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Anaerobic ammonium oxidation for advanced municipal wastewater treatment: is it feasible?

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Abstract: Anaerobic ammonium oxidation(ANAMMOX) is a recently developed process to treat ammonia-rich wastewater. There were numerous articles about the new technology with focus on the ammonium-rich wastewater treatment, but few on advanced municipal wastewater treatment. The paper studied the anaerobic ammonium oxidation(ANAMMOX) process with a down flow anoxic biofilter for nitrogen removal from secondary clarifier effluent of municipal wastewater with low COD/N ratio. The results showed that ANAMMOX process is applicable to advanced wastewater treatment with normal temperature as well as ammonia-rich high temperature wastewater treatment. The results indicated that ammonia removal rate was improved by raising the nitrite concentration, and the reaction rate reached a climax at 118.4 mgN/L of the nitrite nitrogen concentration. If the concentration exceeds 118.4 mgN/L, the ANAMMOX process was significantly inhibited although the ANAMMOX bacteria still showed a relatively high reactivity. The data also indicated that the ratio of NO_2^--N : NH_4^+-N = 1.3 : 1 in the influent was appropriate for excellent nitrogen removal. The pH increased gradually along the ANAMMOX biofilter reactor. When the ANAMMOX reaction was ended, the pH was tend to calm. The data suggested that the pH could be used as an indicator to describe the course of ANAMMOX reaction.

Keywords: ANAMMOX; anoxic biofilter; advanced treatment; nitrogen removal; nitrite

Introduction

Along with the improvement of the living standard, less C/N exists in the urban sewage, which affects the biological nitrogen removal. Due to the increasing cost for extra-carbon source, it is necessary to develop new processes for nitrogen removal, which are more effective with less material and energy consumption. Recently, the discovery of ANAMMOX bacteria produces a promising opportunity to improve the traditional biological nutrient removal(BNR) process. Since the discovery of the ANAMMOX process by Mulder(Mulder, 1995) and other researchers(Van de Graaf, 1995), which proved the prediction made by Broda(Broda, 1977), lots of researches have been conducted on the new biological nitrogen removal technology, and various reactors have been invented (Graaf, 1996; Strous, 1997; Konrad, 2001; Dapena-Mora, 2004) for the purpose of enriching the generation time up to 3 weeks ANAMMOX bacteria(Jetten, 2001). However, all the current researches on ANAMMOX focused on the treatment of ammonia-rich high temperature wastewater, such as sludge digestion fluid, waste leachate; if the ANAMMOX technology can be applied to the advanced treatment of the municipal wastewater, such technology will be widely utilized for its advantages of less consumption of oxygen, no request of additional carbon source and neutralizer.

The chemical measurement relation for ANAMMOX concluded by Strous(Strous, 1998) based on element balance is:

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H \rightarrow 1.02N_2 + 0.26NO_3^- + 0.66CH_2O_{0.5}N_{0.5} + 2.03H_2O \quad (1)$$

The above equation shows that the ANAMMOX bacterium is an autotrophic organism. The substance involved in the ANAMMOX reaction is ammonia and nitrite, and a certain quantity of inorganic carbon is required as the carbon source. For most of germs, nitrite is harmful. According to the report presented by Christian (Christian, 2002) and Strous(Strous, 1999), when the concentration of nitrite was higher than 100 mgN/L, the oxidation activity of anaerobic ammonia would be completely inhibited. Yet Jetten(Jetten, 1999) believed that only when the concentration of nitrite was higher than 280 mgN/L would the ANAMMOX process be restricted. However, when the concentration of NO_2^--N was higher than 140 mgN/L, the effect might be not ideal. In spite of the different conclusions of the inhibit concentration of NO_2^--N made by the researchers, which may be due to the water quality for experiment and the employed processes, a consensus that the strong concentration of nitrite will inhibit the ANAMMOX process has been reached. Till now, no report states whether nitrite will cause inhibitation and what the inhibit concentration is when ANAMMOX is applied to the advanced treatment of municipal wastewater.

Hence, the purpose of the research was to investigate the influence of nitrite and the control factor for ANAMMOX reaction when ANAMMOX was used to treat ammonia-low wastewater in order to promote the application of such a process in advanced municipal wastewater treatment for water reuse.

1 Materials and methods

1.1 Experimental set-up

The experimental reactor was a down flow anoxic biofilter made from organic glass, whose inner diameter and height were 7 cm and 2 m respectively. Shale grain(with the diameter between 2.5—5 mm) was used as the filtering material and was filled up to 1.6 m(Fig.1). The raw water was from the secondary clarifier of municipal wastewater treatment system. The NH_4^+-N, COD, TOC, and temperature of the raw water were 36 ± 2, 35 ± 10, 10 ± 2 mg/L, and 26 ± 2℃, respectively. About two months later, the ANAMMOX bacteria were successfully accumulated in the biofilter and the filtering rate was kept at 2.74 m/h. In order to satisfy the requirement of the influent for ANAMMOX process, nitrite was added into the raw water during the experiment, so as to meet the demand of removing ammonia with ANAMMOX bacteria.

1.2 Analytical methods

Ammonium was measured by Nesselerization/spectrophotometry method(precision ≥ 0.01 mgN/L(GB7479-87; NEPA, 1987a). Nitrite was measured by Diazotization/spectrophotometry method (precision ≥ 0.003 mgN/L, GB7493-87) (NEPA, 1987c). Nitrate was measured colorimetrically after a reaction with 14764 cell test(detection range 1.0—50.0 mgN/L, WTW PhotoLab S12; German). Total nitrogen was measured by Multi_NC 3000 (Analytik Jena AG, German). pH value was measured by Thermo Orion Model 868(USA).

2 Results and discussion

2.1 Removal of nitrogen

According to the results of Van de Graaf(Van de Graaf,

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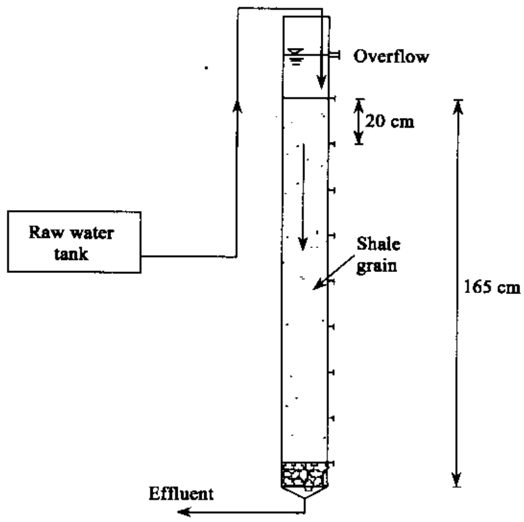

Fig.1 Sketch map of ANAMMOX biofilter

1997), during the process of ANAMMOX, the ratio between the ammonia and nitrite consumption and the nitrate production was 1 : 1.31 : 0.22. During this experiment, the relations among the ΔTN, ΔNH4$^+$-N, ΔNO2$^-$-N and ΔNO_3^--N (Fig. 2) were in good agreement with the ANAMMOX reaction [Eq. (1)]. The data show that the ammonia nitrogen in the filter was removed by the ANAMMOX bacteria. The ANAMMOX process could be used not only for the treatment of ammonia-rich high temperature wastewater, but for the advanced treatment of municipal wastewater with normal temperature, serving as the last process for the biological treatment of sewage for reuse.

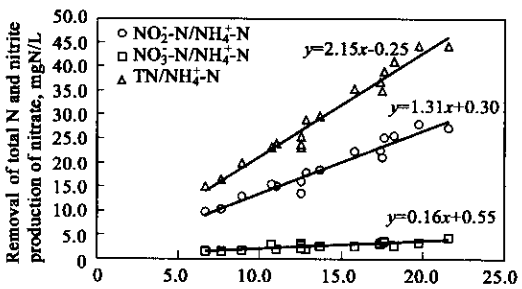

Fig.2 Relation between ΔNH_4^+-N and ΔTN, ΔNO_2^--N and ΔNO_3^--N in ANAMMOX biofilter

2.2 Effect of nitrite on ANAMMOX reaction

As the ANAMMOX reaction continued in the biofilter, the concentration of ammonia and nitrite decreased accordingly. The average removal rate for ammonia nitrogen in the biofilter of 0—20 cm height along with the water flow direction was used to indicate the inhibition of nitrite for the purpose of analyzing the impact imposed by NO_2^--N on ANAMMOX reaction(Fig.3).

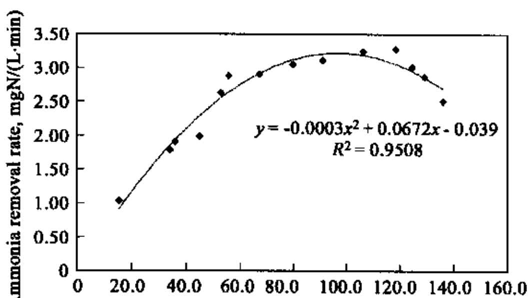

Fig.3 Ammonium removal rate with various concentrations of nitrite

As shown in Fig. 3, the removal rate for ammonia nitrogen increased as the concentration of NO_2^--N existing in the influent was higher. When NO_2^--N = 118.4 mgN/L, the highest removal rate of ammonia nitrogen was up to 3.28 mgN/(L · min). However, as the concentration of nitrite nitrogen went up further, the removal rate for ammonia nitrogen slowed down instead of rising, which revealed that high concentration of nitrite(the conclusion of the experiment showed greater than 118.4 mgN/L) would inhibit ANAMMOX reaction.

Therefore, the concentration of nitrite rose to a certain degree would help speed up the reaction process of ANAMMOX when ANAMMOX was used for advanced treatment of municipal wastewater. However, the over high concentration of nitrite-nitrogen might have inhibit effect accordingly. As indicated by this experiment, when the concentration of NO_2^--N exceeded 118.4 mgN/L, it was not ideal for ANAMMOX reaction because the removal rate for ammonia nitrogen decreased due to the strong inhibit of ANAMMOX process by nitrite. As shown in Fig.3, when the concentration of NO_2^--N reached 136.0 mgN/L, the removal rate for ammonia nitrogen was 2.51 mgN/(L · min), a decrease of 23.5% comparing to 3.28 mgN/(L·min). The rate, however, was still higher than that under NO_2^--N(< 60 mgN/L). The data demonstrated that when the concentration of NO_2^--N became too high, the ANAMMOX reaction did not stop and the ANAMMOX bacteria remained a high activity. Hence, when ANAMMOX was used for advanced treatment of municipal wastewater (ammonia-low wastewater), the inhibition produced by NO_2^--N became apparently different with the results that Christian(Christian, 2002) and Strous (Strous, 1999) reported for the treatment of ammonia-rich wastewater.

2.3 Determination of appropriate mixture ratio for NO_2^--N:NH_4^+-N in the influent

To keep the NH_4^+-N = 35 mgN/L (because the ammonium concentration from the secondary clarifier of municipal wastewater treatment system is about 35 mgN/L), the performances of ANAMMOX biofilter at different ratio of NO_2^--N:NH_4^+-N were shown in Fig.4.

As shown in Fig.4a, when the ratio of NO_2^--N:NH_4^+-N = 1.0 : 1 existed in the influent, ANAMMOX reaction stopped in the filter bed of 60 cm height along with the water direction. Although some NH_4^+-N remained, the reaction stopped because the ANAMMOX bacteria could not get enough electron acceptors due to the shortage of NO_2^--N, which led to the incomplete removal of NH_4^+-N.

When the ratio of NO_2^--N : NH_4^+-N = 1.5 : 1 existed in the influent(Fig.4c), there were adequate electron acceptors NO_2^--N, the removal rate for ammonia nitrogen was much higher than that under the condition of NO_2^--N : NH_4^+-N ≤ 1.3 : 1 (the slope of fitting a straight line represented the removal rate for ammonia nitrogen, as shown in Fig. 4). However, excessive NO_2^--N still existed in the effluent when NH_4^+-N was completely removed. As NO_2^--N : NH_4^+-N = 1.3 : 1 (Fig.4b), the electron acceptors completely reacted with the electron donors, very little NO_2^--N and NH_4^+-N existed in the effluent from the ANAMMOX biofilter. The above data showed that when ANAMMOX was applied to the advanced treatment of municipal wastewater (ammonia-low wastewater), the ratio of NO_2^--N : NH_4^+-N = 1.3 : 1 existing in the influent was appropriate for the best removal of nitrogen, which further proved the conclusion of the chemical

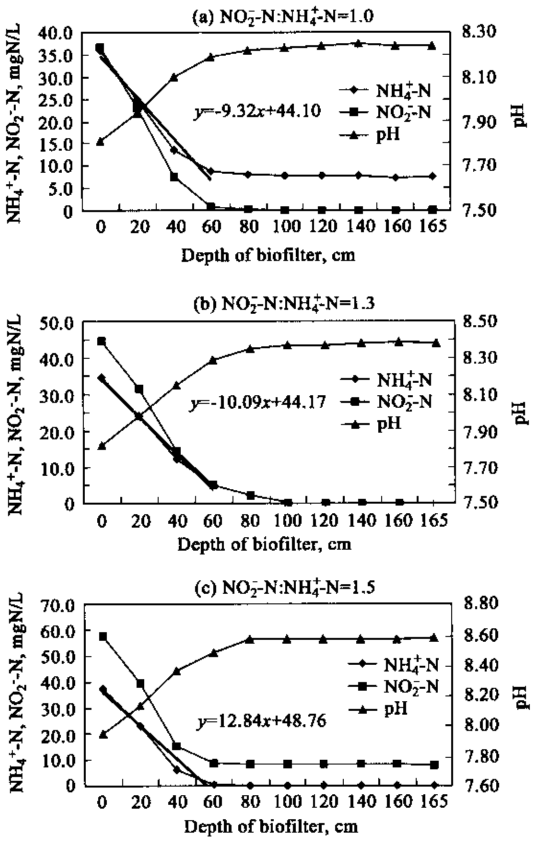

Fig.4 Performances of ANAMMOX biofilter at different ratio of NO_2^- -N : NH_4^+ -N

measurement relation for ANAMMOX made by Strous(Strous, 1998; Eq.(1)) based on element balance.

2.4 Variation of pH value in the ANAMMOX biofilter

The variation of pH value in the ANAMMOX biofilter was shown in Fig.4. The results showed that the pH value increased gradually along the ANAMMOX biofilter reactor. When the ANAMMOX reaction was ended, the pH tended to calm, as shown in Fig.4a, 4b and 4c. The data suggested that the pH could be used as an indicator to describe the course of ANAMMOX reaction. Strous (Strous, 2002) had inferred that the alkalinity of the surrounding environment might rise due to the autotrophic stable CO_2 required to be the carbon source for the ANAMMOX process that was fed by the autotrophic microorganism. So far, the report on the variation of the pH value had not been published under the current laboratory or engineering conditions. The author holds such an opinion that most of the current ANAMMOX processes employed fluidized-bed or SBR processes, therefore the reactant, the resultant and the microorganism in the ANAMMOX reaction were fully mixed up in the reactor, making it difficult to monitor the variation regularity of the pH value in such a fully mixed-up reactor during the ANAMMOX reaction in spite of the rise of the pH value in the effluent from the ANAMMOX reactor comparing with that in the influent.

3 Conclusions

This experiment used the effluent from the clarifier of municipal wastewater treatment process as raw water to successfully apply ANAMMOX biofilter to the advanced treatment of municipal wastewater, showing that the ANAMMOX can be used not only for the treatment of ammonia-rich high temperature wastewater, but for the advanced treatment of municipal wastewater, serving as the last process for the biological treatment of wastewater for reuse. Besides, the following conclusions have also been drawn:

During the experiment, the relation between the consumption of ammonia and nitrite and the production of nitrate is ΔNH_4^+ -N : ΔNO_2^- -N : ΔNO_3^- -N = 1 : 1.31 : 0.16. The results indicate that the removal of ammonia nitrogen in the filter mainly relies on the function of ANAMMOX bacteria.

The ammonia removal rate is improved by raising the nitrite concentration but may not benefit much when the concentration of the nitrite nitrogen exceeds 118.4 mgN/L, because the ANAMMOX process will be significantly inhibited although the ANAMMOX reaction does not stop and the ANAMMOX bacteria still remain a high reactivity.

The ratio of NO_2^- -N : NH_4^+ -N = 1.3 : 1 existing in the influent is appropriate for the best removal of nitrogen.

The pH value increased gradually along with the ANAMMOX biofilter reactor. When the ANAMMOX reaction ended, the pH value tended to calm. The data suggested that the pH could be used as an indicator to describe the course of ANAMMOX reaction.

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