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Article

N_2O Emission from Partial Nitrification and Full Nitrification in Domestic Wastewater Treatment Process

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Abstract: Using actual domestic wastewater as the research object, nitrogen compounds and their combinations were added to different nitrification (partial nitrification, full nitrification) processes to investigate nitrous oxide (N_2O) emission and its nitrification mechanisms. The presence of influent NH_4^+ was the driving force of N_2O emission during nitrification. Compared with full nitrification, NO_2^- in partial nitrification more readily generated N_2O by denitrification. Under the proportional gradient of NH_4^+-N:NO_2^--N/NO_3^--N, 30:0, 20:10, 10:20, and 0:30, total N_2O emissions during partial nitrification were 2.81, 11.30, 65.20, and 11.67 times greater than the total N_2O emissions during full nitrification. Full nitrification was more beneficial to N_2O emission reduction. This provides a control strategy for N_2O emission reduction in wastewater treatment processes under the background of reducing the production of greenhouse gases.

Keywords: N_2O; domestic wastewater; partial nitrification; full nitrification; greenhouse gas reduction

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1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas whose greenhouse effect exceeds CO_2 by ~300 times [1]. N_2O is also a potential ozone depleting substance (ODS) [2]. Wastewater biological treatment is an anthropogenic source of N_2O emissions, and both nitrification and denitrification processes produce N_2O [3–6]. Full nitrification involves two steps: NH_4^+ oxidization to NO_2^- via NH_2OH utilizing Ammonia Oxidizing Bacteria (AOB) followed by subsequent oxidation of NH_2OH to NO_2^- by AOB (the energy generation step); Secondly, NO_2^- is further oxidized to NO_3^- using Nitrite Oxidizing Bacteria (NOB). In this process, ammonia mono-plus oxidase (AMO) catalyzes the oxidation of NH_3 to NH_2OH and O_2 acts as the electron acceptor [7]. Hydroxylamine oxidase (HAO) catalyzes the oxidation of NH_2OH to NO_2^- and O_2 acts as the main electron acceptor [8]. In the nitrification process, there are two possible pathways for N_2O emission as a byproduct: (1) N_2O is produced during autotrophic denitrification by AOB, NO_2^- acts as an electron acceptor, and is converted into N_2O via NO using nitrite reductase and nitric oxide reductase [9,10]; (2) N_2O is produced by the incomplete oxidation of NH_2OH [11–13].

A few studies have reported some operational control factors related to N_2O emission regarding full nitrification, such as dissolved oxygen (DO), temperature, pH, Sludge Retention Time (SRT), salinity, and toxic substances [14–21]. However, fewer studies on N_2O emission during partial nitrification have been published. Most studies were conducted using culture medium and artificial wastewater, which does not accurately simulate the complex actual nitrification.

In this study, a Sequencing Batch Reactor (SBR) and specific test rules explored N_2O emission and some nitrification mechanisms using partial and full nitrification of sludge cultivated with actual domestic wastewater. These results provide a theoretical basis for the control of N_2O emission in wastewater treatment.

2. Methods

2.1. Sludge and Wastewater

Two 12L SBRs were used for cultivation of partial and full nitrification sludge and the index of domestic wastewater inflow is shown in Table 1. The traditional full nitrification operation mode was as follows. The average operational cycle was 420 min, which included feeding (30 min), aeration (240 min), anoxic denitrification (120 min), and settling (30 min), 3 cycles per day, with the DO was 2 mg/L and Mixed Liquid Suspended Solids (MLSS) remaining at about 3000 mg/L. SRT was 20 days, and the rate of nitrate accumulation during full nitrification was about 99%. The partial nitrification operation mode was similar to that for full nitrification, except the DO was 1 mg/L and running temperature was 30 °C, SRT was 11 days; the rate of nitrite accumulation during partial nitrification was about 98%. After anoxic denitrification, the effluent's composition, consisting of NH_4^+-N, NO_2^--N, and NO_3^--N were all below 1 mg/L. The full nitrification and partial nitrification sludge taken from the SBRs was aerated for 12 h, then washed 3 times with deionized water repeatedly, for batch testing. The effluent's COD was less than 50 mg/L and could not be oxidized for longer.

Table 1. The quality of real domestic wastewater.

	COD (mg/L)	**NH_4^+-N (mg/L)**	**NO_2^--N (mg/L)**	**NO_3^--N (mg/L)**	**TN (mg/L)**	**pH**	**Alkalinity**
minimum	88	39.6	0	0	56.4	6.9	262
maximum	276	91.2	2.8	1.2	98.5	7.7	343
average	182	65.4	1.4	0.6	77.4	7.3	303

2.2. Batch Test Rules

The experimental batch test reactor is shown in Figure 1. The effective volume of the reactor was 3 L. At the beginning of each batch test, 1 L of concentrated full nitrification and partial nitrification sludge was added into the reactor, followed by 2 L of wastewater, and the MLSS were controlled at 3000 mg/L. Nitrogen compounds, DO and pH levels were then adjusted for the batch set upon commencing operation (Table 2). The running time for batch tests was 180 min.

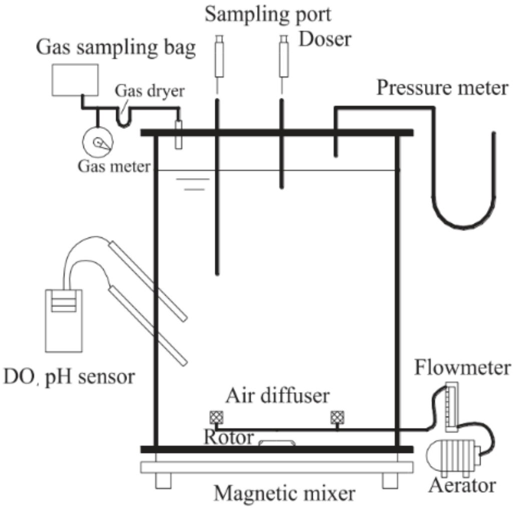

Figure 1. N_2O emission during partial nitrification (partial nitrification effluent +NH_4Cl-N/$NaNO_2$-N, DO = 0.5 mg/L).

Table 2. Batch test rules.

Batch Test Number	Sludge—Water Mixture Type	Initial pH	Reaction Time (h)	NH_4^+-N (mg/L)	NO_2^--N (mg/L)	NO_3^--N (mg/L)	DO (mg/L)
1	partial nitrification sludge + effluent	7.5	3	30	0		0.5
	partial nitrification sludge + effluent	7.5	3	20	10		0.5
	partial nitrification sludge + effluent	7.5	3	10	20		0.5
	partial nitrification sludge + effluent	7.5	3	0	30		0.5
2	full nitrification sludge + effluent	7.5	3	30		0	0.5
	full nitrification sludge + effluent	7.5	3	20		10	0.5
	full nitrification sludge + effluent	7.5	3	10		20	0.5
	full nitrification sludge + effluent	7.5	3	0		30	0.5
3	full nitrification sludge + effluent	7.5	3		20		0.5
	full nitrification sludge + effluent	7.5	3		20		1
	full nitrification sludge + effluent	7.5	3		20		2
	full nitrification sludge + effluent	7.5	3		20		3

2.3. Detection Method

COD, NH_4^+-N, NO_2^--N, NO_3^--N were measured according to methods previously described [22]. DO, pH, T were measured by an oxygen, pH and temperature meter (WTW 340i, WTW Company, Munich, Germany). The Mixed Liquid Suspended Solids concentration was measured at the beginning and at the end of each test to obtain an average value, which was used for the calculation of the NH_4^+-N oxidation rate, NO_x^--N production rate and N_2O emission rate. The total N_2O production consists of the N_2O emitted in the gaseous phase (emission-gas N_2O) and the N_2O dissolved in the mixed liquid phase (dissolved N_2O). The N_2O concentrations in gas samples were analyzed in triplicate using a gas chromatograph (Agilent 6890N, Santa Clara, CA, USA). The overhead space method was used to analyze the dissolved N_2O. Water and N_2O samples were taken at 30-min intervals.

3. Results and Discussion

3.1. N_2O Emission in Partial Nitrification Process

Figure 2 shows the variations of N_2O emissions under different NH_4^+-N and NO_2^--N ratios during partial nitrification (partial nitrification's effluent +NH4Cl/$NaNO_2$). As shown in Figure 2a–c, the maximum N_2O emission occurred when NH_4^+-N was about to be oxidized completely, and its maximum value was 1.20 mg/L, 1.37 mg/L, and 1.48 mg/L. When the ratios of NH_4^+-N to NO_2^--N were 30:0, 20:10, and 10:20, the time for N_2O to reach its highest level decreased, and the N_2O emission rates increased; they were 0.16, 0.30, and 0.49, respectively (in mgN/(gMLSS·L·h). This indicated that the initial emission rate of N_2O increased with added NO_2^- in the presence of NH_4^+-N. This was due to the electrons provided by the NH_4^+ oxidation process being used for autotrophic denitrification of AOB in the partial nitrification process.

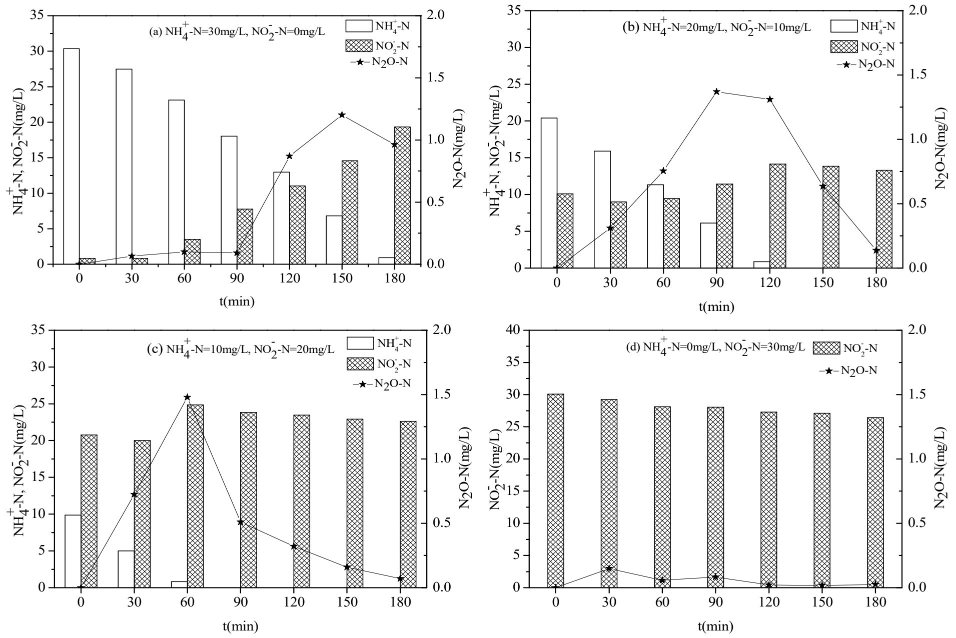

Figure 2. N_2O emission during partial nitrification (partial nitrification effluent +NH_4Cl-N/$NaNO_2$-N, DO = 0.5 mg/L).

When NH_4^+ oxidation provided electrons, higher concentrations of electron acceptor NO_2^- led to increased autotrophic denitrification of AOB. As shown in Figure 2b,c, NO_2^- concentrations decreased with NH_4^+ oxidation in the first 30 min of the reaction. However, in the absence of NH_4^+, as shown in Figure 2d, even a NO_2^- concentration of 30 mgN/L did not result in N_2O emission above 0.15 mg/L. This reaction resulted in denitrification of only 3.5 mgN/L of NO_2^-. The lack of BOD (effluent) suggested its electron source might be internal organic matter (PHB) stored in AOB sludge [23,24], hydrogen, and pyruvate [25]. In addition, under four different ratios of NH_4^+-N and NO_2^--N, the total production of N_2O was 3.29, 4.52, 3.26, and 0.35 mgN/L, respectively. N_2O production was maximized when NH_4^+-N and NO_2^--N ratios were 20:10. This was due to the presence of electron acceptor NO_2^- (10 mgN/L), and contrasted with the minimal levels observed with the ratio of 30:0 (Figure 2b). Compared with 10:20, the reaction in Figure 2b had more electron donors from NH_4^+.

3.2. N_2O Emission in Full Nitrification Process

Figure 3 shows the variation of N_2O emission during full nitrification (full nitrification effluent +NH_4Cl/$NaNO_2$) under different NH_4^+-N and NO_3^--N ratios. As shown in Figure 3a–c, with decreasing NH_4^+-N and increasing NO_3^--N, the time it took for N_2O to maximize decreased; however, the N_2O emission rates also decreased (0.051, 0.029, and 0.005, mgN/(gMLSS·L·h)). When the ratios of NH_4^+-N to NO_3^--N were 30:0, 20:10, and 10:20, the maximum yields of N_2O were 0.46, 0.18, and 0.02 mgN/L, respectively. As shown in Figure 3a–c, the maximum production of N_2O occurred as NH_4^+-N was oxidized, which was the same as for the N_2O emissions in the AOB enrichment system. Figure 3 also shows that under the four proportional gradients, the total N_2O production was 1.17, 0.40, 0.05, and 0.03 (mgN/L), which indicated that with full nitrification (where AOB and NOB co-exist), the production of N_2O mainly depended on the initial concentration of NH_4^+, rather than the concentration of NO_3^-. In addition, as shown in Figure 3d, in the absence of COD, a very small amount of N_2O was still generated when NO_3^- was added to the system, which may be caused by the denitrification of using internal organic matter in sludge.

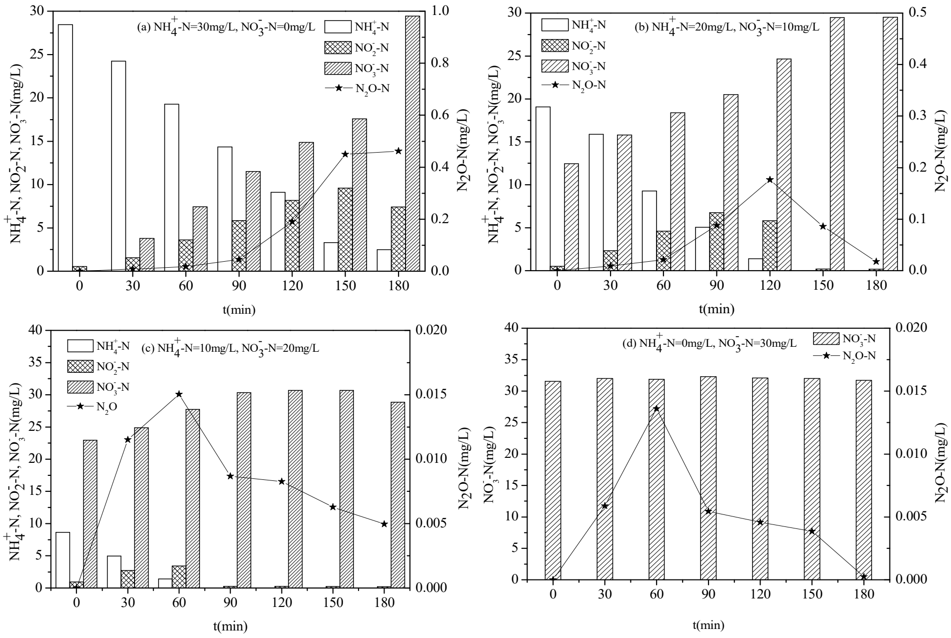

Figure 3. N_2O emission during full nitrification (full nitrification effluent +NH_4Cl-N/$NaNO_2$-N, DO = 0.5 mg/L).

Figure 4 shows the variation of N_2O emissions during full nitrification (full nitrification effluent +$NaNO_2$ 20 mgN/L). This batch test added 20 mgN/L $NaNO_2$ to the nitrification system effluent and investigated the oxidation of NO_2^- by NOB to produce N_2O under different DO concentrations. As shown in this figure, N_2O reached its maximum value after 30 min, and its maximum production decreased with increasing DO, with values of 0.054 mg/L, 0.051 mg/L, 0.014 mg/L, and 0.007 mg/L. The NO_2^- oxidized to NO_3^- within 60 min. After 60 min, no NO_2^- remained in the system (data not shown), but the production of N_2O was not 0, which indicated that during full nitrification, there was still N_2O production during NO_2^- oxidation to NO_3^- by NOB. Although the amount was very small, this N_2O may come from microorganisms using endogenous substances to provide electrons for denitrification. During the reaction, the total production of N_2O was 0.14 mg/L, 0.09 mg/L, 0.04 mg/L, and 0.03 mg/L for the four different DO gradients, and the proportion of N_2O in influent NO_2^--N was 0.70%, 0.45%, 0.20%, and 0.15%. The percentage was smaller than N_2O production in an AOB enriched system (Figure 2d), which was 1.17% (when DO = 0.5 mg/L) and indicated that NO_2^- in an AOB enriched system was more readily denitrified than with full nitrification.

As shown in Figures 2 and 3, under the same ratio of NH_4^+-N to NO_2^--N and NO_3^--N (DO = 0.5 mg/L), and under four proportional gradients, in the AOB system with NO_2^-, the total N_2O emissions were 2.81, 11.30, 65.20, and 11.67 times greater than the total N_2O emission during full nitrification, which indicated that under the same conditions of influent NH_4^+-N, partial nitrification produced more N_2O than full nitrification. During partial nitrification, NO_2^- was more involved in autotrophic denitrification of AOB as a product, while during full nitrification, NO_3^- would not participate in autotrophic denitrification as a nitrification product. Moreover, NO_2^- further oxidized to NO_3^- by NOB as an intermediate product of full nitrification; therefore, only a small amount of NO_2^- was involved in autotrophic denitrification by AOB.

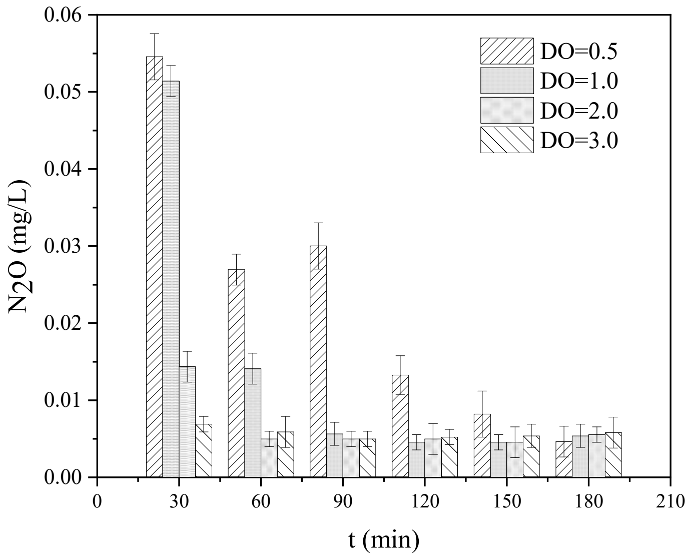

Figure 4. N_2O emission during full nitrification (full nitrification effluent +$NaNO_2$-N 20 mgN/L).

4. Conclusions

The N_2O emission in partial and full nitrification of actual domestic wastewater was investigated under specific conditions and yielded the following conclusions:

(1) The presence of influent NH_4^+ was the driving force of N_2O emissions in full and partial nitrification processes.

(2) Compared with full nitrification, NO_2^- was more likely to participate in denitrification during partial nitrification to produce N_2O.

(3) Under four proportional gradients, the total production of N_2O during partial nitrification was 2.81, 11.30, 65.20, and 11.67 times greater than the total N_2O production during full nitrification.

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Data Availability Statement: The original data is backed up on my computer, ready for investigation.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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