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Hyperhaline Municipal Wastewater Treatment of a Processing Zone through Pilot-Scale A/O MBR, Part II: Nitrogen and Phosphorous Removal

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Abstract

An integrated anoxic/aerobic membrane bio-reactor (A/O MBR) was designed to treat hyperhaline municipal wastewater from a processing zone of Tianjin, China. The removal performance of the system to ammonia nitrogen (NH₃-N), total nitrogen (TN) and total phosphorus (TP) was investigated, and the contribution of membrane and microbes to pollutant removal was evaluated and discussed. The adaptability of the system to a high-loading nitrogen impact was also studied. Experimental results show that the removal efficiencies of NH₃-N and TN of the A/O MBR system were approximately 95% and 50%-70%, respectively, during the four-month investigation period. Very good removal is mainly contributed to the microbial degradation. Membrane interception to nitrogenous matters is insignificant. The contribution of membrane interception is to keep nitrifying bacteria (having a long generation cycle) in the reactor, thus strengthening nitrogen removal. Total phosphorus removal of the A/O MBR system is as high as 60%-80%. Such high removal of TP is unexpected since there was only once sludge discharge from the system during four-month operation period, that is traditional biological phosphorus removal cannot be achieved. Nontraditional biological functions (including sludge particle adsorption to phosphoric matters and microbial assimilation) and membrane interception to insoluble phosphoric matters (mainly organic phosphorus and a small quantity of phosphorus complex) are the main mechanisms of TP removal of the A/O MBR system. Moreover, biological function is predominant, therefore sludge concentration in the reactor is increased and TP removal is enhanced.

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1. Introduction

Compared with traditional wastewater treatment processes, membrane bio-reactor (MBR) has many advantages, such as good effluent quality, small occupy area of equipment, high sludge concentration, low sludge production, and available automatic control, etc. Compared with MBR, the anoxic/aerobic membrane bio-reactor (A/O MBR) with prepositive anoxic zone has a new breakthrough in nitrogen removal. The total nitrogen removal efficiency increased from approximately 47% to 70% [1-3]. Therefore, A/O MBR has broad prospects in municipal and industrial wastewater treatment [2-5].

MBR process has many problems in practical application, such as membrane pollution and high operation expense, etc. To solve the problems, present researches on MBR are mainly focused on membrane pollution prevention [6-7], sludge quantity reduction [8], development of new membrane filtration technology [9-10] and improvement of nitrogen and phosphorus removal [11-12], etc.

For a long time, phosphorus removal ability of A/O MBR is controversial. The reactor rarely discharges sludge during operation period, thus theoretically the ability of phosphorus removal was limit (only by biological assimilation). However, many experimental results [13-15] showed that phosphorus removal efficiency of MBR was mainly between 40%-70%.

The objectives of the study are to investigate the performance of the designed A/O MBR system for hyperhaline municipal sewage treatment to recycled water quality standard in a processing zone of Tianjin, China (the sewage is consisted of around 80% industrial wastewater and 20% sewage, with approximately 1000 mg/L salinity), to study characteristics of mixture liquor and to evaluate the efficiencies and mechanisms of COD_{Cr}, total nitrogen, ammonia nitrogen and total phosphorus removal of the A/O MBR system. Because of the space limit, only removal performances of nitrogen and phosphorous are presented in this article. The characteristics of mixture liquor and the removal performance of COD_{Cr} are presented in another article.

2. Material and method

2.1. Influent and effluent water quality

The raw wastewater was from municipal sewer system of a processing zone in Tianjin, China. It consists of approximately 80% industrial wastewater and 20% domestic wastewater. Raw wastewater quality fluctuated in a relatively large range during investigation period, as shown in Table 1.

Table 1. Index of raw wastewater quality

Index	COD _{Cr} (mg/L)	Total nitrogen (mg/L)	Ammonia nitrogen (mg/L)	Nitrate nitrogen (mg/L)	Total phosphorus (mg/L)	Salinity (mg/L)	pH
Range	42.5-615.1	11.1-41.4	1.7-36.4	0-15.8	1.6-7.4	882-1310	6.88-9.02
Average value	189.4	27.6	16.4	1.36	4.7	1024.6	7.83

According to Tianjin local standard of Integrated Wastewater Discharge Standard (DB12/356-2008) and national standard of Discharge Standards of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002), sewage treatment plant of industrial park in Tianjin carry out the level I-B standard of GB18918-2002. However, recycled water is required to achieve the level I-A standard of GB18918-2002. The main usage of the recycled water in the processing zone are to flush street, water flowers and plants, and supply water to rivers in processing zone (used in unamused landscape environment), which have no

requirement or no more than 1.0 mg/L (the same as the level I-B of GB18918-2002) for phosphorus standard. Therefore, in the recycled water plant of the processing zone, Total Phosphorus carries out the level I-B standard of GB18918-2002 and all other pollutant indices carry out the level I-A standard of GB18918-2002.

2.2 Experimental equipment and process

The experimental equipments and technical process are shown in Fig. 1.

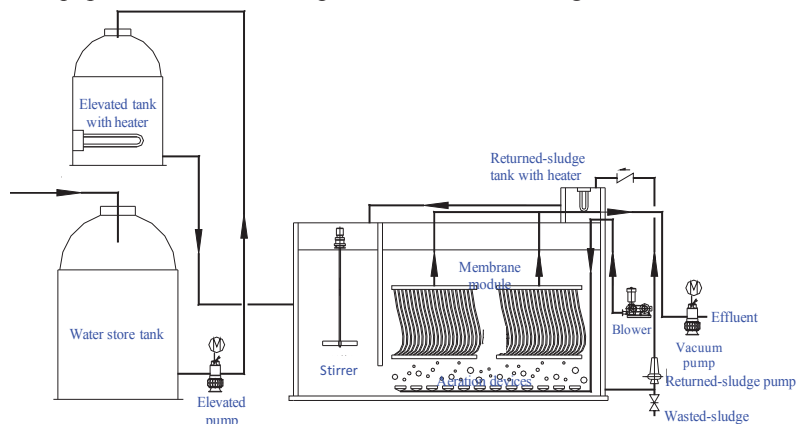


Fig. 1 Experimental equipments and technical process

Raw wastewater of the system was pumped to a water store tank after going through the bar screen and grit chamber of a wastewater treatment plant, and was further pumped to an elevated tank with heater to keep the influent water more than 10°C before flowing into A/O MBR system. The influent water of anoxic zone (briefly A zone, be equipped with stirrer) of A/O MBR was mixed with back flow nitrification fluid from aerobic zone (briefly O zone) to denitrify before flowing to O zone (be equipped with membrane module and aeration devices). The effluent was drawn out through the membrane module intermittently by a vacuum pump. Sludge discharging pipe in the bottom of the A zone was designed to connect with returned-sludge pump and wasted-sludge valve. When the temperature of returned sludge was below 10°C, the heater in the return-sludge tank was started up.

Experimental devices of the A/O MBR system operated automatically through PLC electrical apparatus control system. The integrated A/O MBR system was made from stainless steel 304 with a thickness of 2mm. The total available volume of the bio-reactor was 0.54m³ with 1.5m in length, 0.6m in width, and 0.6m in available water depth (0.9m in total height). The integrated A/O bio-reactor was divided into anoxic zone with available volume of 0.13m³ and aerobic zone with available volume of 0.41m³ by clapboard. Two hollow fibre microfiltration membrane modules were made of Polyvinylidene fluoride (PVDF) with a pore size of 0.22μm and a total membrane area of 9m². The dimension of each membrane module was 0.30m in length, 0.24m in width and 0.25m in height. The designed maximum trans-membrane pressure was 0.04MPa and the designed membrane flux was 10-15L/(m²·h). The treatment capacity of the A/O MBR system was 40L/h.

2.3. Analytical Methods

The analysis of each index referred to Monitoring and Analysis Method of Water and Wastewater (Editor 4) [16]. Ammonia Nitrogen was detected by Nessler's Reagent Spectrophotometer method (GB7479-87), Total Nitrogen was detected by Alkaline Potassium Persulfate Digestion - Ultraviolet Spectrophotometry method (GB11894-89), Total Phosphorus was detected by Ammonium Molybdate Spectrophotometry method (GB11893-89).

3. Result and discussion

The inoculated sludge of the bio-reactor came from the returned sludge of aerobic zone of the third MBR in the recycled wastewater treatment plant of the Tianjin processing zone, China. After more than one-month cultivation, domestication and stabilization of the A/O MBR system, the experimental investigation started from August 24th (the first day of the investigation operation) to December 24th, i.e. total 123 days. From November 3rd (the 72nd day) to 6th (the 75th day), 60g urea (equivalent to 28mg/L nitrogen, calculated by N) was dosed to raw wastewater each day to investigate the adaptability of the system to a high-loading nitrogen impact.

3.1. Removal performance and mechanism of ammonia nitrogen (NH_3-N)

The NH_3-N removal efficiency, concentrations of influent, supernatant of aerobic zone and effluent of the A/O MBR system are shown in Fig. 2.

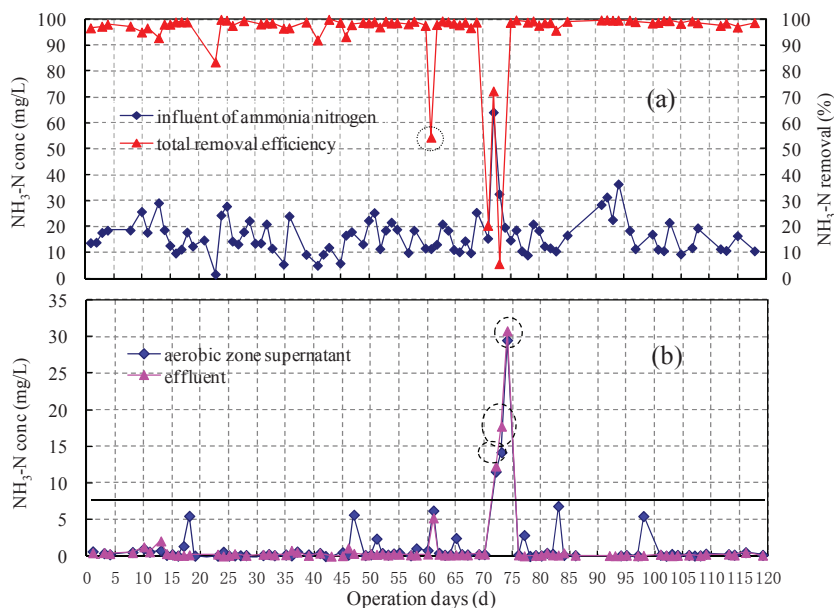


Fig. 2 Removal performance of ammonia nitrogen of A/O MBR

Figure 2 shows that the A/O MBR system has very nice removal performance to NH_3-N . The NH_3-N concentration of effluent was mostly below 1mg/L and all below 5 mg/L (the level I-A standard of GB18918-2002, see Fig. 2b) under an influent fluctuating in a range of 1.7 to 36.4 mg/L (see Fig. 2a) during the normal investigation period. The removal efficiency of NH_3-N was mostly more than 95% (see Fig. 2a). However, the NH_3-N concentration of effluent increased suddenly to around 5 mg/L or

$\text{NH}_3\text{-N}$ removal efficiency dropped suddenly to approximately 54% in the 61st day. The most possible reason was believed to be that COD_{Cr} concentration of influent increased suddenly to 615mg/L in this day (it mostly fluctuated in a range of 100-400 mg/L). Such high and sudden increase of COD_{Cr} concentration restrained the bioactivity of autotrophic nitrifying bacteria and nitrification process.

During the period of a high-loading nitrogen impact test (the 72nd to 75th day), rapid increase of influent $\text{NH}_3\text{-N}$ concentration resulted in an extremely high $\text{NH}_3\text{-N}$ concentration of aerobic zone supernatant and also an extremely high $\text{NH}_3\text{-N}$ concentration of effluent. The removal efficiency of $\text{NH}_3\text{-N}$ decreased rapidly from more than 95% to less than 30% during the impact-test period (see Fig. 2a). Moreover, $\text{NH}_3\text{-N}$ concentration of effluent was higher than that of aerobic zone supernatant (see Fig. 2b, the data points surrounded by “O”). This indicates that the adaptability of the system to a high-loading nitrogen impact is not good. The most possible reason is that when $\text{NH}_3\text{-N}$ concentration rose suddenly, a portion of $\text{NH}_3\text{-N}$ cannot be biodegraded in the retention time and was adsorbed to the surface of activated sludge. This portion of $\text{NH}_3\text{-N}$ may be released during drawing effluent through vacuum pump. However, the removal efficiency of $\text{NH}_3\text{-N}$ rose back to more than 95% or effluent $\text{NH}_3\text{-N}$ concentration decreased to approximately 0.5 mg/L in the day of impact-test finish (the 76th day).

Figure 2b shows that $\text{NH}_3\text{-N}$ concentration of aerobic zone supernatant and effluent was very low and their difference was little. This indicates biodegradation is the predominant mechanism of ammonia nitrogen removal in the A/O MBR system. The contribution of membrane is to keep nitrifying bacteria (having a long generation cycle) in the bioreactor, thus to strengthen nitrify removal performance. Membrane interception of $\text{NH}_3\text{-N}$ was insignificant, even under the unsatisfied biodegradation or very high $\text{NH}_3\text{-N}$ concentration of the aerobic zone supernatant during the impact-test period. This is because the form of ammonia nitrogen are mainly in ion form of NH_4^+ and molecule form of NH_3 in water, which can penetrate through the membrane pores and flow out the system with effluent.

3.2. Removal performance and mechanism of total nitrogen (TN)

The TN concentrations and removal efficiencies of the A/O MBR system in the investigation period are shown in Fig. 3a and 3b, respectively.

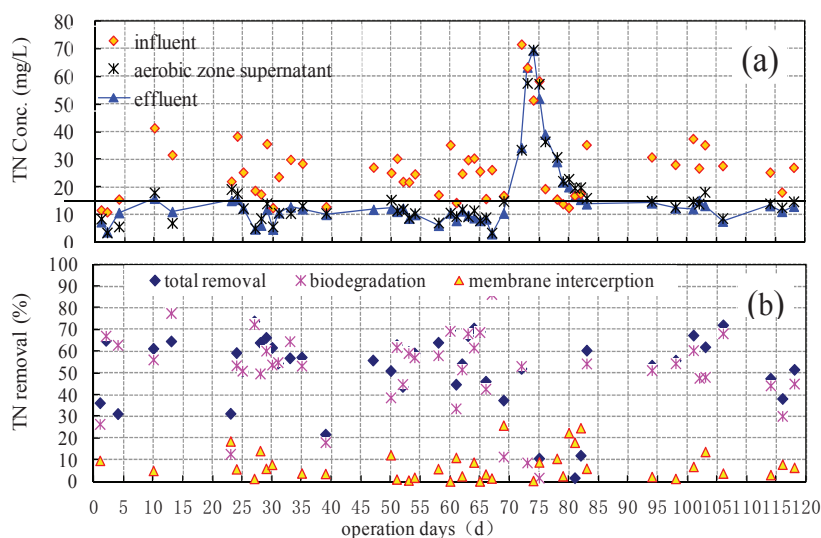


Fig. 3 Removal performance of total nitrogen of A/O MBR

Figure 3 shows that the A/O MBR system has a very nice removal performance to total nitrogen. The TN concentration of effluent was all below 15 mg/L (the level I-A standard of GB18918-2002) under an influent fluctuating in a range of 11.8 to 41.4 mg/L during the normal investigation period (see Fig. 3a). The removal efficiency of TN was mostly lying between 50%-70% (see Fig. 3b). However, in the 1st, 4th, 23rd, 39th, 69th and 116th days, TN removal efficiencies were below 40%. TN concentrations of influent in the aforementioned days were lower than 20 mg/L is believed to be the main reason of low TN removal efficiencies.

During the period of a high-loading nitrogen impact test (the 72nd to 75th day), rapid increase of influent TN concentration (50 to 70 mg/L) resulted in an extremely high TN concentration of aerobic zone supernatant (33.5 to 69.6 mg/L) and also an extremely high TN concentration of effluent (39.1 to 69.4 mg/L) (see Fig. 3a). The removal efficiency of TN decreased rapidly from 50%-70% to less than 15% during the impact-test period (see Fig. 3b). The removal efficiency of TN rose back to more than 50% or effluent TN concentration decreased to below 15 mg/L after 7 days of impact-test finish (the 83rd day). Moreover, TN concentration of effluent was equal to or even higher than that of aerobic zone supernatant during the impact-test period and the followed days (see Fig. 3a). This indicates that the adaptability of the system to a high-loading nitrogen impact is not good. Similar phenomena are found in NH₃-N removal performance and the reasons are similar.

Figure 3a shows that the difference of TN concentration between aerobic zone supernatant and effluent was little. This indicates biodegradation is the predominant mechanism of total nitrogen removal in the A/O MBR system. Membrane interception of TN was insignificant, even under the unsatisfied biodegradation or very high TN concentration of the aerobic zone supernatant during the impact-test period. Similar phenomena were found in NH₃-N removal performance. The reasons and mechanisms are also similar.

3.3. Removal performance and mechanism of total phosphorus (TP)

The TP concentrations and removal efficiencies of the A/O MBR system in the 53rd to 61st investigation days (October 15th to 23rd) are shown in Fig. 4a and 4b, respectively.

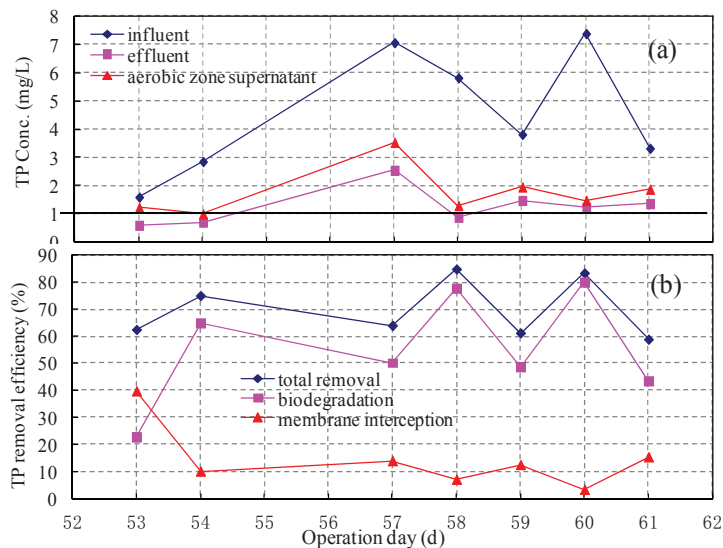


Fig. 4 Removal performance of total phosphorus of A/O MBR

Figure 4 shows that the A/O MBR system has a very nice removal performance to total phosphorous. The TP concentration of effluent was fluctuated around 1mg/L (the level I-B standard of GB18918-2002) under an influent in a range of 1.6 to 7.4 mg/L during the investigation days (see Fig. 4a). The removal efficiency of TP was between 60%-80% (see Fig. 4b), much better than expected since no sludge was wasted from the A/O MBR system in the first two-month operation period and the traditional biological TP removal through sludge wasting cannot be achieved. Adsorption of sludge particles and other glutinous matters as EPS to phosphorous compounds as well as microbial assimilation are the main function to TP removal. Therefore, increase of activated sludge concentration is effective to enhance TP removal. The removal efficiency of TP was affected slightly by influent TP concentration (in a range of 1.6 to 7.4 mg/L) under more than 5000 mg/L MLSS during the investigation days.

Figure 4b shows that the trend of TP removal efficiency by biological function was similar to that of total removal efficiency. The difference of TP concentration between aerobic zone supernatant and effluent was not significant. This indicates biological functions (sludge adsorption and microbial assimilation) are the predominant mechanism of TP removal in the A/O MBR system. The contribution of membrane to TP removal is to keep activated sludge (adsorbed/absorbed large phosphorus) in the bioreactor and to intercept insoluble phosphorous matters (mainly organic phosphorus and a small portion of phosphorus complex). The contribution of membrane interception cannot be neglected under an unsatisfied biological functions and a high portion of particulate phosphorus in influent.

4. Conclusion

The A/O MBR system had a very nice removal performance to $\text{NH}_3\text{-N}$ and TN. The effluent quality was stable and below their corresponding Level I-A standard of GB18918-2002 (5mg/L for $\text{NH}_3\text{-N}$ and 15mg/L for TN) under influent $\text{NH}_3\text{-N}$ concentration in a range of 1.7-36.4 mg/L and TN concentration in a range of 11.8-41.4 mg/L. Biodegradation is the predominant mechanism in $\text{NH}_3\text{-N}$ and TN removal. The contribution of membrane is to keep nitrifying bacteria (have a long generation cycle) in the bioreactor and strengthen nitrogen removal performance of activated sludge.

The results of high-loading nitrogen impact test indicate that the adaptability of the system to a high-loading nitrogen impact is not good. The difference between $\text{NH}_3\text{-N}$ and TN removal performance was that the removal performance of $\text{NH}_3\text{-N}$ recovered in the next day of impact-test finish while that of TN recovered after 7 days of impact-test finish.

The A/O MBR system has a very nice removal performance (60%-80% removal) to total phosphorous. The TP concentration of effluent was fluctuated around 1mg/L (the level I-B standard of GB18918-2002) under an influent in a range of 1.6 to 7.4 mg/L during the investigation days. Biological functions (sludge adsorption and microbial assimilation) are the predominant mechanism of TP removal. Increase of activated sludge concentration is effective to enhance TP removal. The contribution of membrane interception cannot be neglected under an unsatisfied biological functions and a high portion of particulate phosphorus in influent.

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