N₂O emission and control strategy in different wastewater treatment processes

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Abstract. N₂O (Nitrous oxide) is a strong greenhouse gas, and wastewater treatment process is one of the important artificial sources of N₂O. Controlling N₂O production and discharge in wastewater treatment process is beneficial to alleviate the greenhouse effect. Based on the mechanism of N₂O production in biological nitrogen removal process, emission characteristics and influencing factors of N₂O in three traditional biological nitrogen removal processes, A/A/O, SBR and oxidation ditch, and two new biological nitrogen removal processes, SBBR and CANON, have been reviewed. Furthermore, a control strategy for slowing the generation and release of N₂O is proposed, which provides a reference for researchers in related field.

Introduction

Nitrous oxide (N₂O) is one of the six greenhouse gases regulated by the Kyoto. Its single-molecule warming potential is 298 times that of carbon dioxide [1]. (IPCC 2007) N₂O has a long residence time in the atmosphere of up to 114 years and can be transported to the stratosphere, causing ozone depletion and ozone holes.

Sewage treatment is one of the important anthropogenic sources of N₂O emissions. Therefore, developing an emission reduction strategy for nitrous oxide in wastewater treatment is an important way to alleviate the greenhouse effect.

1. N₂O production mechanism

The removal of nitrogen in a typical sewage biological treatment process is completed by two processes of nitrification and denitrification. The production pathway of N₂O in the nitrification and denitrification process is shown in Figure 1.

A: Nitrification process

B: Denitrification process

Figure 1. N₂O production pathway during nitrification and denitrification

In the traditional aerobic nitrification process, N₂O is produced by the following two pathways: 1. the intermediate product NH₂OH or NOH in the oxidation process is chemically decomposed or enzymatically reacted to produce N₂O; second, if the concentration of NO₂⁻ is too high, AOB denitrification occur.

Heterotrophic bacteria can also produce N₂O in the denitrification stage. The denitrification process involves four enzymes: Nitrate reductase (NAR), Nitrite reductase (NIR), and Nitric Oxide Reductase (Nitric oxide reductase, NOR) and Nitrous oxide reductase (NOS). Changes in external conditions can inactivate NOS in heterotrophic bacteria, leading to the denitrification process only to the third stage, and some heterotrophic bacteria do not have a system for producing NOS, so that the final product of the denitrification stage is N₂O.

2. N₂O emissions from traditional wastewater treatment processes

2.1 N₂O emission and its influencing factors in A/A/O process

For the A/A/O process, the dissolved N₂O produced in the anoxic denitrification stage is released by a large amount of ablation during the aerobic process, so the main emission unit of N₂O is an aerobic tank. Wang [2] et al. found that nitrite concentration had a significant effect on N₂O release flux, and the increase in nitrite concentration led to an increase in N₂O release flux. The lower the DO concentration in the aerobic pool, the higher the

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NO_2^- concentration, the more N_2O is released. Therefore, sufficient DO is provided to complete the nitrification reaction and reduce the production of N_2O .

Yan ^[3] et al. revealed the effects of DO and carbon sources on N_2O production in the denitrification stage from the gene level. Studies have shown that the amount of N_2O produced is negatively correlated with the content of NOS Z in the sludge. The carbon source and DO have a significant effect on the denitrifying bacteria containing the NOS Z gene. The low DO environment and sufficient carbon source can greatly promote the increase of the content, thereby significantly reducing the production of N_2O . Therefore, providing sufficient carbon source and lower dissolved oxygen concentration in the denitrification stage can increase the abundance of N_2O reductase, thereby reducing the release of N_2O .

2.2 N_2O emission and its influencing factors in SBR process

In the SBR (Sequencing Batch Activated Sludge Reactor) process, N_2O is mainly produced in the aerobic phase. Zhang ^[4] et al. found that the four key factors that have a greater impact on N_2O are DO, C/N, carbon source species and pH. The mechanism of action of DO and C/N is consistent with the A/A/O processes. When a single carbon source is used, the carbon source will cause different particle sizes of the activated sludge particles. The larger the particle size, the stronger the denitrification of the nitrifying bacteria and the higher the N_2O production. Therefore, a mixed carbon source should be used in the actual sewage treatment process. The pH can affect the concentration of free ammonia (FA) in the system. The effect of free ammonia on AOB and NOB is significant. As the pH increases, the concentration of free ammonia increases, and the inhibition of NOB by the system increases. The accumulation of nitrous acid in the system increases the N_2O production. Lv ^[5] et al. also confirmed that the amount of N_2O produced in the system decreased with increasing pH.

2.3 N_2O emission and its influencing factors in oxidation ditch process

Due to the aerobic aeration of the aeration ditch, the dissolved N_2O in the water is released in a large amount, and the dissolved N_2O concentration is very low. Due to the frequent alternating aerobic and anoxic environments, the nitrification and denitrification are not completely performed. Therefore, the dissolved N_2O concentration in the non-aerated zone is higher. Li ^[6] et al. found that if the C/N ratio is low, the denitrification reaction was not complete, and the denitrifying bacteria would reduce NO_2^- or NO_3^- to N_2O . The competition of NOS for electrons under C/N is weak and is suppressed during the synthesis phase, resulting in the accumulation and release of N_2O . When the DO concentration is relatively low, the reduction rate of NO_2^- is smaller than the NO_2^- production rate, resulting in a large accumulation of NO_2^- . Therefore, providing sufficient carbon source, increasing the DO

concentration, and reducing the concentration of NO_2^- as much as possible can reduce the production of N_2O .

3. Emissions of N_2O in new sewage treatment process

3.1 N_2O emission and its influencing factors in SBBR process

SBBR is a new type of composite biofilm reactor developed by charging different fillers (such as fiber filler, activated carbon, ceramsite) in the SBR reactor. Su ^[7] et al. found that N_2O is mainly produced in the nitrification process during SBBR denitrification. The addition of carbon source can reduce the release of N_2O during nitrification. Liang ^[8] et al. found that low carbon to nitrogen ratio, high concentration of NO_2^- and intracellular storage as carbon source are the key factors for N_2O production and accumulation in denitrification. When carbon and nitrogen are relatively high, the rate of utilization of exogenous carbon is fast, and the inhibition of N_2O reductase is small. When the concentration of NO_2^- in the reactor is high, N_2O reductase is inhibited; while the rate of utilization of the internal carbon source is slow, the N_2O reductase is inhibited by electronic competition and becomes a limiting factor for N_2O production. Ge ^[9] et al. believed that the increase in aeration and the increase in DO concentration were beneficial to the N_2O production in the control system. Zou ^[10] et al. also reached the same conclusion.

3.2 N_2O emission and its influencing factors in CANON process

The whole process of autotrophic denitrification (CANON) is a new type of denitrification process based on anammox oxidation technology (ANAMMOX) with NO_2^- as an electron acceptor to convert NH_4^+ to N_2 . The short-range nitrification process is N_2O release. The main route is mainly derived from the oxidation of NH_2OH and the denitrification of AOB. When the concentration of NO_2^- is too high, it may inhibit the activity of NOS enzyme, which leads to more release of N_2O . Fu ^[11] et al. found that in the CANON process, DO affects the accumulation of NO_2^- . With the increase of the initial NH_4^+ concentration, the total amount of N_2O released gradually increased, Fu ^[12] et al. proved that this is due to the first one in the oxidation process of NH_4^+-N . The intermediate NH_2OH is prone to accumulate under high NH_4^+ conditions. The lower the pH, the more NO_2^- will produce more FNA, and when $\text{FNA} > 0.004 \text{ mg/L}$, the reduction of N_2O can be completely inhibited. Therefore, the reduction of N_2O in the CANON process can be mainly carried out in two aspects. On the one hand, the control conditions during system operation are optimized to avoid NO_2^- accumulation and low DO; on the other hand, microorganisms adapted to high NO_2^- concentration can be cultured.

4. Proposal of N₂O control strategy

4.1 Reasonable regulation of DO concentration in nitrification and denitrification processes

In the nitrification process, it is necessary to ensure sufficient DO so that NH₂OH and NO₂⁻ are oxidized in time. At the same time, in the denitrification process, the concentration of DO should be controlled, such as reducing the reflux of the nitrifying solution, to reduce the inhibition of N₂O reductase. For processes such as CANON based on anaerobic ammonium oxidation, it is necessary to control the lower DO concentration to avoid excessive accumulation of NO₂⁻ and reduce the inhibition of denitrifying bacteria.

4.2 Improve the utilization of influent carbon sources in the anoxic denitrification stage

Providing sufficient carbon source for the denitrification stage is an important way to reduce the production of N₂O in the denitrification stage. It is possible to increase the utilization rate of the influent carbon source in the denitrification stage by extending the SRT, adding a mixed carbon source, and changing the type of the carbon source, thereby reducing the generation and emission of N₂O.

4.3 Regulate microbial populations and metabolic activity

Increasing the activity of nitrification and denitrifying bacteria can make nitrification and denitrification better, thereby reducing the release of N₂O. The central ion of the NOS enzyme contains elemental copper, so that the activity of NOS can be increased by flowing a part of (small flow) industrial wastewater containing copper ions without exceeding the microbial inhibitory concentration and the standard water quality. Some scholars have also found that carbon fiber helped to increase the activity of denitrifying bacteria, so that denitrification can be carried out thoroughly. Therefore, regulation of microbial populations and their metabolic activities can reduce N₂O emissions.

4.4 Adjust other operating conditions

The stepwise water inlet method can effectively control the precursors NO₂⁻ and NH₄⁺ of N₂O, thereby reducing the amount of N₂O produced. Therefore, adjusting the water inlet method is a method to effectively reduce the N₂O emissions in the sewage treatment process. In addition to affecting the activity of nitrifying bacteria and denitrifying bacteria, N₂O is also more likely to overflow in the acid phase. Therefore, proper pH can reduce N₂O overflow. The pH of the reaction system can be increased and stabilized by adding a buffer solution to the wastewater system to reduce the escape of N₂O in the biological nitrogen removal process of the sewage. In

addition, intermittent aeration produces and emits less N₂O than continuous aeration.

5. Summary and outlook

N₂O is produced in both the nitrification and denitrification stages of the biological nitrogen removal process, and the N₂O release characteristics of different sewage treatment processes are different. DO and C / N are the main factors affecting the release of N₂O. The sewage treatment plant can reduce the N₂O by properly controlling the DO concentration and the influent C / N of the nitrification process and the denitrification process, and can also adjust the pH, operating conditions such as the influent mode to reduce the generation and release of N₂O. The research on N₂O release in China's sewage treatment process is still in its infancy, and it is urgent to carry out research on N₂O control strategy.

Acknowledgements

This work was financially supported by the Shandong Provincial Key Research and Development Program(2017GSF17105).

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