Partial nitritation and anaerobic ammonium oxidation in biofilter reactors treating low ammonium strength wastewater

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Abstract. Partial nitritation (PN) and anaerobic ammonium oxidation (ANAMMOX) were applied in biofilter reactors to treat low ammonium strength wastewater. The removal efficiency and contribution of PN-ANAMMOX process to CODₐr, BOD₅, NH₃-N, TN and TP were investigated. The results showed that the average removal rates of CODₐr, BOD₅, NH₃-N, TN and TP via PN-ANAMMOX process were 91.9%, 96.7%, 98.9%, 92.8% and 93.3% respectively when hydraulic load was 1.0 m/d. The effluent CODₐr, BOD₅, NH₃-N, TN and TP concentrations were lower than 13.8, 4.8, 0.76, 4.4 and 0.28 mg/L, respectively. The PN-ANAMMOX process showed high efficiency and stability in removing C, N and P pollutants from wastewater. PN reactor played a major role in the removal of CODₐr, BOD₅, NH₃-N and TP. ANAMMOX reactor played a leading role in TN removal.

1. Introduction

Traditional biological nitrification and denitrification process consumes a lot of oxygen, needs to supplement organic carbon sources, and has a high sludge yield. The single anaerobic ammonium oxidation (ANAMMOX) process needs to add NO₂⁻-N to provide electron acceptor for ANAMMOX bacteria (AAOB) [1,2]. Both of them have certain limitations, while the partial nitritation (PN) and ANAMMOX coupling process could remedy their shortcomings. It could not only reduce energy consumption and sludge yield, but also do not require additional organic carbon sources. NH₃-N and NO₂⁻-N produced by PN process could be directly used as the reaction matrix of ANAMMOX process to achieve efficient and stable denitrification while reducing operating costs [3-5].

PN-ANAMMOX process has been paid more and more attention by researchers in recent years. Li et al. [6] realized PN and ANAMMOX in SBR and UASB systems respectively and coupled them to treat late landfill leachate. When the nitrogen load was 1 kgN/(m³·d), the nitrogen removal rate could be stable at 85±1%. Wang et al. [7] used PN-ANAMMOX process in treating anaerobic sludge digestion, and the nitrogen removal rate reached 1.23 kgN/(m³·d). However, the existing research on PN-ANAMMOX coupling process was mostly focused on wastewater with high ammonium concentration, and there were few reports on low ammonium strength wastewater. In addition, the existing research...
mostly used activated sludge system to start PN-ANAMMOX, and there were few reports on fixed-bed biofilm system. Therefore, biofilters were selected as the PN and ANAMMOX reactors in this study to treat low ammonium strength wastewater. On the premise of relatively stable operation, the removal performance of COD, BOD, NH$_3$-N, TN and TP by PN-ANAMMOX coupling processes was investigated. The contribution of PN reactor and ANAMMOX reactor to pollutant removal was also analyzed, which could provide scientific guidance for future production practice.

2. Materials and Methods

2.1. Experimental Reactors

The schematic diagram of experimental reactors is shown in Fig. 1.

![Figure 1. Schematic diagram of PN-ANAMMOX reactors.](image)

The height of PN reactor is 100 cm and the inner diameter is 7.04 cm. The filter layer is 75 cm high and is uniformly mixed with natural river sand, shell sand and zeolite sand of 0.5~1.0 mm in diameter according to the volume ratio of 6:3:1. The top and bottom of the filter layer are paved with 2.5 cm thick gravel layer (particle size 5~18 mm), which plays the role of buffer and support respectively. Drip-infiltration water distribution was used to feed water, adjustable flow rate pump and rotor flowmeter were used to adjust the water intake, and relay was used to control the water intake time. Partial nitritation was initiated via starvation-pH coordinated regulation. After 15 days of starvation, when the influent pH value was adjusted to 8.7, the accumulation rate of NO$_2^-$-N appeared a jump point, the removal rate of NH$_3$-N was stable at about 60%, the accumulation rate of NO$_2^-$-N was stable at over 90%, and the ratio of NO$_2^-$-N/NH$_3$-N in effluent was 1.21~1.33, which realized the rapid start-up of partial nitritation.
The height of ANAMMOX reactor is 70 cm and its inner diameter is 7.04 cm. The filter layer is 50 cm high. The composition of the filter material is the same as that of the PN reactor. The upper and lower parts of the filter layer are also provided with gravel layer. The wastewater is pumped from the bottom of the reactor by a peristaltic pump and discharged from the outlet above the top gravel layer. The gas generated during the reaction is discharged from the top outlet. During the start-up period, the operating temperature was controlled at 30±1°C, and the volume ratio of aerobic nitrification sludge to heterotrophic denitrification sludge was 1:2. After 87 days, the ANAMMOX was successfully activated, and the average removal rate of volumetric nitrogen reached 0.0827 kgN/(m³·d).

2.2. Operating Conditions
The wastewater is pumped into PN reactor by peristaltic pump 1#. The effluent of PN reactor enters into the header tank, and the pH and DO of the wastewater in the header tank are monitored by sensors in real time. The wastewater enters the ANAMMOX reactor from the bottom by peristaltic pump 2# and finally discharges into the effluent tank from the right outlet. During the experiment, the temperature of the reaction zone was 20~30 °C.

During stable operation, the concentration of COD₉, BOD₅, NH₃-N, NOₓ-N and TP in the effluent of the influent tank were 120~140, 83.2~115.4, 45~50, 0~0.5 and 2.5~4.2 mg/L, respectively. pH was 7.2~7.8, hydraulic load was 1.0 m/d, wet-dry ratio was 1:3, and the pH of the effluent in the header tank was 7.0~8.2, DO was lower than 3.0 mg/L.

2.3. Analysis Methods
Concentrations of COD₉, BOD₅, NH₃-N, NOₓ-N, NO₃-N and TP were determined by potassium dichromate method, dilution and inoculation method, Nessler reagent spectrophotometry, N-(1-naphthyl)-ethylenediamine spectrophotometry, ultraviolet spectrophotometry and ammonium molybdate spectrophotometry, respectively.

3. Results and Discussion

3.1. Removal of Organic Pollutants
The removal of COD₉ and BOD₅ during stable operation period is shown in Fig. 2. It can be seen that the COD₉ and BOD₅ concentration in the effluent of PN reactor were 14.1~25.5 and 8.5~19.6 mg/L respectively. The COD₉ and BOD₅ concentration in the effluent of ANAMMOX reactor were 7.1~13.8 and 2.1~4.8 mg/L respectively. The average removal rates of COD₉ and BOD₅ were 91.9% and 96.7%, respectively. It can be seen that PN-ANAMMOX processes have a good removal effect on organic pollutants. The removal of organic pollutants mainly depends on the adsorption and interception of filter materials and the degradation of microorganisms.

![Figure 2. Variations of COD₉ and BOD₅ removal.](image-url)
3.2. Removal of Nitrogen Pollutants

Fig. 3 shows the removal characteristics of NH$_3$-N and TN during stable operation period. The concentration of NH$_3$-N and TN in the effluent of ANAMMOX reactor was lower than 0.76 and 4.4 mg/L respectively. The average removal rates of NH$_3$-N and TN were 98.9% and 92.8% respectively, which showed that PN-ANAMMOX processes could maintain high efficiency of nitrogen removal.

![Figure 3. Variations of NH$_3$-N and TN removal.](image)

3.3. Removal of Phosphorus Pollutants

Fig. 5 shows the removal of TP by PN-ANAMMOX processes. The concentration of TP in effluent of PN reactor ranged from 0.33 mg/L to 0.83 mg/L. After further treatment by ANAMMOX reactor, the concentration of TP in effluent decreased to 0.11~0.28 mg/L, and the average removal rate of TP reached 94.3%. It can be seen that the processes not only had good removal effect on COD$_{cr}$, BOD$_5$, NH$_3$-N and TN, but also had good removal effect on TP, which mainly depends on the good adsorption ability of filter media to phosphorus and the assimilation of microorganisms to phosphorus.

![Figure 4. Variations of NO$_2$-N/NH$_3$-N ratio in PN and ANAMMOX reactors.](image)
3.4. Contribution of PN and ANAMMOX reactor to C, N and P removal

Fig. 6 shows the contribution of PN and ANAMMOX reactor to C, N and P removal. It can be seen that the removal rates of COD$_{cr}$ and BOD$_5$ in PN reactor were 85.8±1.8% and 86.3±3.4% respectively, which were 14.2 and 8.3 times higher than those in ANAMMOX reactor, indicating that the removal of organic matter in wastewater mainly depends on PN reactor. Firstly, the diversity of filter media in PN reactor was conducive to the retention or adsorption of pollutants, which provided a good condition for the removal of organic matter. Secondly, PN reactor used alternate operation of flooding and drying. During the flooding period, most of the organic matter was intercepted or adsorbed. During the drying period, oxygen in the air entered the reactor with the infiltration of wastewater, creating a good oxygen environment for aerobic microbial degradation [9]. Therefore, the removal efficiency of COD$_{cr}$ and BOD$_5$ by PN reactor was better. For the dissolved oxygen content in ANAMMOX reactor was relatively low, the organic matter adsorbed or retained on the filter material was mainly used as carbon source of denitrifying microorganisms in ANAMMOX reactor. Additionally, the removal rate of TP in PN reactor was 83.9±2.9%. It can be seen that the removal of TP mainly occurred in PN reactor.

The average removal rates of NH$_3$-N by PN and ANAMMOOX reactors were 60.2±1.4% and 38.2±1.4% respectively, which indicated that PN reactor played a major role in NH$_3$-N removal from wastewater. The removal mechanism of NH$_3$-N in PN reactor was similar to COD$_{cr}$. NH$_3$-N was adsorbed by biofilm on filter material in flooding period and transformed by microorganism on biofilm in drying period. Nitrification in PN reactor mainly depended on AOB, so most of NH$_3$-N was oxidized to NO$_2^-$-N. During stable operation, the concentration of NO$_2^-$-N in the effluent of PN reactor was 20.4–26.7 mg/L, while the concentration of NO$_3^-$-N was only 0.9–1.9 mg/L, the average accumulation rate of NO$_2^-$-N was 94.6%, and the corresponding effluent NO$_2^-$-N/NH$_3$-N ratio was 1.21–1.33, which conformed to the theoretical influent water demand for ANAMMOX.
The removal rate of TN by ANAMMOX reactor was 84.6±3.5%, while the contribution of PN reactor to TN removal was only 8.2±3.2%, which showed that ANAMMOX reactor played a leading role in TN removal. Although about 60% of NH$_3$-N was removed from PN reactor, most of NH$_3$-N was only converted to NO$_2$-N, and only a few were converted to gaseous nitrogen, so the TN content of wastewater after PN reactor was still high. When the effluent of PN reactor entered ANAMMOX reactor, NO$_2$-N and NH$_3$-N were removed as the reaction substrates of ANAMMOX [10]. The average removal rates of NO$_2$-N and NH$_3$-N were 98.3% and 97.2% respectively.

4. Conclusion
The average removal rates of COD$_{cr}$, BOD$_5$, NH$_3$-N, TN and TP by PN-ANAMMOX processes were higher than 90% when the influent COD$_{cr}$, BOD$_5$, NH$_3$-N, NO$_x$-N and TP concentrations were 120~140, 83.2~115.4, 45~50, 0~0.5, 2.5~4.2 mg/L and hydraulic load was 1.0 m/d, respectively. The effluent NO$_2$-N/NH$_3$-N ratio of PN reactor and the removal NO$_2$-N/NH$_3$-N ratio of ANAMMOX reactor fluctuated around 1.3. The PN-ANAMMOX coupling system showed high and stable removal efficiency of C, N and P pollutants. During stable operation, PN reactor played a major role in COD$_{cr}$, BOD$_5$, NH$_3$-N and TP removal, while ANAMMOX reactor played a leading role in TN removal.

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