Membrane module assembly enhances the performance of A/O-MBBR in treating mariculture wastewater

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Abstract. The anoxic-aerobic moving bed biofilm reactors (A/O-MBBR) run stably with influent of low C/N ratio and present a promising application in treating mariculture wastewater. However, the nitrogen pollutants removal is still not acceptable and fails to meet the strict effluent standards. Thus, in this study, a membrane module assembly was installed in the sedimentation tank of the A/O-MBBR to improve the water quality of effluent. The results showed that the removal rates of different nitrogen species were highly enhanced by installing the membrane instrument and 98.16% ammonia and 92.61% nitrate were finally removed. which led to significant reduction of total nitrogen pollutants to 0.70 mg/L in the effluent and thus met the requirement of national standard of the mariculture wastewater discharge. This study indicates that the combination of A/O-MBBR and the membrane module assembly is of great strategy for the efficient treatment of mariculture wastewater.

1. Introduction

Mariculture is a rapidly developing global industry. Currently, China has become the leader in the seafood production around the world, accounting for about 71% of the total seafood supply [1]. Mariculture wastewater commonly contains high suspended organic granular and dissolved nutrients due to the redundant bait and fish feces, which easily leads to eutrophication of coastal waterbody [2]. In addition, the high salinity and complex chemicals in wastewater also pose negative effects on the microbial community in nitrogen removal. Under such conditions, the nitrification and denitrification are seriously impacted, resulting in poor water quality of the effluent [3].

Anoxic/aerobic (A/O) process has the advantages of simple flow and high volumetric loading, and is suitable for treating high-salinity wastewater. However, the inoculated sludge is hard to domesticate and the operation cost is usually high [4]. Moving bed biofilm reactor (MBBR) makes the carriers move by aeration and thus promotes the growth of microorganisms. It gains stable operation under low C/N conditions due to large surface of mass transfer and strong anti-impact load capacity. However, the dead zones may be formed in the reactor, thus blocking the complete mixing of carriers and the influent [5, 6]. Application of the membrane module assembly can effectively improve the biomass, prevent sludge bulking, and reduce the amount of residual sludge [7]. However, Membrane-based bioreactors (MBR) are not suitable for treating wastewater of high salinity [8].
Hence, A/O-MBBR combines the advantages of A/O and MBBR, suitable for mariculture wastewater treatment under low C/N conditions. To further improve the water quality in effluent and meet the discharge standards, this study applied a membrane module assembly in the sedimentation tank of the A/O-MBBR. The parameters of wastewater before and after the membrane installation were monitored to reveal the performance of the combined bioreactor.

2. Materials and methods

2.1. Bioreactor
The A/O-MBBR (Figure 1a) is divided into anoxic zone, aerobic zone and sedimentation zone. The anoxic zone is equipped with an agitator, and the aerobic zone is supplied with oxygen by a micro-porous aeration device. In the sedimentation zone, there is a u-shaped hollow fiber ultrafiltration membrane assembly (working principle refers to Figure 1b). The material of the reactor is plexiglass, with an effective volume of 11.88 L. In the anoxic and aerobic zones, 30% of volume is filled with K3 biofilm carriers, with 25mm in diameter and 500m²/m³ in an effective surface area. The anoxic zone is 10cm×10cm×30cm in size. The size of aerobic zone is 10cm×36cm×27cm. And the sedimentation zone is 5 cm×12 cm×14cm in size.

The artificial mariculture wastewater, with the C/N ratio of 12, was prepared according to Table 1. The inoculated sludge in the reactor was taken from the sewage treatment plant of Tuandao in Qingdao, China. The reactor was started following the sequential batch mode and the startup last for 4 weeks. After the reactor started up, ρ(mixed liquid suspended solids) was maintained at about 2.00 mg/L with a stable salinity of 30‰ and pH of 6.9~8.2. During the experiment, the outside temperature was maintained at 20~25°C.

| Material     | Concentration | NH₄Cl | NaNO₃ | NaNO₂ | KH₂PO₄ | CH₃COONa | Na₂CO₃ |
|--------------|---------------|-------|-------|-------|--------|----------|--------|
|              |               | 18.00 | 30.00 | 3.30  | 15.00  | 159.00   | 130.00 |

2.2. Analytical methods
During 10 days’ operation, influent and effluent of the reactor were sampled daily before and after installing the membrane module. ρ(CODₗ), ρ(NH₄⁺-N), ρ(NO₂⁻-N) and ρ(NO₃⁻-N) were determined respectively by potassium dichromate method, sodium nitrate reagent spectrophotometry, N-(1-naphthyl)-ethylenediamine spectrophotometry and ultraviolet spectrophotometry. ρ(DO) and pH in aerobic zone and anaerobic zone were detected by a portable dissolved oxygen analyzer and a precise pH meter.
3. Results and Discussion

3.1. Effects of membrane module assembly on the performance of A/O-MBBR

Figure 2 shows the changes of NH$_4^+$-N, NO$_2^-$-N, NO$_3^-$-N, TN, COD$_C$, before and after the installation of the membrane module assembly in the A/O-MBBR in a stable operation period (10 days). After application of the membrane module assembly, the capacity of the reactor to remove NH$_4^+$-N was significantly improved. Before the membrane module was applied, the average influent $\rho$(NH$_4^+$-N) was 6.47 mg/L and the average effluent $\rho$(NH$_4^+$-N) was 0.81 mg/L, with the average removal efficiency of 87.62%. Compared with that, after application of the membrane module, the average influent $\rho$(NH$_4^+$-N) was 6.11 mg/L and the average effluent $\rho$(NH$_4^+$-N) was 0.11 mg/L, with the average removal efficiency of 98.16%. The removal efficiency reached 99% and $\rho$(NH$_4^+$-N) in the effluent was 0.05 mg/L after operation of one week. This results indicate that the nitrification process is improved with the membrane module installing in the sedimentation zone, which is obviously beneficial to enrich the nitrifying bacteria. Since the effluent $\rho$(NH$_4^+$-N) meets the discharge standard of Water Quality Standard for Fisheries of China (GB 11607-89) , this combined process might be used in the recirculating aquaculture system.

![Figure 2](image_url)
The addition of ultrafiltration membrane showed no significant effects on the removal of NO$_2$-N. After adding ultrafiltration membrane, the average removal rate of NO$_2$-N was slightly improved from 85.60% to 86.10%. However, the removal efficiency of NO$_3$-N was highly improved from 89.42% to 92.61%. Before the ultrafiltration membrane was used, the average influent ρ(NO$_3$-N) was 6.73 mg/L and the average effluent ρ(NO$_3$-N) was 0.71 mg/L, while the average effluent ρ(NO$_3$-N) dropped to 0.50 mg/L after the application of the membrane. By comparing the effluent ρ(NH$_4$+N), ρ(NO$_2$-N) and ρ(NO$_3$-N), it can be found that decrease of NO$_3$-N is the main contribution of nitrogen pollutants removal. The improvement of TN removal efficiency by the combined system mainly benefits from the increase of the removal rate of NO$_3$-N.

The average effluent ρ(TN) of the bioreactor without membrane module was 1.61 mg/L and the removal rate was only 88.38%. After adding the membrane module, the TN removal rate increased to 94.83% and average ρ(TN) of effluent decreased to 0.70 mg/L, which met the effluent quality requirements of Mariculture Wastewater Discharge Standard of China (SC/T 9103-2007). This result indicates that the removal of nitrogen pollutants in aquaculture wastewater has been greatly improved by combining A/O-MBBR process and a membrane module assembly. The installation of the membrane module assembly presented no effect on the COD$_c$ removal. The influent ρ(COD$_c$) was 90-120 mg/L and the effluent ρ(COD$_c$) decreased to 20 mg/L. The average removal rate of COD$_c$ was about 90%.

3.2. Factors influencing the performance of the bioreactor
The removal efficiency of nitrogen pollutants by the combined A/O-MBBR and the membrane module assembly is affected by many factors. For instance, temperature effects the biological transformation performance of microorganisms, and the relative high temperature is beneficial to the removal efficiency [9]. Meanwhile, under the same conditions, the increase of temperature difference between day and night will significantly improve the effluent ρ(TN) [10]. Similarly, great changes of pH also effect the removal efficiency of pollutants, which is not conducive to the growth of microorganisms [11]. The concentration of dissolved oxygen (DO) has an important effect on the synthesis of membrane fatty acids in the reactor, and the abundance of biofilms is also related to ρ(DO) [12]. Therefore, during the experiment, ρ(DO) of anaerobic zone (A) and aerobic zone (O) significantly affected the contents of various organic compounds in the water by affecting the membrane properties and microbial community structures of nitrifying and denitrifying bacteria.

For this reason, the temperature, pH and ρ(DO) in the aerobic and anaerobic zones of the reactor were monitored daily in fixed time during the experiment (Figure 3). The overall temperature of the reactor was maintained at about 20°C during the whole operation of bioreactor, and the temperature variation between day and night was less than 5°C. Before and after applying the membrane, the average pH of the aerobic zone was 8.20 and 8.15, and the average pH of the anaerobic zone was 7.39 and 7.45 respectively. Thus, it can be concluded that the operating temperature and pH were stable in the appropriate range. In addition, the installation of membrane showed little effect on ρ(DO) in the aerobic zone of the reactor, with the mean value of ρ(DO) reaching 7.54 mg/L and 7.56 mg/L respectively. The average ρ(DO) in the anaerobic region was 0.63 mg/L and 1.02 mg/L respectively. According to the previous study [13], when ρ(DO) was 0.71-1.32 mg/L, the synthesis of microbial membrane fatty acids increased. This indicates that the application of membrane component is conducive to the nitrification and further improves the removal efficiency of ammonia nitrogen.
Figure 3. Changes of temperature, pH, ρ(DO) during operation before(a) and after(b) applying the membrane module assembly.

4. Conclusion
At the influent C/N ratio of 12, a combined mariculture wastewater treatment process containing A/O-MBBR and membrane module assembly was constructed to explore the removal efficiency of various pollutants. The results showed that the application of the membrane module assembly significantly improved the removal efficiency of ammonia and nitrate and the nitrogen pollutants in the effluent were significantly reduced. The study provided a support for the practical application of integrated membrane module and MBBR system in treating mariculture wastewater.

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