Nitrous Oxide Generation, Influencing Factors and Emission Reduction in Anaerobic-Anoxic-Oxic Process Wastewater Treatment Plant

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Abstract: To achieve the reduction of emissions and control of non-CO₂ greenhouse gases in municipal wastewater treatment plants, this study conducted a one-year monitoring of N₂O in the A²O process of a large municipal wastewater treatment plant in Beijing. N₂O released from the water surface of the A²O process was collected by using a gas flux chamber, and the key influencing factors affecting N₂O were analysed using statistics. The results showed that N₂O was not easy to be released under non-aerated conditions, and the aerobic zone was its main emission area. Temperature leads to high N₂O emissions in winter and low in summer. Correlation analyses showed that NO₂⁻-N is one of the most critical factors affecting N₂O production, and its accumulation level directly affects the amount of N₂O produced in the system. DO also has a great influence on the production of N₂O, and the amount of N₂O produced decreases with the increase of the DO concentration, and the effect on the enzyme activity also makes the pH have a significant effect on the production of N₂O.

1 Introduction

With the world's average temperature reaching a record high in 2023, the trend of climate change characterized by global warming is accelerating, and greenhouse gas (GHG) emission reduction is imminent. Nitrous oxide (N₂O), the third largest greenhouse gas, damages the ozone layer and forms acid rain, seriously affecting ecological degradation[1]. The carbon footprint of China's municipal wastewater treatment plants is two to three times higher than that of other countries[2]. With policies such as the "dual carbon" target in place, the reduction and control of N₂O emissions from wastewater treatment plants is particularly urgent in China.

Research on N₂O in wastewater treatment in China has mainly focused on the mechanism and influencing factors, while less research has been conducted on the generation of N₂O in actual wastewater treatment plants. N₂O generation in actual sewage plants is affected by process types, operating parameters, environmental factors and influent water quality, resulting in complex N₂O emission patterns[3]. As a result, the results of small and pilot experiments are difficult to be accurately used for the calculation of N₂O emissions in actual wastewater treatment plants. Therefore, to achieve the current goal of low-carbon operation of wastewater treatment plants, it is necessary to carry out long-term measurements of N₂O generation and emission in actual wastewater treatment plants to promote the reduction of greenhouse gas emissions from wastewater treatment plants. The A²O process, oxidation ditch, and SBR processes are currently the most used biological nitrogen removal processes for wastewater in China, and thanks to the advantages of easy operation and good operating results, the A²O process is used in more than 31% of the cases[4], and its N₂O emission problem needs to be paid attention to.

In this study, a one-year N₂O monitoring was conducted in an A²O process urban wastewater treatment plant in Beijing to determine the characteristics of N₂O generation and emission in different seasons; the key influencing factors of N₂O generation in urban wastewater treatment plants were determined by analyzing the changes in water quality parameters, operational parameters and microbial community structure, with a view to providing a basis for N₂O emission reduction in wastewater treatment plants.

2 Material and methods

2.1. Introduction of A²O process

The A²O process urban wastewater treatment plant has a planned watershed area of 223.5km² and a design capacity of 600,000m³/d. The average influent NH₄⁺-N, total nitrogen, total phosphorus, and COD concentrations of the A²O process are40, 50, 4.5, and 160 mg/L, respectively. Average sludge concentration about 4000 mg/L. One site in the influent, two in the anaerobic and anoxic zones, respectively, and four evenly spaced sites in the aerobic zone for sampling.
2.2. Gas collection method

A hemispherical floating surface gas collector is used for gas collection, the collector material is polymethyl methacrylate (PMMA), the main body is a ring-shaped float and hemispherical gas collector with a diameter of 40cm, an air inlet is set at the side of the collector on the upper part of the float, and an air outlet is set at the top of the collector.

2.3. Methods of analysis

Water quality indicators analyzed according to standard methods[5]. The pH and dissolved oxygen (DO) were monitored on-line using a multi-parameter water quality meter (WTW 3620i, Germany) and the environmental conditions were monitored using a wind speed detector (PM6252B, China).

The N₂O concentration of the collected gases was determined by gas chromatography using an Agilent 7890N (Agilent, USA) gas chromatograph with an HP-PLOTQ capillary column (30m×0.53mm×25μm) and an ECD detector. The chromatographic conditions were 110 °C at the inlet temperature, 180 °C at the oven temperature and 300 °C at the ECD detector. The dissolved N₂O (Dis-N₂O) concentration was determined according to the upper space method described by Yang[6]. All the samples were measured three times and averaged.

3 Results and discussion

3.1. Characteristics of N₂O production during winter operation of the A²O process

The typical changes of NH₄⁺-N, NO₂⁻-N, NO₃⁻-N and COD during the winter operation of A²O process are given in Fig.1. COD is mainly removed in anaerobic zone and anoxic zone, and the concentration of anaerobic sludge in anaerobic zone is greatly reduced by the external reflux dilution of anaerobic zone, and the concentration of effluent is about 30mg/L, with a COD removal rate of up to 79%. In the influent water of A²O process NH₄⁺-N is about 35mg/L, which is basically converted to NO₃⁻-N in aerobic zone, and the removal rate can reach 100%. The NO₂⁻-N and NO₃⁻-N in the influent water is nearly zero, the appearance of NO₂⁻-N in the anaerobic zone may be related to the reflux sludge of the secondary sedimentation tank, and there is about 0.4mg/L of NO₂⁻-N in the whole process of A²O. NO₃⁻-N is only in the aerobic zone and increases with the conversion of NH₄⁺-N, and the effluent water has NO₃⁻-N about 16mg/L.

The average DO was controlled at about 0.7 mg/L in winter, and it can be observed that NO₂⁻-N has a similar trend with DO in the aerobic section, which indicates that the level of DO control also affects the accumulation of NO₂⁻-N in the aerobic zone. The influent of the A²O process contained about 0.015 mg/L Dis-N₂O, and its concentration increased rapidly to 0.042 mg/L after entering the anaerobic zone, and the effluent of the A²O process increased to 0.042 mg/L after passing through the anaerobic zone and the anoxic zone. L, and Dis-N₂O was basically removed after passing through the anaerobic and anoxic zones. In the aerobic zone, the Dis-N₂O concentration increased rapidly to 0.060 mg/L. In this study, the N₂O emission from the A²O process mainly occurred in the aerobic zone, and no obvious N₂O emission was detected in the anaerobic and anoxic zones. This suggests that although Dis-N₂O exists in the aerobic and anoxic zones, this part of Dis-N₂O is not easy to be released under non-aerated conditions, and Stripping effect caused by aeration is an important reason for the release of N₂O in the aerobic zone.

The wastewater will accumulate and discharge N₂O rapidly after entering the aerobic zone, which has little relationship with heterotrophic denitrification, because at this time, the COD is basically degraded, and the higher DO will also inhibit the activity of denitrifying bacteria, which does not have the good conditions for the occurrence of heterotrophic denitrification, which indicates that the nitrification process leads to the generation of N₂O in this A²O process. The NO₂⁻-N and N₂O increased rapidly after the wastewater entered the aerobic zone, and the location with relatively high NO₂⁻-N concentration (Points 6 and 8 in Fig.1) also had more N₂O production. Studies have shown that the accumulation of NO₂⁻-N promotes AOB to preferentially utilize it as an electron acceptor instead of O₂, and then denitrification occurs to produce N₂O[7], so AOB denitrification is likely to be the main pathway of N₂O production in this A²O process.

3.2. Characteristics of N₂O production during summer operation of the A²O process

As shown in Fig.2, compared with winter, the pollutant concentration of A²O process influent was slightly lower in summer, and the average DO in the aerobic zone was controlled at 1.20 mg/L, with basically no accumulation of
NO$_2^-$-N. The COD and total nitrogen removal rates were about 67 and 65%, respectively.

In summer, the A$^2$O influent was also basically free of Dis-N$_2$O, but its trend along the course was like that in winter, and the outward return sludge carried about 0.025 mg/L Dis-N$_2$O, which was significantly lower than that of 0.042 mg/L in winter, and it could be removed in the anaerobic section. Intra-sludge reflux in the anoxic zone resulted in the appearance of Dis-N$_2$O, but N$_2$O, as the last step before denitrification to produce N$_2$, would be degraded subsequently under the stronger denitrification in the anoxic zone. Upon entering the aerobic zone, Dis-N$_2$O rises rapidly to 0.026 mg/L at first, but then decreases and stays around 0.003 mg/L. The gaseous N$_2$O (Gas-N$_2$O) was detected only in the aerobic zone, with a maximum release flux of about 0.385 g·m$^{-2}$·d$^{-1}$, which is much lower than that in winter.

**Fig.2** Variations of Water quality indicators, DO and N$_2$O concentration during summer in A$^2$O process. NO$_2^-$-N increased rapidly from 0.04 mg/L to 0.12 mg/L while Dis-N$_2$O peaked after entering the aerobic zone, and thereafter, with the increase of DO concentration along the course, the accumulation of NO$_2^-$-N was alleviated, and the Dis-N$_2$O in the system also decreased rapidly. This suggests that Dis-N$_2$O is affected by changes in NO$_2^-$-N, so the main pathway for N$_2$O production from the A$^2$O process in summer may still be AOB denitrification.

Overall, there was a significant difference in N$_2$O production between the two seasons, which may be due to the fact that the N$_2$O production pathway of the process is dominated by AOB denitrification, so the winter season, where NO$_2^-$-N accumulation is more pronounced, has a higher level of N$_2$O production and emission, with a difference of up to 7.6-fold in the average N$_2$O release flux compared to the summer season.

**3.3. N$_2$O emissions from the A$^2$O process in different seasons**

Fig.3 shows the changes of water temperature and N$_2$O emission in different seasons of A$^2$O process. The N$_2$O emission of A$^2$O process is the highest in winter, about 32.75 kg/month. With the increase of water temperature, the emission of N$_2$O decreased in turn, and the emission of N$_2$O in spring was slightly lower than that in winter, about 22.34 kg/month. The emissions in summer and autumn are similar and are much lower than those in winter and spring, which are 6.06 kg/month and 4.99 kg/month respectively.

**Fig.3** Water temperature, N$_2$O emissions in different seasons of the A$^2$O process.

In a single test event, the water temperature of the A$^2$O process would not change by more than 1°C, and the effect on the N$_2$O production of the A$^2$O process was not obvious, but from the difference between the water temperature and the change of the N$_2$O emission in different seasons, the temperature may also be one of the key factors affecting the N$_2$O production. Different studies for wastewater treatment plants have found significant seasonal variations in N$_2$O emissions, for example, Gruber and Dias found that N$_2$O emissions were higher in the period of low-temperature operation in their studies of N$_2$O emissions from the SBR process of a wastewater treatment plant in Switzerland and from a wastewater treatment plant in a tourist area in Portugal[8,9]. Because the bacterial metabolic activity and enzymatic efficiency will change with the decrease of temperature, the nitrifying bacterial population is affected by the low temperature environment, which makes NO$_2^-$-N accumulation and promotes the occurrence of AOB denitrification, and then increases the N$_2$O emission, which may be the reason why the N$_2$O emission of this process is high in winter and spring, but low in summer and autumn.

**3.4. Key factors affecting N$_2$O generation from the A$^2$O process**

N$_2$O generation in A$^2$O process wastewater treatment plant may be affected by factors such as influent water quality and operating conditions. According to the correlation analysis depicted in Fig.4, it was found that Dis-N$_2$O and Gas-N$_2$O exhibited a notable positive correlation with NO$_2^-$-N and pH, along with negative correlations with DO and T at a significance level of p<0.01. These findings highlight the influence of changes in water quality conditions and operating parameters on the generation of N$_2$O within the A$^2$O process during the test. The most significant effect of NO$_2^-$-N accumulation on N$_2$O production from the A$^2$O process was found by Foley in his study on N$_2$O production and emissions from
A Australian wastewater treatment plants, which found that the peak of N\textsubscript{2}O emissions tends to occur together with the peak of NO\textsubscript{2}--N, and that the systematic NO\textsubscript{2} production will be significantly increased after NO\textsubscript{2}--N exceeds 0.3–0.5 mg/L\textsuperscript{[10]}. In the different seasonal tests of this study, sudden changes in the NO\textsubscript{2}--N concentration in the aerobic zone also led to corresponding changes in Dis-N\textsubscript{2}O and Gas-N\textsubscript{2}O, which suggests that similar NO\textsubscript{2}--N thresholds may exist in this A\textsuperscript{2}O process, resulting in a large difference in N\textsubscript{2}O emissions at different NO\textsubscript{2}--N levels.

Fig. 4 Key factors affecting N\textsubscript{2}O production in the A\textsuperscript{2}O process.

N\textsubscript{2}O production was also affected by the level of DO control, which was due to the oxygen half-saturation coefficients of AOB and NOB were around 0.4 and 1.4 mg/L, respectively, and the NOB with low oxygen affinity would be restricted under limited DO, which would result in NO\textsubscript{2}--N accumulation. Studies have shown that higher N\textsubscript{2}O emission often occurs at lower DO control level, because AOB converts NH\textsubscript{3}--N into NO\textsubscript{2}--N under DO restriction, and then acts as an electron acceptor to produce N\textsubscript{2}O through denitrification\textsuperscript{[11,12]}. In the present study, higher pollutants, sludge concentration and sludge age in winter made the average DO in the aerobic zone controlled at about 0.7 mg/L, which was much lower than the DO level of 1.2 mg/L in summer, resulting in different levels of NO\textsubscript{2}--N accumulation in the two seasons, which in turn resulted in differences in the production of N\textsubscript{2}O, which was the reason for the negative correlation between DO and Gas-N\textsubscript{2}O.

It is very important to control pH to ensure biological nitrogen removal efficiency of wastewater. The positive correlation between pH and N\textsubscript{2}O production in this study is similar to that of Law, who investigated the effect of pH on N\textsubscript{2}O production by enriching AOB\textsuperscript{[13]}, and Su, who found that the rate of N\textsubscript{2}O production increased with the increase of pH in a sequential study of the effect of pH on the rate of N\textsubscript{2}O production, and the difference of the rate of N\textsubscript{2}O production between pH 8.0 and 6.5 could be up to 7 times\textsuperscript{[14]}. This may be since the enzymes involved in nitrogen metabolism have different suitable pH, and the change of enzyme activity due to pH change affects N\textsubscript{2}O production.

4 Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

1. N\textsubscript{2}O is released mainly in the aerobic zone, and the presence of anaerobic and anoxic zones helps to reduce N\textsubscript{2}O.

2. The N\textsubscript{2}O emission of the A\textsuperscript{2}O process with a design capacity of 600,000 m\textsuperscript{3}/d has obvious seasonal changes, and the average N\textsubscript{2}O emission in winter is 32.75 kg/month, which is significantly higher than that of 6.06 kg/month in summer.

3. NO\textsubscript{2}--N is the most critical factor affecting the N\textsubscript{2}O production of A\textsuperscript{2}O process, and water temperature, DO and pH indirectly affect the N\textsubscript{2}O production by influencing the NO\textsubscript{2}--N accumulation.

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References


