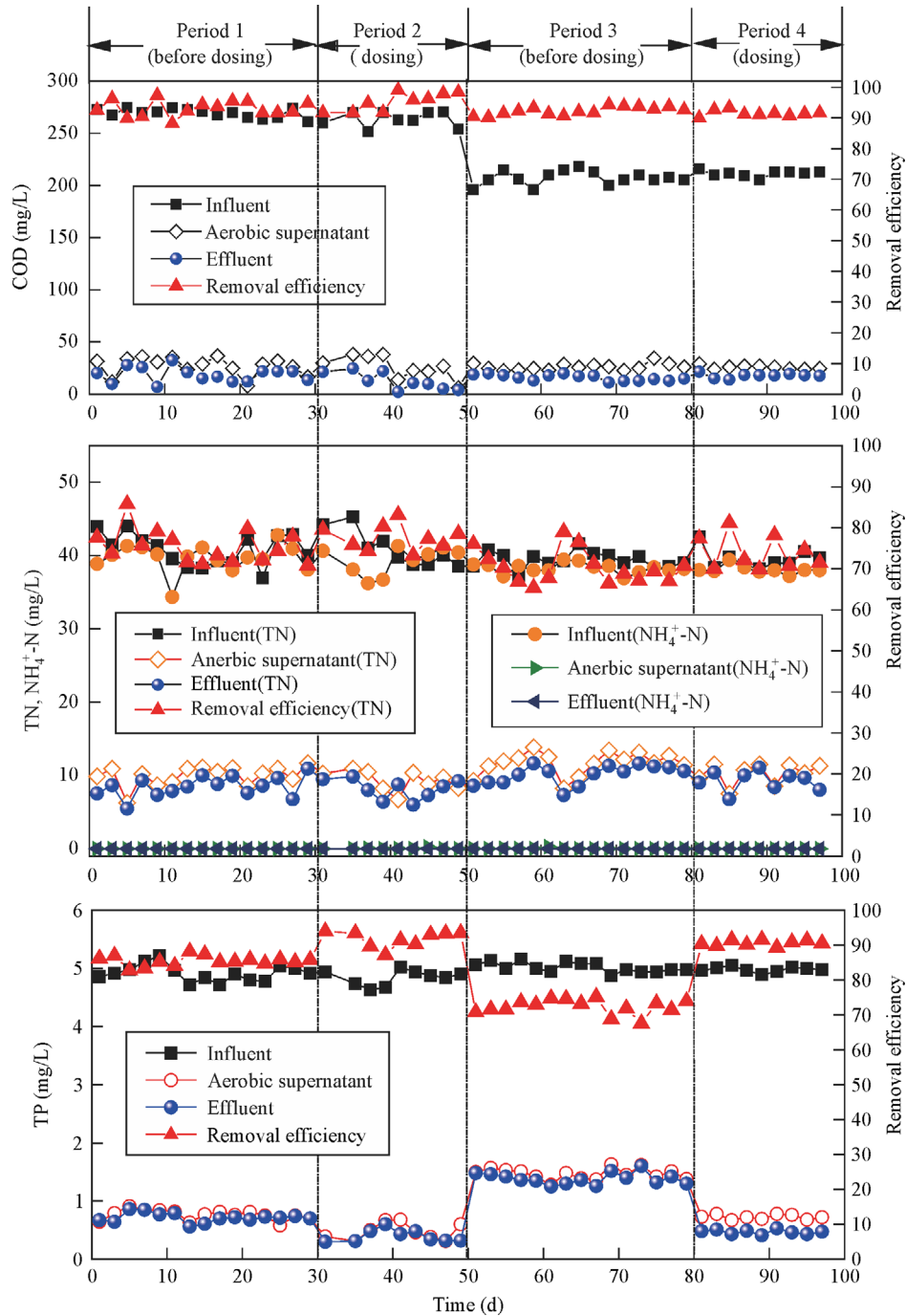
with the final effluent concentration of 18.6 mg/L and 15.9 mg/L, respectively in phase 1 and 3, and the total COD removal efficiency was kept at 93.1%–93.7% regardless of the influent COD. The results obtained were consistent with the report that the membrane separation played an important role in maintaining high and stable COD removal (Díez-Montero et al., 2016). However, COD removal efficiency increased slightly with the addition of aluminum sulfate in phase 2 and 4, and lower effluent concentration ranging from 13.8 to 17.9 mg/L was observed. It could be inferred that part colloid COD fraction could be removed by aluminum sulfate through compressing electric double layer of colloid substances (Caravelli et al., 2012) and some soluble COD fraction could be removed by satisfying some unsaturated coordinate bonds of organics and/or absorption by new sludge flocs (Yan et al., 2008). These findings indicated that aluminum sulfate dosing will not give rise to adverse effects on the COD removal.

With respect to the nitrogen removal, it could be observed that a total nitrification occurred as demonstrated by the negligible value of NH<sub>4</sub><sup>+</sup>-N in aerobic reactor supernatant and effluent throughout the experimental runs. Indeed, a quite high NH<sub>4</sub><sup>+</sup>-N removal efficiency (approximately 100%) was achieved, which was consistent with the results obtained by Monclús et al. (2010). In addition, the system showed excellent TN removal with an average value of 75.4% and 70.3%, respectively in phase 1 and 3, higher than the results (69.0%–70.0%) reported by Cosenza et al. (2013). In details, the average effluent TN concentration was 8.46 mg/L and 10.09 mg/L, respectively, which was lower than the China effluent limit (15 mg/L). These finding indicated that the influent COD concentration had no significant effect on TN removal. With the addition of aluminum sulfate, average TN effluent concentration decreased slightly to 8.16 mg/L and 9.25 mg/L, and the average removal efficiencies were 77.5% and 74.0%, respectively in phase 2 and 4. Consequently, the removal of TN was high-efficient and improved slightly (2.13%–3.65%) by aluminum sulfate addition. This result may be mainly attributed to a slight improvement of denitrification and sludge activity in anoxic reactor with the aluminum sulfate addition, as well as the obvious advantage of MBR (Trapani et al., 2011).

Precipitation is the main mechanisms in terms of chemical P removal. The aluminum sulfate could form precipitates with P, the reaction formulas are:



Polynuclear hydroxy complexes, such as Al(OH)<sub>3</sub>, could be formed during this process. They could stimulate the coagulation performance due to the high positive load and significant sorptive capacity for orthophosphate,



**Fig. 2** The concentrations and removal efficiencies in UCT-MBR during the operational period.

condensed phosphate and organic phosphate (Wu et al., 2016). The precipitates could be intercepted by MBR, hence, it demonstrated that the addition of aluminum sulfate could enhance P removal.

In general, TP removal efficiency showed an increasing trend with the increase of influent COD concentration. After phosphorus release in anaerobic reactor and excessive phosphorus uptake in aerobic reactor by polyphosphate-accumulating organisms (PAOs), the

average concentration in aerobic supernatant was just 0.76 mg/L and a part of residual TP (5.3%) was removed by membrane physical filtration. Indeed, TP removal efficiency during phase 1 achieved an average value of 85.4%, consistent with findings by Leyva-Díaz et al. (2016) but higher than biological TP removal efficiency of 60% reported by Ferrero et al. (2011). However, the final effluent concentration was 0.72 mg/L, higher than the discharge limit in the wastewater treatment plant

(0.5 mg/L). Hence, aluminum sulfate dose was applied in phase 2 and 10 mg/L aluminum sulfate was dosed to aerobic reactor continuously. Therefore, with the effort of chemical P removal, the residual phosphorus concentrations in the effluent reduced to 0.40 mg/L with the increased removal efficiency of 92.0%. Therefore, the proportions of chemical phosphorus and biological phosphorus removals are 85.6% and 6.4%, respectively.

However, the decrease of average influent COD to 210 mg/L in phase 3 had significantly worsened TP removal. It was mainly due to insufficient PHB production for phosphate uptake which limited the TP removal. Particularly, it was noted a decreased to 71.1% in TP removal efficiency and the residual phosphorus concentrations were increased rapidly to 1.57 mg/L and 1.45 mg/L, respectively in aerobic supernatant and effluent. Therefore, 50mg/L aluminum sulfate was dosed to aerobic reactor continuously in phase 4. Correspondingly, the removal efficiency increased to 90.6% and the effluent TP concentration reduced rapidly to 0.47 mg/L, below the effluent discharge limits (0.5 mg/L). The proportions of chemical phosphorus and biological phosphorus removals are 71.0% and 19.6%, respectively. The improvement of TP removal should

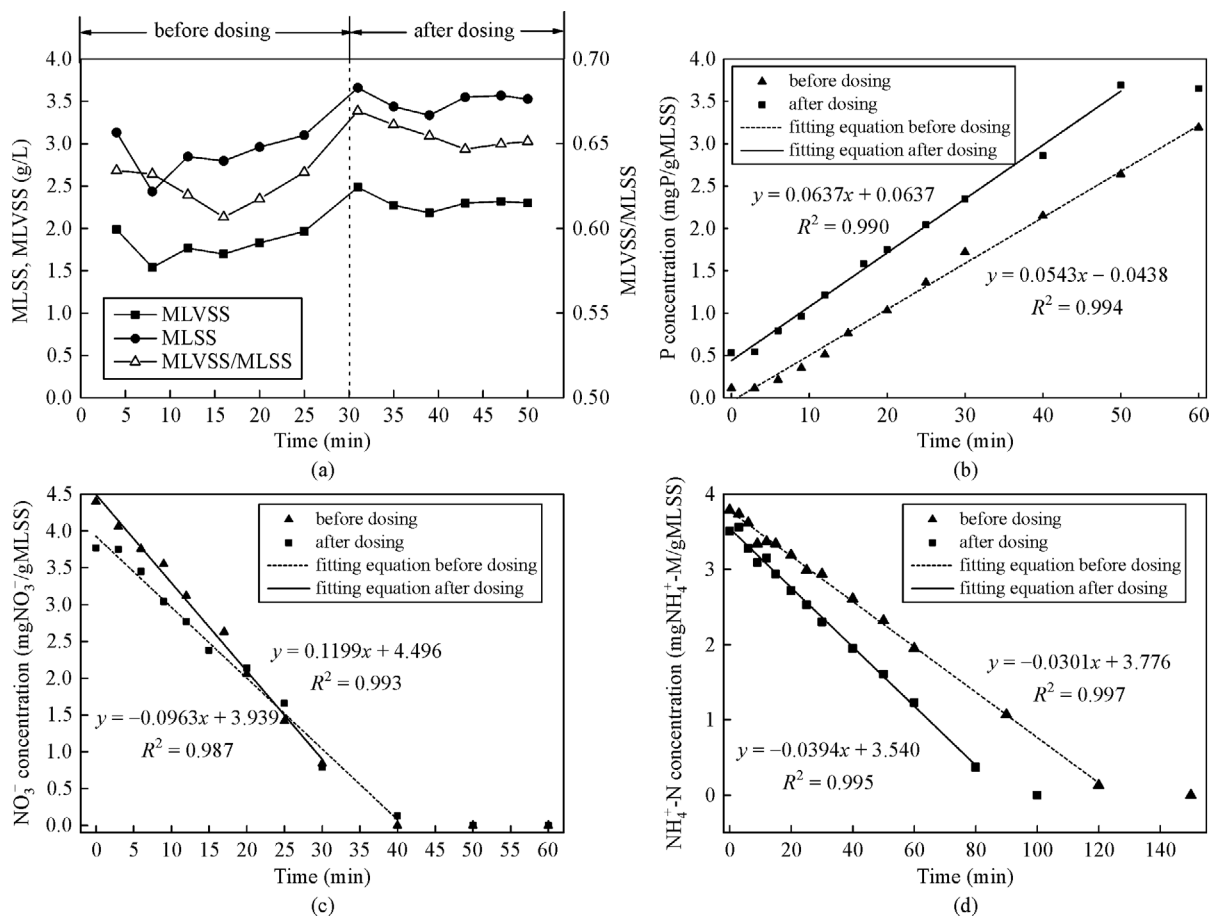
mainly result from chemical precipitation of sparingly soluble phosphates with the addition of aluminum sulfate. Thus, it has been proved that the feasibility of enhancing phosphorus removal with aluminum sulfate addition.

### 3.2 Analysis of sludge characteristics

#### 3.2.1 MLSS and MLVSS

The variation of MLSS and MLVSS concentrations in aerobic reactor (Fig. 3a) was observed in order to investigate the effects of aluminum sulfate addition on the microbial biomass of sludge. Usually, MLVSS/MLSS ratio was also used to characterize the microbial activity in activated sludge macroscopically and the content of the inorganic matters.

Compared with phase 1, aluminum sulfate addition (in phase 2) had promoted the increase of MLSS from 1.5–2.0 g/L to 2.2–2.5 g/L (average 28.56% increase) and MLVSS from 2.4–3.1 g/L to 3.3–3.7 g/L (average 22.04% increase), respectively. These improvements may be attributed to the increased adsorption of organic matters in colloidal form by Al hydroxides complexes formed in



**Fig. 3** Sludge characteristics: Changes of MLSS, MLVSS and ratio of MLVSS/MLSS in aerobic reactor (a), phosphorus release rate (b), denitrification rate (c) and nitrification rate (d) in different reactors before/after the dose of aluminum sulfate.

the mixed liquor, transferring the colloidal particles from the liquid to the sludge. Besides, MLVSS/MLSS ratio was also improved from 0.61–0.63 to 0.65–0.67. In other words, the slight improvement implied that the microbial biomass and microbial activity were improved slightly and there were no adverse effects on the microbial biomass and microbial activity when aluminum sulfate was dosed directly into the reactors during the long-term operation, Xu et al. (2010) also found that the coagulants addition had no adverse effect on sludge activity.

### 3.2.2 Activity of sludge

Further research was conducted regarding phosphorus release rate, denitrification rate and nitrification rate to investigate the influences of aluminum sulfate addition on the activity of sludge. The results were shown in Fig. 3b–3d.

After linear fitting, it was obvious that phosphorus release rate and maximum amount of phosphorus release increased from 0.054 mgP/gMLSS and 9.64 mg/L to 0.064 mgP/gMLSS and 11.42 mg/L, respectively after the addition of aluminum sulfate. Correspondingly, the average ratio of P-release to COD-uptake also increased from 0.036 to 0.042. Hence, the results obtained demonstrated that the addition of aluminum sulfate increased the activity of PAOs and phosphorus release rate effectively.

In anoxic reactor, the consumption of  $\text{NO}_3^-$ -N was basically linear with time passing by. Before dosing aluminum sulfate, the concentration of  $\text{NO}_3^-$ -N was about 3.77 mg $\text{NO}_3^-$ /gMLSS at the beginning and then decreased to 0.13 mg $\text{NO}_3^-$ /gMLSS at 40 min, the denitrification rate was 0.096. However, it increased slightly to 0.120 after the addition of aluminum sulfate, the result meant the denitrification rate and denitrifying bacteria activity was improved, in line with the slight improvement of TN removal efficiency (2.13%–3.65%) analyzed in Section 3.1. Wang et al. (2014a) also found the enhancement on denitrification by dosing  $\text{Fe}^{2+}$  in a modified BAF process and there was no adverse impact in removing other nutrients by dosing  $\text{Fe}^{2+}$  salt. Similarly, a linear positive relationship was also found between the consumption of  $\text{NH}_4^+$  and the pass of time. As shown in Fig. 4d, nitrification rate has increased slightly from 0.030 to 0.039 with the addition of aluminum sulfate.

In conclusion, the sludge activity was not inhibited, but improved slightly, therefore no negative effect on nutrients removal efficiency with the addition of aluminum sulfate was found. The results were similar with the findings reported by Xu et al. (2010). Wu (2016) also reported that addition of  $\text{Fe}^{2+}$  lower than 0.07 mmol/L could enhance the activity of microorganisms. Previous studies (Wvon, 1991) have suggested that the addition of aluminum sulfate could promote the dehydrogenase activity (DHA) and the degradation rate of organic matters effectively, which also

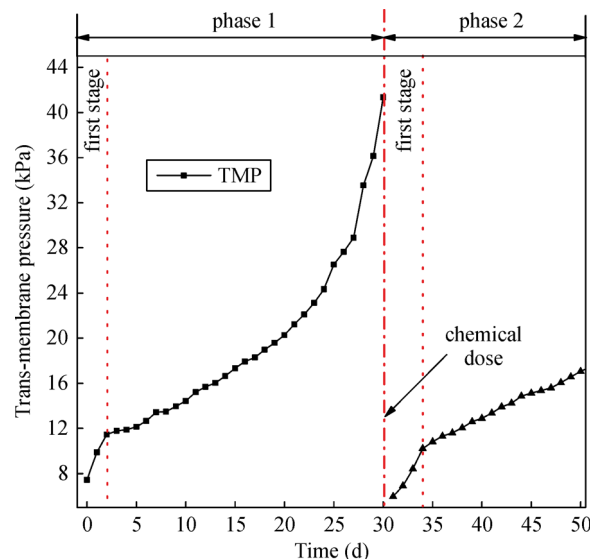


Fig. 4 Effect of aluminum sulfate dosing on the changes of TMP.

meant the sludge activity was improved effectively, providing the theoretical support for the practical application. Seen from the engineering view, the enhancement on the sludge activity signed an advantage of dosing aluminum sulfate over no aluminum sulfate dose in the proposed synergistic nitrification and chemical precipitation process, and hence the volume of the reactor could be reduced.

## 3.3 Membrane fouling

### 3.3.1 Variation curves of TMP

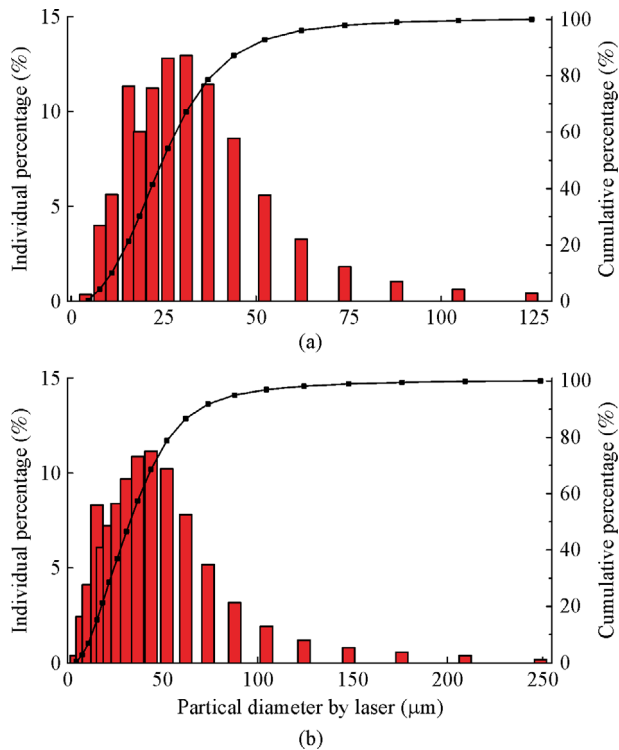
The effects of dosing aluminum sulfate on TMP were assessed with operating time by comparing to the cases of no additional chemical dose, and the results were illustrated in Fig. 4. Since the MBR was operated at constant flux (16 L/m<sup>2</sup>/h), the development of fouling was indicated according to the TMP increase. Obviously, the trend of TMP showed a rapid increase at the initial stage (first stage) with TMP increase rate was 1.06 kPa/d after the addition of aluminum sulfate, much lower than 1.99 kPa/d before the addition. Similarly, the increasing trend of TMP was also alleviated during the entire experimental phase. After the addition of aluminum sulfate, a slight decrease of TMP increase rate from 1.13 kPa/d to 0.57 kPa/d implied that the goal of mitigating the membrane fouling was achieved.

The surface negative charges of sludge particles changed to almost neutral when cationic flocculations ( $\text{Al}^{3+}$ ) were added into mixed liquid, which was conducive to producing larger particles. Therefore, the decrease of TMP increase rate might be owing to the enlarged sludge particles by the perfect adsorption effect of aluminum

sulfate, leading to a decreasing accumulation of the small sludge particles on the membrane surface. In addition, the aluminum sulfate addition could also improve sludge settle ability and structure in activated sludge, which is beneficial for membrane fouling control (Fan et al., 2007).

### 3.3.2 Sludge particle sizes

The distributions of sludge particle sizes before and after the addition of aluminum sulfate were evaluated, shown in Fig. 5.



**Fig. 5** Distribution of sludge particle sizes before (a) and after (b) the dose of aluminum sulfate.

Before the addition of aluminum sulfate, the sludge particle sizes in the aerobic reactor were mainly in the range of 3.3–124.5  $\mu\text{m}$  and the average particle size was 24.7  $\mu\text{m}$ . After dosing aluminum sulfate, an improvement in the sludge particle sizes was observed. The sludge particle sizes were becoming larger and varying from 4.6 to

248.9  $\mu\text{m}$  with the average particle size of 32.9  $\mu\text{m}$ . Moreover, the cumulative percentage of particle sizes lower than 10  $\mu\text{m}$  and 20  $\mu\text{m}$  with the addition of aluminum sulfate were 6.9% and 28.5%, respectively, much lower than that of no addition, which were 10% and 41.5% correspondingly.

The characteristics of particles in the aerobic reactor have a significant influence on the composition of the sludge layer that forms on the membrane surface and resulting in membrane fouling (Liu et al., 2016). The small sludge particles could cause the relatively higher density of the cake layer through blocking the inner pores and a higher hydraulic resistance, consequently, they were reported as the main factor resulting in the membrane fouling (Song et al., 2008). However, aluminum sulfate was an effective flocculant for removing the supernatant organics and producing flocs with larger size by charge neutrality and bridging (Wu et al., 2006), resulting in the decreased accumulation of the small sludge particles on membrane surface (Li et al., 2017b), which was favorable for the membrane fouling control. Therefore, the results demonstrated that the membrane fouling was controlled effectively, in accordance with the conclusion in Section 3.3.1. However, Xu et al. (2018) found that higher viability and abundance of PAOs in small-size sludge flocs could lead to more effective removal of TP when compared with those in large-size sludge flocs. In our study, adding aluminum sulfate could lead to the increase of sludge particle sizes, as well as TP removal efficiency. The performance of phosphorus removal with different particle sizes has not been studied in our study. Thus, further research on particle sizes is still needed in the future.

### 3.3.3 Analysis of EPS content in mixed liquid

The EPS was well known as the major fouling component of membrane fouling (Wang et al., 2009), it was widely distributed in activated sludge. In addition, PN and PS are the main hydrophilic substances in EPS and the sum of PN and PS was considered as the total EPS in this study. The content of EPS with and without the addition of aluminum sulfate in three reactors was shown in Table 2.

According to the Table 2, it was found that there was no obvious difference of EPS concentrations in three reactors (anaerobic, anoxic and aerobic) and they were in the range

**Table 2** The content of EPS before and after the addition of aluminum sulfate (mg/gMLSS)

Parameter	Anaerobic reactor		Anoxic reactor		Aerobic reactor		
	PN	PS	PN	PS	PN	PS	
Before dosing	Concentration	73.15	8.99	73.67	9.15	71.85	9.30
	Total EPS	82.14		82.82		81.15	
After dosing	Concentration	38.13	10.12	37.33	9.22	35.09	13.42
	Total EPS	48.25		46.55		48.50	



of 81.15–82.82 mg/gMLSS before aluminum sulfate dosing. However, it was evident that PN was the dominant component in EPS, accounting for 88.54%–89.06%. These results were somewhat in line with other studies (Ramesh et al., 2007; Satyawali and Balakrishnan, 2009; Tang et al., 2010). In terms of composition, TB-EPS was the majority of total EPS while LB-EPS was almost seldom detected, hence TB-EPS showed the outstanding potential for membrane fouling. The findings also corresponded well to previous study (Hu et al., 2014). However, Wang et al. (2009) reported that TB-EPS had no obvious relations to membrane fouling rate while LB-EPS demonstrated positive correlations. Moreover, after the addition of aluminum sulfate, it should be noted that PN was also the major components of EPS with the decreased proportion of 72.34%–82.39%, and as a whole EPS concentration decreased to 46.55–48.50 mg/gMLSS in three reactors.

It had to be pointed out that EPS showed stronger significant correlations with membrane fouling and was considered as the main substance leading to the membrane fouling (Huang and Wu, 2008), which was mainly due to the fact that the EPS were consisted of a matrix of microbial polymers, hence high EPS concentrations had been related to high fouling rates (Azami et al., 2011). In addition, sludge with higher PN/PS ratio in EPS resulted in higher stickiness, stimulating the cake layer formation and increasing membrane fouling in the submerged membrane bioreactors (Yao et al., 2010). In this study, the addition of aluminum sulfate has reduced the concentration of EPS and PN effectively, as well as the decreased PN/PS ratio from 8 to 3. These results suggested that the decrease of

EPS, mainly the decrease of PN and PN/PS ratio was the real reason for the mitigation of membrane fouling.

### 3.3.4 The concentration of EPS on membrane surface

EPS on the membrane surface was formed by the accumulation of activated sludge, it could reflect the membrane fouling rate in the long term operation. The concentration was measured after the membrane fouling cycle was finished and results were shown in Fig. 6.

Before the addition of aluminum sulfate, the total EPS concentration on the membrane surface was 540.06  $\mu\text{g}/\text{m}^2$ , PN and PS were 403.98  $\mu\text{g}/\text{m}^2$  (74.8%) and 136.08  $\mu\text{g}/\text{m}^2$  (25.2%), respectively. The ratio of PN/PS was around 2.97, which meant PN was the major substance leading to the membrane fouling. In terms of composition, EPS in the cake layer was 359.03  $\mu\text{g}/\text{m}^2$  (66.5%), which was about 1.99 times of that in the gel layer (181.03  $\mu\text{g}/\text{m}^2$ , 33.5%). Therefore, it was apparent that the cake layer was the main contributor to the membrane resistance.

After the addition of aluminum sulfate, PN concentration decreased to 278.4  $\mu\text{g}/\text{m}^2$ , while PS concentration had a slight increase to 173.5  $\mu\text{g}/\text{m}^2$ , contributing to the final decrease of EPS to 451.91  $\mu\text{g}/\text{m}^2$ . The findings were in good agreement with the decrease of EPS concentration in the mixed liquid reported in Section 3.3.3. With the decrease of PN and EPS, which were considered as the main factors contributing to membrane fouling, membrane fouling was controlled effectively. Moreover, EPS in cake layer and gel layer both decreased to 284.4  $\mu\text{g}/\text{m}^2$  (62.9%) and 167.6  $\mu\text{g}/\text{m}^2$  (37.1%), respectively. No matter viewing

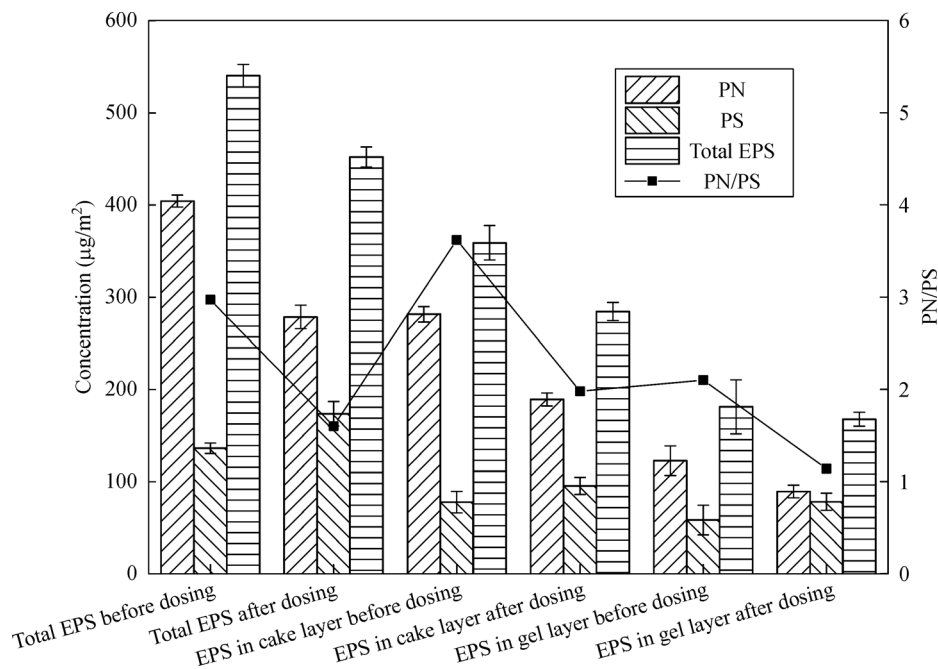


Fig. 6 EPS concentration and distribution on membrane surface before and after the dose of aluminum sulfate.

from the cake layer, gel layer or total EPS, it was demonstrated that the addition of aluminum sulfate could promote the decrease of PN concentration and PN/PS ratio, contributing to the effective mitigation of membrane fouling.

## 4 Conclusions

With the addition of aluminum sulfate, UCT-MBR exhibited a satisfactory removal performance of COD,  $\text{NH}_4^+\text{-N}$ , TN, and TP. It could be concluded that a slight amount addition of aluminum sulfate had improved sludge activity slightly in the long term operation. In addition, the addition of aluminum sulfate could reduce the TMP rising rate effectively. Firstly, the sludge particle sizes were improved obviously while proportions of small particle sizes were decreased. Secondly, EPS concentration both in mixed sludge liquid and on membrane surface was decreased, especially the decrease of PN/PS ratio, which was the real reason for the mitigated membrane fouling.

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## References

- APHA (2012). Standard Methods for the examination of Water and Wastewater 22nd America Public Health Association, Washington DC, USA
- Arrojo B, Mosquera-Corra A, Garrido J M, Méndez R, Ficara E, Malpei F (2005). A membrane coupled to a sequencing batch reactor for water reuse and removal of coliform bacteria. *Desalination*, 179(1-3): 109–116
- Azami H, Sarrafzadeh M H, Mehrnia M R (2011). Fouling in membrane bioreactors with various concentrations of dead cells. *Desalination*, 278(1-3): 373–380
- Buisson H, Cote P, Praderie M, Paillard H (1998). The use of immersed membranes for upgrading wastewater treatment plants. *Water Science and Technology*, 37(9): 89–95
- Caravelli A H, Gregorio C D, Zaritzky N E (2012). Effect of operating conditions on the chemical phosphorus removal using ferric chloride by evaluating orthophosphate precipitation and sedimentation of formed precipitates in batch and continuous systems. *Chemical Engineering Journal*, 209: 469–477
- Cosenza A, Bella G D, Mannina G, Torregrossa M, Viviani G (2013). Biological nutrient removal and fouling phenomena in a University of Cape Town Membrane Bioreactor treating high nitrogen loads. *Journal of Environmental Engineering*, 139(6): 773–780
- Dalmou M, Rodriguez-Roda I, Ayesa E, Odriozola J, Sancho L, Comas J (2013). Development of a decision tree for the integrated operation of nutrient removal MBRs based on simulation studies and expert knowledge. *Chemical Engineering Journal*, 217: 174–184
- Diez-Montero R, De Florio L, González-Viar M, Herrero M, Tejero I (2016). Performance evaluation of a novel anaerobic-anoxic sludge blanket reactor for biological nutrient removal treating municipal wastewater. *Bioresource Technology*, 209: 195–204
- Drews A, Lee C H, Kraume M (2006). Membrane fouling—A review on the role of EPS. *Desalination*, 200(1-3): 186–188
- Dubois M, Gilles K A, Hamilton J K, Rebers P A, Smith F (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, 28(3): 350–356
- Fan F, Zhou H, Husain H (2007). Use of chemical coagulants to control fouling potential for wastewater membrane bioreactor processes. *Water Environment Research A Research Publication of the Water Environment Federation*, 79: 952–957
- Ferrero G, Monclús H, Buttiglieri G, Comas J, Rodriguez-Roda I (2011). Automatic control system for energy optimization in membrane bioreactors. *Desalination*, 268(1-3): 276–280
- Ge S, Peng Y, Wang S, Guo J, Ma B, Zhang L, Cao X (2010). Enhanced nutrient removal in a modified step feed process treating municipal wastewater with different inflow distribution ratios and nutrient ratios. *Bioresource Technology*, 101(23): 9012–9019
- Hu Y, Wang X C, Tian W R, Chen R (2014). Assessment of fouling potentials of extracellular polymeric sub-stances in a membrane bioreactor using modified fouling index (MFI). *Journal of Water Sustainability*, 4: 237–246
- Huang X, Wu J (2008). Improvement of membrane filterability of the mixed liquor in a membrane bioreactor by ozonation. *Journal of Membrane Science*, 318(1-2): 210–216
- Hussain S, Leeuwen J V, Chow C W K, Aryal R, Beecham S, Duan J, Drikas M (2014). Comparison of the coagulation performance of tetravalent titanium and zirconium salts with alum. *Chemical Engineering Journal*, 254: 635–646
- Leyva-Díaz J C, Muñoz M M, González-López J, Poyatos J M (2016). Anaerobic/anoxic/oxic configuration in hybrid moving bed biofilm reactor-membrane bioreactor for nutrient removal from municipal wastewater. *Ecological Engineering*, 91: 449–458
- Li W, Cai Z Y, Duo Z J, Lu Y F, Gao K X, Abbas G, Zhang M, Zheng P (2017a). Heterotrophic ammonia and nitrate bio-removal over nitrite (Hanbon): Performance and microflora. *Chemosphere*, 182: 532–538
- Li X, Liu Y, Liu F, Liu A, Feng Q (2017b). Comparison of ferric chloride and aluminum sulfate on phosphorus removal and membrane fouling in MBR treating BAF effluent of municipal wastewater. *Journal of Water Reuse and Desalination*, 7(4): 442–448
- Liu T, Lian Y, Graham N, Yu W, Rooney D, Sun K (2016). Application of polyacrylamide flocculation with and without alum coagulation for mitigating ultrafiltration membrane fouling: Role of floc structure and bacterial activity. *Chemical Engineering Journal*, 307: 41–48
- Liu Y, Shi H, Li W, Hou Y, He M (2011). Inhibition of chemical dose in biological phosphorus and nitrogen removal in simultaneous chemical precipitation for phosphorus removal. *Bioresource Technology*, 102(5): 4008–4012
- Lowry O H, Rosebrough N J, Farr A L, Randall R J (1951). Protein measurement with the Folin phenol reagent. *Journal of Biological Chemistry*, 193(1): 265–275
- Mannina G, Capodici M, Cosenza A, Trapani D D (2016). Carbon and nutrient biological removal in a University of Cape Town Membrane Bioreactor: Analysis of a pilot plant operated under two different C/N ratios. *Chemical Engineering Journal*, 296: 289–299

- Monclús H, Sipma J, Ferrero G, Comas J, Rodríguezroda I (2010). Optimization of biological nutrient removal in a pilot plant UCT-MBR treating municipal wastewater during start-up. *Desalination*, 250(2): 592–597
- Morgan J W, Forster C F, Evison L (1990). A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges. *Water Research*, 24(6): 743–750
- Rajesh Banu J, Uan D K, Yeom I T, Nair J (2009). Nutrient removal in an A<sup>2</sup>O-MBR reactor with sludge reduction. *Bioresource Technology*, 100(16): 3820–3824
- Ramesh A, Lee D J, Lai J Y (2007). Membrane biofouling by extracellular polymeric substances or soluble microbial products from membrane bioreactor sludge. *Applied Microbiology and Biotechnology*, 74(3): 699–707
- Satyawali Y, Balakrishnan M (2009). Effect of PAC addition on sludge properties in an MBR treating high strength wastewater. *Water Research*, 43(6): 1577–1588
- Song K G, Kim Y, Ahn K H (2008). Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor. *Desalination*, 221(1-3): 467–474
- Tang S, Wang Z, Wu Z, Zhou Q (2010). Role of dissolved organic matters (DOM) in membrane fouling of membrane bioreactors for municipal wastewater treatment. *Journal of Hazardous Materials*, 178 (1-3): 377–384
- Trapani D D, Capodici M, Cosenza A, Bella G D, Mannina G (2011). Evaluation of biomass activity and wastewater characterization in a UCT-MBR pilot plant by means of respirometric techniques. *Desalination*, 269(1-3): 190–197
- Wang H, Dong W, Li T, Liu T (2014a). Enhanced synergistic denitrification and chemical precipitation in a modified BAF process by using Fe<sup>2+</sup>. *Bioresource Technology*, 151: 258–264
- Wang Z, Wu Z, Tang S (2009). Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor. *Water Research*, 43(9): 2504–2512
- Wang Z Z, Jun L I, Gao J H, Jiang C, Ren J Z, Liu B (2014b). Effects of  $\rho(\text{COD})/\rho(\text{TN})$  on performance and membrane fouling in UCT-type Submerged Membrane Bioreactor. *Journal of Beijing University of Technology*, 40: 619–626 (in Chinese)
- Wu C, Zhou Y, Wang Y, Guo M (2016). Innovative combination of Fe<sup>2+</sup>-BAF and ozonation for enhancing phosphorus and organic micropollutants removal treating petrochemical secondary effluent. *Journal of Hazardous Materials*, 323(Pt B): 654–662
- Wu J, Chen F, Huang X, Geng W, Wen X (2006). Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor. *Desalination*, 197(1-3): 124–136
- Wu M, Jiang X, Lv Y, Zhou J, Yuan L, Jia Y, Wang Y (2015). Long-term effect of Cu (II) on the phosphorous removal performance in enhanced biological phosphorous removal systems. *Chemical Engineering Journal*, 281: 164–173
- Wvon M F S (1991). An improved and accurate method for determining the dehydrogenase activity of soils with iodinitrotetrazolium chloride. *Biology and Fertility of Soils*, 11(3): 216–220
- Xu G L, Fan Y B, Yan Y, Yang W J, Yuan D D, Wu G X (2010). Membrane fouling control in MBR achieved by dosing coagulants. *Fresenius Environmental Bulletin*, 19: 1591–1598
- Xu R, Zhou Z, Meng F (2018). The mechanical scouring of bio-carriers improves phosphorous removal and mediates functional microbiome in membrane bioreactors. *Environmental Science. Water Research & Technology*, 4(2): 241–252
- Yan M, Wang D, Ni J, Qu J, Chow C W K, Liu H (2008). Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics. *Water Research*, 42 (13): 3361–3370
- Yao M, Zhang K, Li C (2010). Characterization of protein-polysaccharide ratios on membrane fouling. *Desalination*, 259(1-3): 11–16
- Zhang H, Wang X, Xiao J, Yang F, Zhang J (2009). Enhanced biological nutrient removal using MUCT-MBR system. *Bioresource Technology*, 100(3): 1048–1054