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N_2O generation and emission from two biological nitrogen removal plants in China

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ABSTRACT

Nitrous oxide (N_2O) generation and emission from No. 3 wastewater treatment plant (WWTP) in Xi'an (Orbal oxidation ditch) and No. 4 WWTP in Xi'an (reversed A/A/O) were measured throughout a year following the water environment research foundation protocol. The N_2O generation and emission rates of No. 4 WWTP (generation rate of 14.43 kg (N_2O)/d and emission rate of 13.78 kg (N_2O)/d) were about twice that of No. 3 WWTP (generation rate of 7.09 kg (N_2O)/d and emission rate of 6.52 kg (N_2O)/d). The N_2O emission factor of No. 4 WWTP (54.64 mg (N_2O)/m^3 INF) was about 1.7 times that of No. 3 WWTP (36.20 mg (N_2O)/m^3 INF). The ammonia oxidation rate, nitrite oxidation rate, and nitrous oxide generation rate were also measured. Results showed that the key factors of N_2O generation and emission were the microbial population and aeration strategy.

Keywords: Nitrous oxide; Reversed A/A/O; Orbal oxidation ditch; Wastewater treatment plant (WWTP); Biological nitrogen removal (BNR)

1. Introduction

Nitrous oxide (N_2O) is one of the main greenhouse gases (GHGs) and is present in wastewater treatment processes. Given its strong greenhouse effect (300-times stronger than that of CO_2) [1], even a little amount of it is undesirable. Wastewater treatment processes have recently been identified as a source of N_2O. Based on current field-scale measurement, approximately 7% of the influent nitrogen load of wastewater treatment plants (WWTPs) are converted to gaseous N_2O and nitric oxide (NO) [2]. Environment calls have been made to increasingly tighten regulations on reducing such emissions and on identifying the factors that control GHG emissions from WWTPs.

N_2O is mainly generated and emitted in the biological nitrogen removal (BNR) process, such as the nitrification and denitrification stages. In the nitrification stage, ammonia oxidation bacteria (AOB) convert ammonia into nitrate. Without oxygen, AOB uses NO_2 (an intermediate product of nitrification) as the oxidant to create N_2O. In the denitrification stage, N_2O is the in-process product. Different operation methods and parameters, such as hydraulic retention time (HRT), dissolved oxygen (DO), and aeration methods, certainly

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lead to different BNR efficiency and may cause different N_2O generation and emission rates [3–7]. Different aeration strategies have different effects on the emission of soluble N_2O and on DO concentration. Dominant bacteria are closely related to N_2O generation. Although some studies have been conducted on the N_2O generation and emission from the WWTPs, a cost-effective, energy-efficient, and environment-friendly method of addressing N_2O is still lacking at present. Therefore, a database of the N_2O emission from the WWTPs is necessary to support the development of a new process of nitrogen removal.

The specific objectives of this study were (1) to investigate the N_2O emission from two WWTPs, (2) to compare the N_2O liquid-to-gas transfer process of these two WWTPs, and (3) to determine the effects of different wastewater treatment processes on N_2O generation and emission.

2. Materials and methods

2.1. Overview of the WWTPs and sample point

Two plants in Xi'an, China were selected: No. 3 WWTP (Orbal oxidation ditch process) and No. 4 WWTP (reversed A/A/O process). The Oxidation ditch and A/A/O (including reversed A/A/O) processes are the two most popular processes in China. Nearly 50% of the wastewater in China is treated through these two processes. Therefore, these two WWTPs are excellent objects of study for examining the relationship between N_2O generation and emission from wastewater treatment processes. Some information of these two WWTPs are listed in Table 1; plan drawings and the location of the sample points are shown in Fig. 1.

The selected sample points had the same location as the monitoring points in the WWTPs. According to the data provided by the WWTPs and pre-experiment, these sample points can be used to represent the different zones of the WWTPs.

A total of four sample points were used in No. 3 WWTP: one for the anaerobic selector and three for the oxidation ditch processes (one for each channel), given that the wastewater was completely mixed in the channel. The difference between aqueous N_2O before and after aeration was the N_2O emission in the channel.

Analogous to the oxidation ditch, only one sample point in the anaerobic zone and anoxic zone was selected in No. 4 WWTP. However, given the plug flow in the oxic zone, three sample points were selected, along with the water stream.

The temperature of wastewater, pH, DO, soluble chemical oxygen demand, mixed-liquor suspended

Table 1
Operation parameters of the two plants (mg/L)

	Process	Treatment capacity (m^3/d)	Size (L × B × H) (m)	pH	COD	BOD5	SS	NH_3–N	TN	TP	Aeration method
Xi'an No. 3 WWTP	Orbal oxidation ditch	Influent	1.5×10^5	Anaerobic zone $27 \times 9.8 \times 4.95$	7.0 ± 0.8	390	200	250	20	–	4	Surface aeration
		Effluent		Oxidation ditch $108.2 \times 50 \times 4.95$	7.0 ± 0.8	60	20	20	8	–	1.5	
Xi'an No. 4 WWTP	Reversed A/A/O	Influent	2.5×10^5	Anoxic zone $20.3 \times 50 \times 6$	7.0 ± 0.8	380	190	260	34	45	4.2	Fine bubble aeration
				Anaerobic zone $19.3 \times 50 \times 6$								
		Effluent		Oxic zone $78.7 \times 50 \times 6$	7.0 ± 0.8	60	20	20	8	25	1.5	

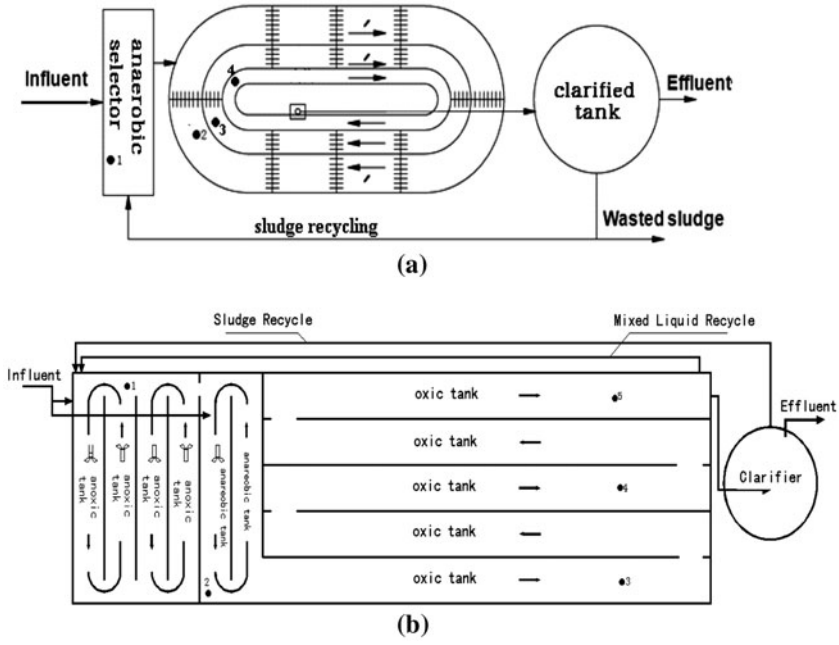

Fig. 1. Plan drawings of the two BNR processes and location of the sample points: (a) the Orbal oxidation ditch process and (b) the reversed A/A/O process.

solids, volatile suspended (VSS) concentrations and the concentration of ammonium (NH_4^+–N), nitrite (NO_2^-–N), and nitrate (NO_3^-–N) were measured using Standard Methods for examination of water and wastewater [8].

2.2. Application of the protocol in measuring the N_2O flux in the BNR process

All of the measurements in this study were conducted as prescribed in the recently developed Water Environment Research Foundation protocol for N_2O concentration and both aqueous and gaseous N_2O flux [6,9,10]. A hand-crafted surface emission isolation flux chamber (SEIFC) with a circular cross-sectional area of 180 cm^2 was used to collect and determine the N_2O flux in the BNR reactors of the two WWTPs.

First, the SEIFC was full of local wastewater, which was completely sunken beneath the surface of the water. The emitted gas from the reactor made it float on the surface of water. After 2–3 d, the gas was collected with a sampling bag. In the aerobic zone, aeration facilitated the direct and immediate collection of the gas samples. Water samples were used for the analysis of aqueous N_2O. The N_2O was measured using a gas chromatograph (PE Clause 600) equipped with an electron capture detector and packed columns of Porapak Q. The detector temperature and column oven temperature were 380 and 50°C, respectively. Pure N_2 (99.999%) was supplied as the carrier gas at a flow rate of 20 mL/min.

The generation and emission rates (E_{N_2O}) were calculated as prescribed by International Water Association (IWA-3762R1). The N_2O generation and emission factors (ωN_2O) were calculated by normalizing the total N_2O mass flux of the reactor to the influent flow rate (m^3/d) and were expressed in $g(N_2O)/m^3$ INF (inflow).

The aqueous N_2O was measured as described by Terry et al. [11] to determine the N_2O generation. The N_2O generation was the sum of the gaseous and aqueous N_2O, which was normalized as mentioned above.

2.3. Ammonia oxidation rate, nitrite oxidation rate, and N_2O generation rate

A non-limiting nutrient substance condition was employed to obtain a zero-order kinetic condition [12]. For the ammonia oxidation rate, a concentration of DO > 5 mg/L and an initial NH_4^+–N of 40 mg/L were used, and the gas and water samples were obtained every 10 min for 2 h. The nitrite oxidation rate was measured similarly to the ammonia oxidation rate, except that the substance was nitrite instead of ammonia.

The N_2O generation rates with the activated sludge of two WWTPs were measured under ideal conditions (20°C) at the nitrification stage (ammonia oxidation

stage), similar to the measurement of the nitrification rate. The gas and liquid samples were obtained to calculate the nitrous oxide generation rate.

3. Results

3.1. N_2O generation and emission from the two BNR plants

A range of values of the N_2O generation and emission from the two BNR plants was calculated and determined throughout one year. On the average, the N_2O emission fraction was different from 6 to 10% (normalized to the influent TKN load), which was in agreement with the findings of previous research (between 0 and 15% of the influent TKN load [6,7,10,13,14]).

Fig. 2 indicated that the N_2O generation and emission from both WWTPs were larger in summer (May–August) than in winter (November–January). The results showed that the N_2O generation and emission were closely related to the wastewater temperature.

The N_2O generation and emission rate of No. 4 WWTP were higher than that of No. 3 WWTP and No. 4 WWTP (generation rate of 9.84–20.45 kg N_2O/d) generated about two to three times as much N_2O as No. 3 WWTP (generation rate of 4.88–8.44 kg N_2O/d). The former also had a larger N_2O emission than the latter.

3.2. Ammonia oxidation rate and nitrite oxidation rate

The ammonia oxidation rate, nitrite oxidation rate, and N_2O generation rate were listed in Figs. 3 and 4 and Table 2.

The two WWTPs had the same ammonia oxidation rate but different nitrite oxidation rate. The nitrite oxidation rate of No. 3 WWTP was not very different from its ammonia oxidation rate, which facilitated the quick oxidization of nitrite and impeded its

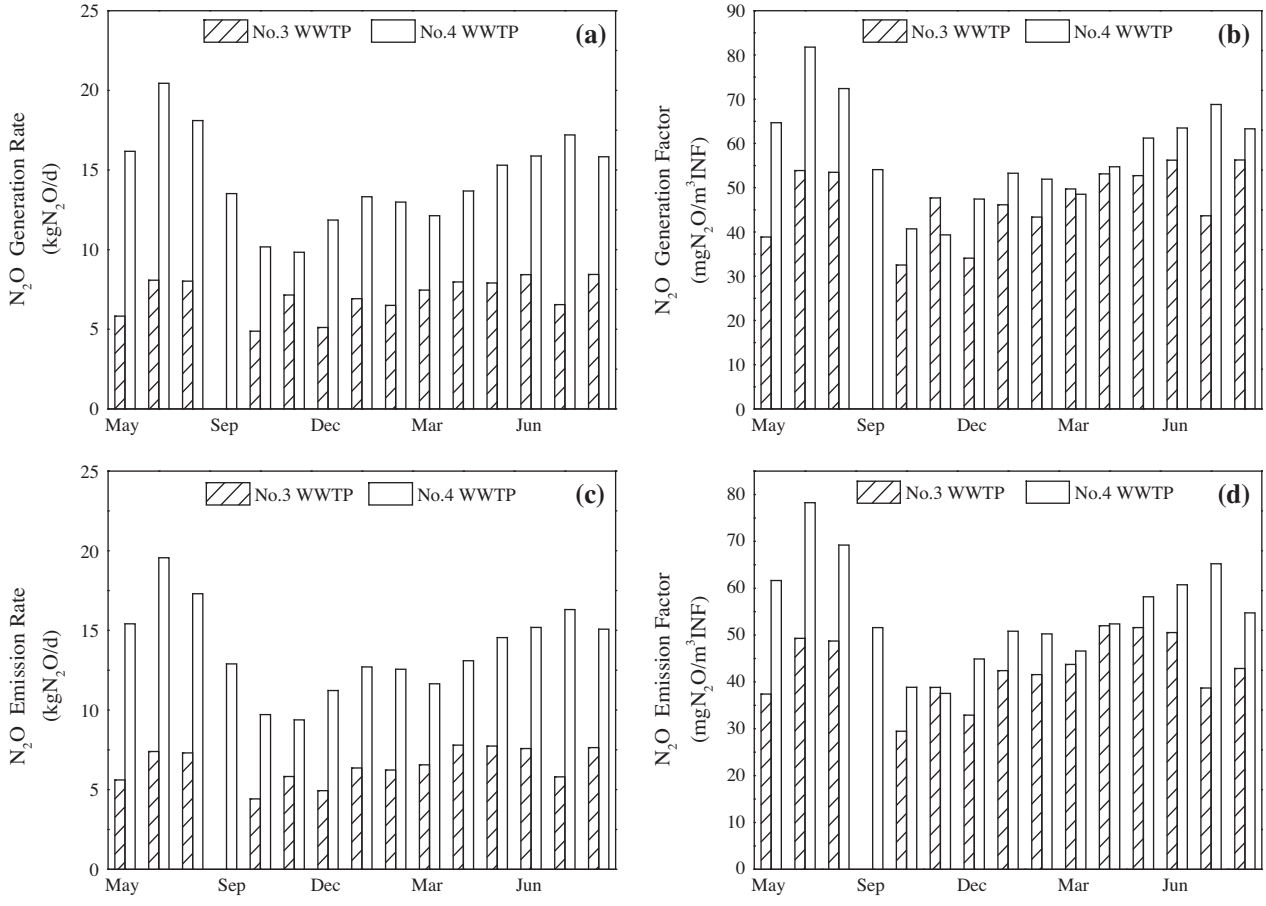

Fig. 2. (a,b) N_2O generation and (c,d) emission from two BNR WWTPs.

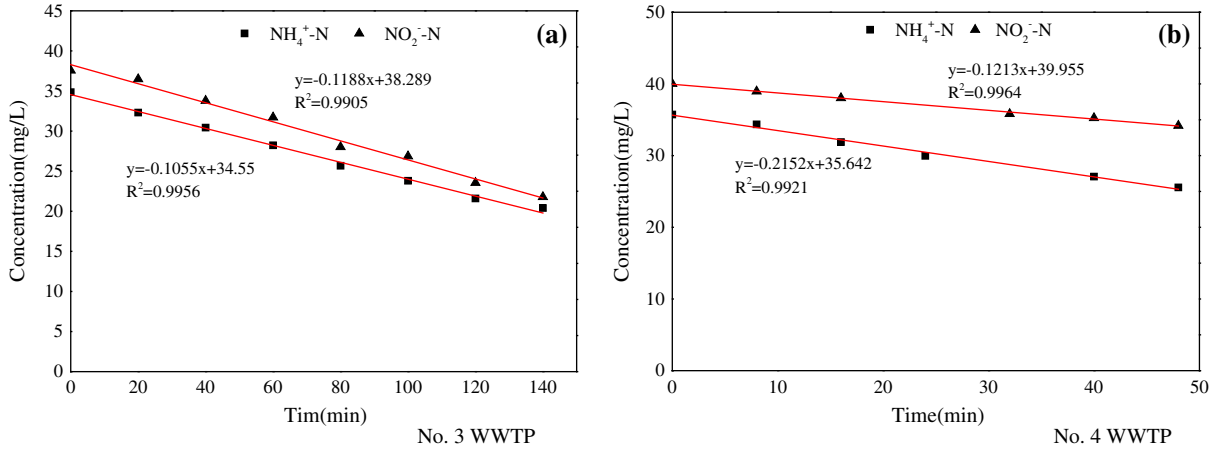

Fig. 3. Nitrification rate of sludge of the two BNR WWTPs: (a) No. 3 WWTP and (b) No. 4 WWTP.

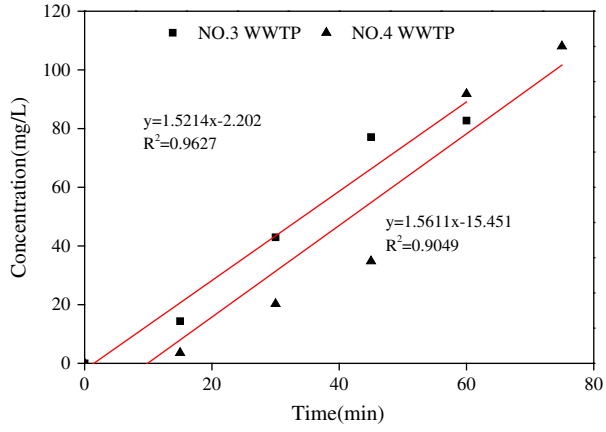

Fig. 4. N_2O generation rate of the two BNR WWTPs.

accumulation. However, the nitrite oxidation rate of No. 4 WWTP was only half of its ammonia oxidation rate, which meant that the nitrite in BNR process of No. 4 WWTP was not be consumed immediately and might be accumulated.

Given that the concentration of nitrite is key to nitrous oxide emission, the higher the nitrite concentration is, the more N_2O is generated. This relation may account for the lager N_2O generation and emission from No. 4 WWTP than No. 3 WWTP. The N_2O generation rate revealed that the N_2O generation rate of No. 4 WWTP was higher than that of No. 3 WWTP, both of which were lower than that of the field survey. The results also indicated that N_2O generation was less under ideal conditions.

4. Discussion

According to the data in Fig. 2, No. 4 WWTP generated and emitted significantly more N_2O than No. 3 WWTP, which meant that the process configuration affected the N_2O generation and emission. Two main factors influenced the generation and emission of N_2O. First, the aeration system had a key role in N_2O emission. Even when the aeration strategy of both WWTPs could meet the demand of DO, the fine bubble aeration in No. 4 WWTP was more efficient than the surface aeration in No. 3 WWTP, which resulted in the emission of aqueous the N_2O with the air bubble. The strategy was closely related to the mass transfer coefficient, which determined the N_2O emission. Another factor was the community structure of the bacteria in the two WWTPs. Given that the reversed A/A/O process was a stepwise nitrification and denitrification process whereas the oxidation ditch process was a simultaneous nitrification and denitrification process, the structure of the microbial

Table 2
Nitrification rate and N_2O generation rate

	Unit	No. 3 WWTP	No. 4 WWTP
Ammonia oxidation rate	mg(NH_4^+–N)/(gVSS h)	2.43	2.58
Nitrite oxidation rate	mg(NO_2^-–N)/(gVSS h)	2.74	1.46
N_2O generation rate	mg(N_2O)/(gVSS h)	18.26	24.65

community in the two WWTPs also had an effect on the N_2O emission [15,16]. HRT was another determinant of the N_2O emission. The strong dilution effect of the relatively longer HRT in No. 3 WWTP (24 h) decreased the nitrite concentration, which was closely related to the N_2O emission [7,17].

The N_2O generation from the two BNR treatment facilities was quite distinctive with similar influent (Table 1), which may be the result of a difference in microbial structure. The ammonia oxidation rate and nitrite oxidation rate were evidence of this hypothesis. In No. 3 WWTP, our previous research had found that the microbial structure [18] and the ratio of AOB/NOB in sludge was around 1.1, which meant that the quantity of microorganisms participating in the ammonia oxidation process and nitrite oxidation process was similar and that the accumulation of nitrite was difficult to achieve. In No. 4 WWTP, the AOB was more than NOB (the ratio was about 2.1), and the ammonia oxidation rate was much higher than the nitrite oxidation rate. *Nitrosomonas europaea*, the dominant microorganism in the ammonia oxidation process, could proceed in denitrification as well as nitrification. The denitrification during the nitrification stage was one of the main sources of N_2O generation [19,20]. Given that the AOB was more than the NOB, nitrite generation was faster than nitrite oxidation, which meant that the nitrite could accumulate in wastewater treatment processes.

The nitrite concentration is critical to nitrous oxide generation and emission. Given that the nitrite is the oxidant of aerobic denitrification and nitrifier denitrification, an increase in the concentration of nitrite strengthens the two processes, both of which are important to nitrous oxide generation.

Aeration strategy is another factor of N_2O emission, given that the liquid-to-gas transfer process may be affected by aeration methods. The DO is controlled by aeration strategy during the nitrification stage. Aerobic processes should avoid incomplete or intermittent nitrification and over aeration is expected to have lower N_2O emission [10,21]. Processes, such as oxidation ditch, which rely on more uniform spatial DO profiles to promote simultaneous nitrification and denitrification probably have less N_2O emission than others. In the denitrification stage, as the inhibiter of both synthesis and activity of denitrification enzymes, DO would relate to N_2O emission when in minimal amount [15,21].

The sustainable management of nitrogenous pollution is one of the great challenges in China. As a consequence, from an engineering perspective, developing comprehensive strategies for BNR design and operations that minimize N_2O generation and emission is beneficial [14,22,23]. This study clearly shows that the N_2O emission originates predominantly from the nitrification stage (aeration zone).

N_2O emission can also be minimized when the peaking factor of the influent nitrogen loading to the activated sludge is conducted via flow equalization [24]. However, this process may be difficult when the flow rate is high, in which case, the influent may be blended with the primary effluent to equalize the nitrogen loads.

According to previous surveys, additional parameters, such as increased nitrite concentration in both the nitrification and denitrification stages and low COD/N ratio in the denitrification stage, result in N_2O emission in BNR WWTPs. The sufficiently long SRT prevents nitrite accumulation during nitrification. Even if the ratio of COD/N in the influent cannot be controlled, the pre-sedimentation of organic carbon in the influent can be minimized; the COD limitation of the denitrification process and the additional organic carbon can be dosed to prevent emission [25].

5. Conclusions

The results and discussion above lead to the following conclusions:

- In both WWTPs, N_2O generated and emitted more in summer than in winter.
- The N_2O generation rate and emission rate of No. 4 WWTP (reversed A/A/O process, generation rate of 14.43 kg $(N_2O)/d$, and emission rate of 13.78 kg $(N_2O)/d$) were about twice that in No. 3 WWTP (Orbal oxidation ditch process, generation rate of 7.09 kg $(N_2O)/d$ and emission rate of 6.52 kg $(N_2O)/d$).
- The N_2O emission factor of No. 4 WWTP (54.64 mg $(N_2O)/m^3$ INF) was about 1.7 times that of No. 3 WWTP (36.20 mg $(N_2O)/m^3$ INF).
- The N_2O generation rate was slower under ideal conditions in the lab than under field conditions. The generation rate of sludge of No. 3 WWTP was 18.26 mg $(N_2O)/(gVSS\ h)$, whereas that of No. 4 WWTP was 24.65 mg $(N_2O)/(gVSS\ h)$.
- Results showed that the key factor of N_2O generation and emission was the microbial population and the aeration strategy.

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