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-CO_2 greenhouse gases in municipal wastewater treatment plants, this study conducted a one-year monitoring of N_2O in the A^2O process of a large municipal wastewater treatment plant in Beijing. N_2O released from the water surface of the A^2O process was collected by using a gas flux chamber, and the key influencing factors affecting N_2O were analysed using statistics. The results showed that N_2O was not easy to be released under non-aerated conditions, and the aerobic zone was its main emission area. Temperature leads to high N_2O emissions in winter and low in summer. Correlation analyses showed that NO_2^--N is one of the most critical factors affecting N_2O production, and its accumulation level directly affects the amount of N_2O produced in the system. DO also has a great influence on the production of N_2O, and the amount of N_2O 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 N_2O.

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 (N_2O), 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 N_2O emissions from wastewater treatment plants is particularly urgent in China.

Research on N_2O in wastewater treatment in China has mainly focused on the mechanism and influencing factors, while less research has been conducted on the generation of N_2O in actual wastewater treatment plants. N_2O generation in actual sewage plants is affected by process types, operating parameters, environmental factors and influent water quality, resulting in complex N_2O emission patterns[3]. As a result, the results of small and pilot experiments are difficult to be accurately used for the calculation of N_2O 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 N_2O generation and emission in actual wastewater treatment plants to promote the reduction of greenhouse gas emissions from wastewater treatment plants. The A^2O 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 A^2O process is used in more than 31% of the cases[4], and its N_2O emission problem needs to be paid attention to.

In this study, a one-year N_2O monitoring was conducted in an A^2O process urban wastewater treatment plant in Beijing to determine the characteristics of N_2O generation and emission in different seasons; the key influencing factors of N_2O 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 N_2O emission reduction in wastewater treatment plants.

2 Material and methods

2.1. Introduction of A^2O process

The A^2O process urban wastewater treatment plant has a planned watershed area of 223.5km^2 and a design capacity of 600,000m^3/d. The average influent NH_4^+-N, total nitrogen, total phosphorus, and COD concentrations of the A^2O 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.

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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 N_2O 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 N_2O (Dis-N_2O) 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 N_2O production during winter operation of the A^2O process

The typical changes of NH_4^+-N, NO_2^--N, NO_3^--N and COD during the winter operation of A^2O 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 COD of effluent is about 30mg/L, with a COD removal rate of up to 79%.In the influent water of A^2O process NH_4^+-N is about 35mg/L, which is basically converted to NO_3^--N in aerobic zone, and the removal rate can reach 100%. The NO_2^--N and NO_3^--N in the influent water is nearly zero, the appearance of NO_2^--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 NO_2^--N in the whole process of A^2O. NO_3^--N is only in the aerobic zone and increases with the conversion of NH_4^+-N, and the effluent water has NO_3^--N about 16mg/L.

The average DO was controlled at about 0.7 mg/L in winter, and it can be observed that NO_2^--N has a similar trend with DO in the aerobic section, which indicates that the level of DO control also affects the accumulation of NO_2^--N in the aerobic zone. The influent of the A^2O process contained about 0.015 mg/L Dis-N_2O, and its concentration increased rapidly to 0.042 mg/L after entering the anaerobic zone, and the effluent of the A^2O process increased to 0.042 mg/L after passing through the anaerobic zone and the anoxic zone. L, and Dis-N_2O was basically removed after passing through the anaerobic and anoxic zones. In the aerobic zone, the Dis-N_2O concentration increased rapidly to 0.060 mg/L. In this study, the N_2O emission from the A^2O process mainly occurred in the aerobic zone, and no obvious N_2O emission was detected in the anaerobic and anoxic zones. This suggests that although Dis-N_2O exists in the anaerobic and anoxic zones, this part of Dis-N_2O is not easy to be released under non-aerated conditions, and Stripping effect caused by aeration is an important reason for the release of N_2O in the aerobic zone.

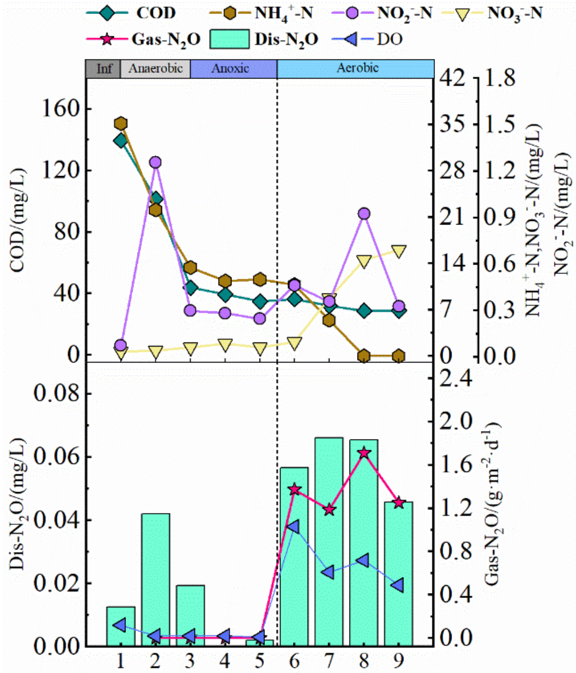

Fig.1 Variations of Water quality indicators, DO and N_2O concentration during winter in A^2O process.

The wastewater will accumulate and discharge N_2O 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 N_2O in this A^2O process. The NO_2^--N and N_2O increased rapidly after the wastewater entered the aerobic zone, and the location with relatively high NO_2^--N concentration (Points 6 and 8 in Fig.1) also had more N_2O production. Studies have shown that the accumulation of NO_2^--N promotes AOB to preferentially utilize it as an electron acceptor instead of O_2, and then denitrification occurs to produce N_2O[7], so AOB denitrification is likely to be the main pathway of N_2O production in this A^2O process.

3.2. Characteristics of N_2O production during summer operation of the A^2O process

As shown in Fig.2, compared with winter, the pollutant concentration of A^2O 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^2O influent was also basically free of Dis-N_2O, but its trend along the course was like that in winter, and the outward return sludge carried about 0.025 mg/L Dis-N_2O, 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_2O, but N_2O, 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_2O rises rapidly to 0.026 mg/L at first, but then decreases and stays around 0.003 mg/L. The gaseous N_2O (Gas-N_2O) was detected only in the aerobic zone, with a maximum release flux of about 0.385 $g{\cdot}m^{-2}{\cdot}d^{-1}$, which is much lower than that in winter.

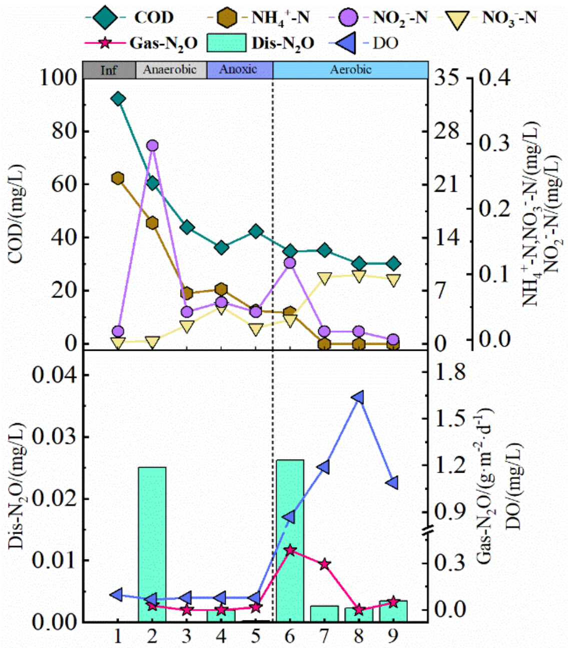

Fig.2 Variations of Water quality indicators, DO and N_2O concentration during summer in A^2O process.

NO_2^--N increased rapidly from 0.04 mg/L to 0.12 mg/L while Dis-N_2O 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_2O in the system also decreased rapidly. This suggests that Dis-N_2O is affected by changes in NO_2^--N, so the main pathway for N_2O production from the A^2O process in summer may still be AOB denitrification.

Overall, there was a significant difference in N_2O production between the two seasons, which may be due to the fact that the N_2O 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_2O production and emission, with a difference of up to 7.6-fold in the average N_2O release flux compared to the summer season.

3.3. N_2O emissions from the A^2O process in different seasons

Fig.3 shows the changes of water temperature and N_2O emission in different seasons of A^2O process. The N_2O emission of A^2O process is the highest in winter, about 32.75 kg/month. With the increase of water temperature, the emission of N_2O decreased in turn, and the emission of N_2O 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.

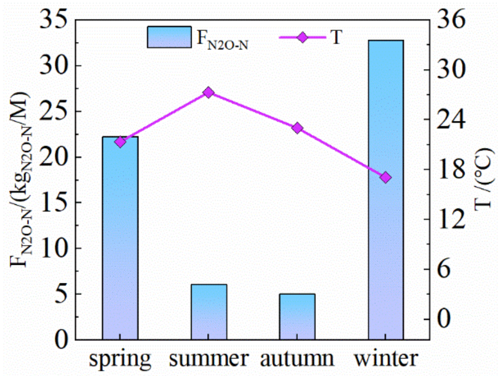

Fig.3 Water temperature, N_2O emissions in different seasons of the A^2O process.

In a single test event, the water temperature of the A^2O process would not change by more than 1°C, and the effect on the N_2O production of the A^2O process was not obvious, but from the difference between the water temperature and the change of the N_2O emission in different seasons, the temperature may also be one of the key factors affecting the N_2O production. Different studies for wastewater treatment plants have found significant seasonal variations in N_2O emissions, for example, Gruber and Dias found that N_2O emissions were higher in the period of low-temperature operation in their studies of N_2O 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_2O emission, which may be the reason why the N_2O emission of this process is high in winter and spring, but low in summer and autumn.

3.4. Key factors affecting N_2O generation from the A^2O process

N_2O generation in A^2O 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_2O and Gas-N_2O 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_2O within the A^2O process during the test. The most significant effect of NO_2^--N accumulation on N_2O production from the A^2O process was found by Foley in his study on N_2O production and emissions from

Australian wastewater treatment plants, which found that the peak of N_2O emissions tends to occur together with the peak of NO_2^--N, and that the systematic N_2O production will be significantly increased after NO_2^--N exceeds 0.3~0.5 mg/L[10]. In the different seasonal tests of this study, sudden changes in the NO_2^--N concentration in the aerobic zone also led to corresponding changes in Dis-N_2O and Gas-N_2O, which suggests that similar NO_2^--N thresholds may exist in this A^2O process, resulting in a large difference in N_2O emissions at different NO_2^--N levels.

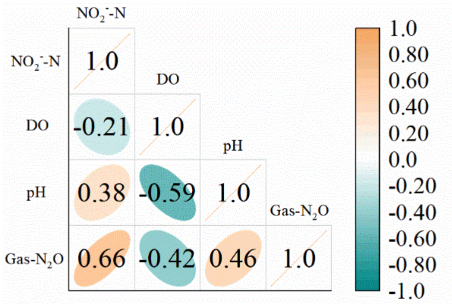

Fig.4 Key factors affecting N_2O production in the A^2O process.

N_2O 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_2^--N accumulation. Studies have shown that higher N_2O emission often occurs at lower DO control level, because AOB converts NH_4^+-N into NO_2^--N under DO restriction, and then acts as an electron acceptor to produce N_2O through denitrification[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_2^--N accumulation in the two seasons, which in turn resulted in differences in the production of N_2O, which was the reason for the negative correlation between DO and Gas-N_2O.

It is very important to control pH to ensure biological nitrogen removal efficiency of wastewater. The positive correlation between pH and N_2O production in this study is similar to that of Law, who investigated the effect of pH on N_2O production by enriching AOB[13], and Su, who found that the rate of N_2O production increased with the increase of pH in a sequential study of the effect of pH on the rate of N_2O production, and the difference of the rate of N_2O production between pH 8.0 and 6.5 could be up to 7 times[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_2O production.

4 Conclusion

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

(1) N_2O is released mainly in the aerobic zone, and the presence of anaerobic and anoxic zones helps to reduce N_2O.

(2) The N_2O emission of the A^2O process with a design capacity of 600,000 m^3/d has obvious seasonal changes, and the average N_2O emission in winter is 32.75 kg/month, which is significantly higher than that of 6.06 kg/month in summer.

(3) NO_2^--N is the most critical factor affecting the N_2O production of A^2O process, and water temperature, DO and pH indirectly affect the N_2O production by influencing the NO_2^--N accumulation.

Acknowledgments

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