N$_2$O emission and control strategy in different wastewater treatment processes

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Abstract. N$_2$O (Nitrous oxide) is a strong greenhouse gas, and wastewater treatment process is one of the important artificial sources of N$_2$O. Controlling N$_2$O production and discharge in wastewater treatment process is beneficial to alleviate the greenhouse effect. Based on the mechanism of N$_2$O production in biological nitrogen removal process, emission characteristics and influencing factors of N$_2$O 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 N$_2$O is proposed, which provides a reference for researchers in related field.

Introduction

Nitrous oxide (N$_2$O) 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) N$_2$O 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 N$_2$O emissions. Therefore, developing an emission reduction strategy for nitrous oxide in wastewater treatment is an important way to alleviate the greenhouse effect.

1. N$_2$O 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 N$_2$O in the nitrification and denitrification process is shown in Figure 1.

Figure 1. N$_2$O production pathway during nitrification and denitrification

In the traditional aerobic nitrification process, N$_2$O is produced by the following two pathways: 1. the intermediate product NH$_2$OH or NOH in the oxidation process is chemically decomposed or enzymatically reacted to produce N$_2$O; second, if the concentration of NO$_2^-$ is too high, AOB denitrification occur.

Heterotrophic bacteria can also produce N$_2$O 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 N$_2$O.

2. N$_2$O emissions from traditional wastewater treatment processes

2.1 N$_2$O emission and its influencing factors in A/A/O process

For the A/A/O process, the dissolved N$_2$O produced in the anoxic denitrification stage is released by a large amount of ablation during the aerobic process, so the main emission unit of N$_2$O is an aerobic tank. Wang [2] et al. found that nitrite concentration had a significant effect on N$_2$O release flux, and the increase in nitrite concentration led to an increase in N$_2$O release flux. The lower the DO concentration in the aerobic pool, the higher the
NO\textsubscript{3}\textsuperscript{-} concentration, the more N\textsubscript{2}O is released. Therefore, sufficient DO is provided to complete the nitrification reaction and reduce the production of N\textsubscript{2}O.

Yan \cite{3} et al. revealed the effects of DO and carbon sources on N\textsubscript{2}O production in the denitrification stage from the gene level. Studies have shown that the amount of N\textsubscript{2}O 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\textsubscript{2}O. Therefore, providing sufficient carbon source and lower dissolved oxygen concentration in the denitrification stage can increase the abundance of N\textsubscript{2}O reductase, thereby reducing the release of N\textsubscript{2}O.

2.2 N\textsubscript{2}O emission and its influencing factors in SBR process

In the SBR (Sequencing Batch Activated Sludge Reactor) process, N\textsubscript{2}O is mainly produced in the aerobic phase. Zhang \cite{4} et al. found that the four key factors that have a greater impact on N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O production. Lv \cite{5} et al. also confirmed that the amount of N\textsubscript{2}O produced in the system decreased with increasing pH.

2.3 N\textsubscript{2}O emission and its influencing factors in oxidation ditch process

Due to the aerobic aeration of the aeration ditch, the dissolved N\textsubscript{2}O in the water is released in a large amount, and the dissolved N\textsubscript{2}O 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\textsubscript{2}O concentration in the non-aerated zone is higher. Li \cite{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\textsubscript{3}\textsuperscript{-} or NO\textsubscript{2}\textsuperscript{-} to N\textsubscript{2}O. 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\textsubscript{2}O. When the DO concentration is relatively low, the reduction rate of NO\textsubscript{3}\textsuperscript{-} is smaller than the NO\textsubscript{2}\textsuperscript{-} production rate, resulting in a large accumulation of NO\textsubscript{2}. Therefore, providing sufficient carbon source, increasing the DO concentration, and reducing the concentration of NO\textsubscript{2} as much as possible can reduce the production of N\textsubscript{2}O.

3. Emissions of N\textsubscript{2}O in new sewage treatment process

3.1 N\textsubscript{2}O emission and its influencing factors in SBBR process

SBBR is a new type of composite biofilm reactor developed by changing different fillers (such as fiber filler, activated carbon, ceramsite) in the SBR reactor. Su \cite{7} et al. found that N\textsubscript{2}O is mainly produced in the nitrification process during SBBR denitrification. The addition of carbon source can reduce the release of N\textsubscript{2}O during nitrification. Liang \cite{8} et al. found that low carbon to nitrogen ratio, high concentration of NO\textsubscript{2} and intracellular storage as carbon source are the key factors for N\textsubscript{2}O 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\textsubscript{2}O reductase is small. When the concentration of NO\textsubscript{2} in the reactor is high, N\textsubscript{2}O reductase is inhibited; while the rate of utilization of the internal carbon source is slow, the N\textsubscript{2}O reductase is inhibited by electronic competition and becomes a limiting factor for N\textsubscript{2}O production. Ge \cite{9} et al. believed that the increase in aeration and the increase in DO concentration were beneficial to the N\textsubscript{2}O production in the control system. Zou \cite{10} et al. also reached the same conclusion.

3.2 N\textsubscript{2}O 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\textsubscript{2} as an electron acceptor to convert NH\textsubscript{4}\textsuperscript{+} to N\textsubscript{2}. The short-range nitrification process is N\textsubscript{2}O release. The main route is mainly derived from the oxidation of NH\textsubscript{3}OH and the denitrification of AOB. When the concentration of NO\textsubscript{2} is too high, it may inhibit the activity of NOS enzyme, which leads to more release of N\textsubscript{2}O. Fu \cite{11} et al. found that in the CANON process, DO affects the accumulation of NO\textsubscript{2}. With the increase of the initial NH\textsubscript{3}OH concentration, the total amount of N\textsubscript{2}O released gradually increased, Fu \cite{12} et al. proved that this is due to the first one in the oxidation process of NH\textsubscript{3}OH-N. The intermediate NH\textsubscript{3}OH is prone to accumulate under high NH\textsubscript{3}OH conditions. The lower the pH, the more NO\textsubscript{2} will produce more FNA, and when FNA > 0.004 mg / L, the reduction of N\textsubscript{2}O can be completely inhibited. Therefore, the reduction of N\textsubscript{2}O 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\textsubscript{2} accumulation and low DO; on the other hand, microorganisms adapted to high NO\textsubscript{2} concentration can be cultured.
4. Proposal of N\textsubscript{2}O 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 NH\textsubscript{3}-OH and NO\textsubscript{2} 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 N\textsubscript{2}O 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 NO\textsubscript{2} 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 N\textsubscript{2}O 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 N\textsubscript{2}O.

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 N\textsubscript{2}O. 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 N\textsubscript{2}O emissions.

4.4 Adjust other operating conditions

The stepwise water inlet method can effectively control the precursors NO\textsubscript{2} and NH\textsubscript{4}+ of N\textsubscript{2}O, thereby reducing the amount of N\textsubscript{2}O produced. Therefore, adjusting the water inlet method is a method to effectively reduce the N\textsubscript{2}O emissions in the sewage treatment process. In addition to affecting the activity of nitrifying bacteria and denitrifying bacteria, N\textsubscript{2}O is also more likely to overflow in the acid phase. Therefore, proper pH can reduce N\textsubscript{2}O 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 N\textsubscript{2}O in the biological nitrogen removal process of the sewage. In addition, intermittent aeration produces and emits less N\textsubscript{2}O than continuous aeration.

5. Summary and outlook

N\textsubscript{2}O is produced in both the nitrification and denitrification stages of the biological nitrogen removal process, and the N\textsubscript{2}O release characteristics of different sewage treatment processes are different. DO and C/N are the main factors affecting the release of N\textsubscript{2}O. The sewage treatment plant can reduce the N\textsubscript{2}O 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 N\textsubscript{2}O. The research on N\textsubscript{2}O release in China's sewage treatment process is still in its infancy, and it is urgent to carry out research on N\textsubscript{2}O control strategy.

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