Characteristics of N₂O Emission and Nitrogen Removal at A DO Controlled Intermittent Aeration Activated Sludge Process

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Abstract

N₂O is emitted through the wastewater treatment process, especially through biological nitrification and denitrification. Recently much attention has come to be paid to N₂O emission, because N₂O is one of the greenhouse effect gases, which is causing global warming. In this study, examination on the effectiveness of DO controlled intermittent aeration activated sludge process was made with respect to suppression of N₂O emission and improvement of nitrogen removal. The results obtained were as follows: DO control operation was superior to former timer control operation for the ability of both suppression of N₂O emission and nitrogen removal. Judging from ORP in the aeration tank, DO control operation could change the surroundings in it periodically for the effective progress of nitrification and denitrification. At the pilot plant experiments, DO control operation was confirmed to be very effective way to suppress N₂O emission and to enhance nitrogen removal efficiency; The conversion ratio from removed nitrogen to N₂O-N was restrained to 0.05% and nitrogen removal efficiency reached over 80%. It was clarified that coagulant dosed and DO controlled intermittent aeration activated sludge process would be very promising way to prevent global warming and to improve water environment.

Key words: global warming, nitrous oxide (N₂O), nitrification, denitrification, wastewater treatment

INTRODUCTION

In recent years, global warming has caused worldwide attention. And many kinds of

human activities are reported to be responsible for the emission of the greenhouse effect gases, which cause global warming¹⁻³⁾. Among such greenhouse effect

gases, CO_2 , CH_4 and N_2O are emitted from the wastewater treatment processes⁴⁻⁷⁾. It is considered that the greenhouse effect per one molecule of CH_4 is 20 - 30 times, and that of N_2O is 200 - 300 times, as large as that of CO_2 ¹⁻³⁾. As for N_2O , its atmospheric concentration is about 310 ppbv; about 8 % greater than that during the pre-industrial era, and it is increasing at a rate of 0.2 - 0.3 % per year¹⁻³⁾. It is true that the concentration of N_2O in the air is about 1/1,000 of that of CO_2 , but by reason of its potential of greenhouse effect and so on, N_2O is by no means neglected as a greenhouse effect gas. Therefore, it is regarded of great importance to develop the technology that can suppress N_2O emission from several kinds of anthropogenic sources including wastewater treatment processes.

Through the biological nitrogen removal, N_2O is said to be emitted from both nitrification⁸⁻¹³⁾ and denitrification^{14, 15)}. Denitrification with N_2O emission is also made by fungi¹⁶⁾. There is a report of N_2O generation through simultaneous nitrification and denitrification¹⁷⁾. It is considered that application of anoxic process would be able to remove nitrogen. However, the characteristic of N_2O emission from this process has not been clarified well. In this study, intermittent aeration activated sludge process was examined for its ability of suppression of N_2O emission with high nitrogen removal. The experiments were made using laboratory scale reactors and a pilot plant. At the laboratory scale experiment, two types of the intermittent aeration operation, that is DO control operation and timer control operation, were compared. At the pilot plant experiment, characteristics of N_2O emission and nitrogen removal at the coagulant dosed and DO controlled intermittent aeration activated sludge process was investigated.

MATERIALS AND METHODS

Comparison of the two modes of the intermittent aeration Examination was made on the intermittent aeration activated sludge process by two operational modes; one was DO control operation (run 1), the other was timer control operation (run 2). Each apparatus was composed of an aeration tank (5.4l) and a settling tank (2.5l). On the top of the aeration tank, there was a cover to seal up the headspace in the aeration tank if necessary. The settled sludge was recirculated from the settling tank to the aeration tank. At run 1, DO concentration in the aeration tank was measured and the intermittent aeration was controlled as follows: For the aerobic period, aeration was carried out till the DO concentration reached 3.0 mg/l. Then aeration was stopped and the DO concentration fell down gradually. When the DO concentration dropped to 0.5 mg/l, the timer started and the anoxic period continued for 60 minutes. One cycle was composed of these processes and the cycle was operated periodically. At run 2, one cycle was composed of 60 minute-aerobic period, and 60 minute-anoxic period, and the cycle was operated periodically. Synthetic wastewater with 40 mg/l of its total nitrogen (T-N) (Organic-N 15 mg/l, $\text{NH}_4\text{-N}$ 25 mg/l, $\text{NO}_2\text{-N}$ 0 mg/l, $\text{NO}_3\text{-N}$ 0 mg/l) and 5 mg/l of its total phosphorus (T-P) was used. HRT was fixed to 12 hours. MLSS in the aeration tank was maintained at about 3,000 mg/l and the experiment was conducted at 20°C. The schematic apparatus is shown in Fig. 1.

Sampling was made for each gas and water. At gas sampling, both the emitted gas into the atmosphere from the aeration tank and the dissolved gas in the water in the aeration tank were collected. The emitted gas into the atmosphere was collected into gas sampling bag by using air pump. For the

aerobic period, aeration made it possible to collect gas sample directly. For the anoxic period, the headspace in the aeration tank was sealed up and was replaced by argon gas at the beginning of the period, then sampling was made at the end of it.

Dissolved gas in the water in the aeration tank was also sampled by following the head gas method: 30 ml of each water and argon gas was sealed into a 60 ml syringe, then 1 ml of $2\text{N-H}_2\text{SO}_4$ was added to it to reduce microbial activity. After shaking, the syringe was kept for 1 hour without moving. Afterwards, the gas phase in it was collected as gas sample.

Water samples were collected from the influent and the water in the aeration tank.

Investigation at a pilot plant Investigation on the characteristics of N_2O emission and nitrogen removal was made at a pilot plant, where coagulant dosed and DO controlled

intermittent aeration activated sludge process was operated to treat actual domestic wastewater. The plant was located in the middle part of Ibaraki prefecture in Japan, and was designed to treat 15 m^3 of wastewater from 75 persons/day. Volume of the aeration tank was 12 m^3 and its HRT was 19 hours. In the aeration tank, each aeration and mixing was made by the blower and the stirrer. About the intermittent aeration, the operation was automatically controlled by measuring DO concentration and the water temperature in the aeration tank. One operational cycle was 120 min. And based on the calculation of the oxygen consumption rate, distribution of each aerobic and anoxic period was made. ORP in the aeration tank was also monitored. For the removal of phosphorus, FeSO_4 was dosed as a coagulant, and pH was adjusted to about 7.0 by adding NaOH. The treatment facilities are shown in Fig. 2.

Fig. 1 Schematic apparatus of laboratory experiment.

Fig. 2 Scheme of pilot plant for coagulant dosed and DO controlled intermittent aeration activated sludge process.

Taking into account of the fluctuation of the influent loading, the experiment was made through 24 hours in each investigation. Sampling was made for gas and water. In order to collect the gas emitted into the atmosphere, a gas collecting chamber with the float fixed by its side was settled on the surface of the water in the aeration tank, then emitted gas was collected by using it (Fig. 3). For the aerobic period, aeration made it possible to collect gas sample directly. For the anoxic period, gas in the chamber was replaced by argon gas at the beginning of the period and sampling was made at the end of it. Sampling of dissolved gas in the water in the aeration tank was also made as same as the laboratory experiment. Water samples were collected from the influent, the water in the aeration tank, and the effluent. Each sampling for gas and water was made when aerobic or anoxic period was converted to each other.

Analysis Gas samples were analyzed for N₂O by ECD-GC (GC-8A, Shimadzu Co., Japan). Water samples were collected from the influent and the water in the aeration

tank. NH₄-N and NO₂-N were measured by the indophenol method and the N-ethylendiamine absorptiometry method, respectively. NO₃-N was reduced to NO₂-N and measured by the N-ethylendiamine absorptiometry method. T-N was oxidized to NO₃-N by K₂S₂O₈ first, then reduced to NO₂-N and measured by the N-ethylendiamine absorptiometry method. PO₄-P was measured by the molybdenum method. T-P was oxidized to PO₄-P by K₂S₂O₈, then measured by the molybdenum method. These methods were according to the "Japanese Standard Method on Sewage" by the Japanese Sewage Works Association, published in 1984.

RESULTS AND DISCUSSION

Comparison of N₂O emission between the two modes of the intermittent operation Rate of N₂O emission into the atmosphere and change of dissolved N₂O concentration for each run are shown in Fig. 4. At run 1, the emission rate took relatively a high value during the aerobic period. And both the emission rate and the concentration were the highest at the middle of the aerobic period.

Fig. 3 Method of gas sampling.

Judging from these phenomena, it was supposed that, at run 1, N_2O should be generated predominantly through nitrification. At run 2, the emission rate took relatively a high value during the aerobic period similar to that at run 1. However, it was about 3 times as large as that at run 1. Moreover, the emission rate took the highest value at the beginning of the aerobic period, and the concentration decreased during the aerobic period and increased during the anoxic period. It was supposed that, in the case of run 2, N_2O should be generated rather through denitrification than through nitrification, and that N_2O generated and accumulated in the water during mainly anoxic process should be emitted into the atmosphere when the aeration started at the aerobic period.

It appeared that DO and ORP would have some influences on N_2O generation. Transition of DO concentration and ORP in each run's aeration tank are shown in Fig. 5. Judging from them, aerobic condition and anoxic condition were clearly divided at

run 1. On the other hand, at the run 2, DO concentration reached nearly 8 mg/l during aerobic period, and it took 30 minutes until the concentration fell down to nearly 0 mg/l during anoxic period. N_2O is the intermediate of denitrification. As the anoxic condition seemed to be not enough at run 2, denitrification should be finished at N_2O during the anoxic period. At run 2, if the ratio of the anoxic period was larger, or K_1a value was smaller, surroundings in the aeration tank would be less aerobic, then denitrification would also make progress more smoothly. However, in this experiment, denitrification did not progress sufficiently during anoxic period. As mentioned before, N_2O is generated through both nitrification and denitrification processes. Progress of these reactions could be examined from the water quality in the aeration tank, and these consideration was made in the next paragraph.

N_2O emission in detail was classified in Table 1. At the DO control operation (run 1), total amount of N_2O emission could be

Fig. 4 Rate of N_2O emission into the atmosphere and transition of dissolved N_2O concentration at run 1 (a) and run 2 (b). Symbols: $\square$, N_2O emission; $\bullet$, N_2O concentration.

Fig. 5 DO concentration and ORP in the aeration tank at run 1 (a) and run 2 (b). Symbols : ○, DO concentration ; ●, ORP.

Table 1. Classification of N₂O emission.

Run	Aerobic period		Anoxic period	
	Emission into the atmosphere (mg-N ₂ O day ⁻¹)	Emission into the effluent (mg-N ₂ O day ⁻¹)	Emission into the atmosphere (mg-N ₂ O day ⁻¹)	Emission into the effluent (mg-N ₂ O day ⁻¹)
1 (DO control)	1.718	0.065	0.075	0.083
2 (timer control)	4.073	0.156	0.227	0.144

reduced to 1/3 of that of the timer control operation (run 2). N₂O generation is to be dependent of the progress of nitrification and denitrification. Especially when ORP during anoxic period was higher, dissolved N₂O concentration would become higher, and consequently N₂O emission into the atmosphere during aerobic period would be higher.

Comparison of nitrogen removal between the two modes of the intermittent operation
 Nitrogen form and its change in each run's aeration tank are shown in Fig.6. Similar tendency was observed at both runs. During the aerobic period, NH₄-N concentration decreased and NO₃-N concentration increased, which meant the progress of nitrification. During anoxic period, both NO₃-N and simultaneously T-N concentrations decreased, which meant the progress of denitrification. No NO₂-N accumulation was observed all through the aerobic-anoxic cycle at any runs. T-N concentrations were approximately 15 mg/l at run 1, and approximately 20 mg/l at run 2. In terms of nitrogen removal efficiency, each value at the DO control operation and the timer control operation was 62.5 % and 56.9 %, respectively. Conversion ratios from the removed nitrogen to N₂O-N were 0.45 % and 1.17 %, respectively. As mentioned in the previous paragraph with the discussion of the DO concentration and the ORP, the efficiency

of the oxygen supply at this apparatus was relatively high, and the surroundings in the aeration tank had a tendency of being aerobic. Hochstein *et al.*¹⁸⁾ reported that activity of the N₂O reductase was decreased under existence of oxygen during denitrification. By reason of the existence of the oxygen during the anoxic period, denitrification might be completed at N₂O at run 2. Consequently N₂O conversion ratio might have increased and nitrogen removal efficiency might have decreased at run 2. However, if K₁a value of the aeration system would be smaller, the surroundings in the aeration tank should be more anoxic. In such case, the progress of nitrification and denitrification, and N₂O emission through them would be different. Besides, the timer control operation would not be able to cope with the various conditions of influent loading. Generally, as DO control operation can control aerobic and anoxic conditions in the aeration tank for the effective progress of nitrification and denitrification, it would be superior to timer control operation with respect to nitrogen removal. And from this experiment, it was clarified that DO control operation was also superior to timer control operation for the suppression of N₂O emission.

Characteristic of N₂O emission at a Pilot Plant
 Characteristics of N₂O emission and nitrogen removal were investigated at a pilot plant,

Fig. 6 Nitrogen concentration in the aeration tank at run 1 (a) and run 2 (b). Symbols :
○, NH₄-N; ●, NO₂-N; □, NO₃-N; ■, T-N.

at the facilities coagulant dosed and DO controlled intermittent aeration activated sludge process was operated to treat domestic wastewater. Typical tendency of N_2O emission rate into the atmosphere from 1 m^3 of the water in the aeration tank is shown in Fig.7. As same as the results of the laboratory experiment, N_2O was emitted largely during aerobic period, and the emission rate during aerobic period was about 4 times as large as that during anoxic period.

Transition of dissolved N_2O concentration in the aeration tank corresponding to the date shown in Fig.7. is shown in Fig.8. From the results of several investigation, N_2O emission into the atmosphere and that into the effluent is summarized in Table 2. Judging from ORP, the surroundings in the aeration tank tended to be more anoxic, compared with that at each laboratory

experiment. There was not so much difference on the amount of N_2O emitted into the atmosphere among each investigation. On the other hand, dissolved N_2O concentration varied at each sampling time or each investigating day. It was supposed that ORP in the aeration tank should have a considerable influence on N_2O emission as similar to laboratory experiment. From the results of the investigation at the pilot plant, estimation for the N_2O emission through wastewater treatment in Japan was made. There live approximately 120,000,000 people in Japan. Assuming that the wastewater from all of the people in Japan would be treated by the intermittent aeration activated sludge process, the amount of N_2O emission would be $2.7 \times 10^8 \text{ g- N}_2\text{O/yr.}$

Characteristic of nitrogen removal efficiency at a pilot plant Nitrogen form and its behavior

Fig. 7 Rate of N_2O emission into the atmosphere at the pilot plant. Symbols: ■, aerobic period; □, anoxic period.

Fig. 8 Transition of dissolved N_2O concentration at the pilot plant.

Table 2. Classification of N_2O emission (average value).

Aerobic period			Anoxic period		
Emission into the atmosphere (mg- N_2O day ⁻¹)	Emission into the effluent (mg- N_2O day ⁻¹)	ORP at the end of the period (mV)	Emission into the atmosphere (mg- N_2O day ⁻¹)	Emission into the effluent (mg- N_2O day ⁻¹)	ORP at the end of the period (mV)
229.2	18.6	+32.0	65.6	26.1	-31.8

in the aeration tank corresponding to the date shown in Fig.7 is shown in Fig.9. The concentration of each nitrogen form behaved as similar to that in the laboratory experiment. The composition of the influent was about T-N of 30 mg/l and $\text{NH}_4\text{-N}$ of 17 mg/l. Neither $\text{NO}_2\text{-N}$ nor $\text{NO}_3\text{-N}$ was detected in the influent. Water quality of the effluent was much the same as that in the aeration tank. Table 3 shows the nitrogen removal efficiency and the N_2O conversion ratio. As same as the results at the laboratory experiment, the effectiveness of

the DO control operation was confirmed. Nitrogen removal efficiency reached over 80% and the N_2O conversion ratio could be reduced to about 0.05%.

Anthropogenic N_2O emission in Japan was estimated¹⁹⁾ to be 1.1×10^{11} g- N_2O /yr. And with the value of N_2O emission in the previous paragraph, 2.7×10^8 g- N_2O /yr, the amount of N_2O emission from wastewater treatment would correspond to only 0.25 % of whole anthropogenic emission. However, N_2O emission through the only aerobic treatment process was much higher than

Fig. 9 Nitrogen concentration in the aeration tank at the pilot plant. Symbols: ○, $\text{NH}_4\text{-N}$; ●, $\text{NO}_2\text{-N}$; □, $\text{NO}_3\text{-N}$; ■, T-N.

Table 3. Nitrogen removal efficiency of the pilot plant.

Nitrogen removal efficiency (%)	$\text{N}_2\text{O-N}$ conversion ratio ⁽¹⁾ (%)	$\text{N}_2\text{O-N}$ conversion ratio ⁽²⁾ (%)
83.7	0.05	0.06

(1) Ratio from the nitrogen influent to $\text{N}_2\text{O-N}$.

(2) Ratio from the removed nitrogen to $\text{N}_2\text{O-N}$.

aerobic/anoxic process²⁰⁾. $\text{N}_2\text{O-N}$ conversion ratio reached 1.23 % of the nitrogen influent, at our investigation at the real domestic wastewater treatment facilities. In such case, N_2O emission through wastewater treatment process would not be negligible at all. Consequently it was clarified that DO controlled intermittent aeration process would be very effective way to enhance nitrogen removal efficiency and to suppress N_2O emission.

CONCLUSIONS

In this study, the ability of suppression of N_2O emission and nitrogen removal in an intermittent aeration activated sludge process was examined. And the following conclusions could be drawn.

- 1) DO control operation was superior to timer control operation for the ability of both suppression of N_2O emission and nitrogen removal.

- 2) Judging from ORP in the aeration tank, it was clarified that DO control operation could control aerobic and anoxic condition in the aeration tank suitably, for the purpose of effective progress of nitrification and denitrification.
- 3) In a pilot plant investigation, nitrogen removal efficiency reached over 80 % under DO control operation, and the N₂O-N conversion ratio could be restrained to about 0.05 %.
- 4) From the results of the pilot plant investigation, N₂O emission through the wastewater treatment in Japan was estimated to 2.7×10^8 g- N₂O/yr.
- 5) From the results of the pilot plant investigation, it was confirmed that DO control operation would be very effective way to suppress N₂O emission and improve nitrogen removal efficiency.

REFERENCES

- 1) IPCC.: Climate Change 1992. The Supplementary Report to The IPCC Scientific Assessment, Cambridge University Press, Cambridge, UK. (1992).
- 2) IPCC.: Climate Change 1995. Science of Climate Change. IPCC Working Group I Technical Summary, Cambridge University Press, Cambridge, UK. (1996).
- 3) IPCC.: Climate Change 1995. Impacts, Adaptations, and Mitigation. IPCC Working Group II Summary for Policymakers, Cambridge University Press, Cambridge, UK. (1996).
- 4) Peter, C., Patric, C. and Robert, H.: Nitrous oxide emissions from municipal wastewater treatment, Environ. Sci. Technol., 29, 2352-2356 (1995).
- 5) Sümer, E., Weiske, A., Benckiser, G. and Ottow, J. C. G.: Influence of environmental conditions on the amount of N₂O released from activated sludge in a domestic waste water treatment plant, Experientia, 51, 419-422 (1995).
- 6) Bernet, N., Delgenes, N. and Moletta, R.: Denitrification by anaerobic sludge in piggery wastewater, Environ. Technol., 17, 293-300 (1996).
- 7) Schülthess, R. V., Kuhni, M. and Gujer, W.: Release of nitric and nitrous oxide from denitrifying activated sludge, Wat. Res., 29, 215-226 (1995).
- 8) Wu, X. L., Kong, H. N., Mizuochi, M., Inamori, Y., Xia, H. and Yi, Q.: Nitrous oxide emission from microorganisms, Japanese J. of Water Treatment Biol., 31 (3), 151-160 (1995).
- 9) Ritchie, G. A. F. and Nicholas, D. J. D.: Identification of the sources of nitrous oxide produced by oxidative and reductive processes in *Nitrosomonas europaea*, Biochem. J., 126, 1181-1191 (1972).
- 10) Hynes, R. K. and Knowles, R.: Production of nitrous oxide by *Nitrosomonas europaea*: Effects of acetylene, pH, and oxygen, Can. J. Microbiol., 30, 1397-1404 (1984).
- 11) Anderson, I. C., Poth, M., Homstead, J. and Burdige, D.: A comparison of NO and N₂O production by the autotrophic nitrifier *Nitrosomonas europaea* and the heterotrophic nitrifier *Alcaligenes faecalis*, Appl. Environ. Microbiol., 59, 3525-3533 (1993).
- 12) Castingnetti, D. and Thomas, C. H.: Heterotrophic nitrification among denitrifiers, Appl. Environmen. Microbiol., 47 (4), 620-623 (1984)
- 13) Thomas, J. G., Warren, A. K., Steven, C. W., Michael, B. M., Frederica, W. V. and Stanley, W. W.: Production of NO₂⁻ and N₂O by nitrifying bacteria at reduced concentration of oxygen, Appl. Environ. Microbiol., 40 (3), 526-532 (1980).
- 14) Mckenney, D. J., Drury, C. F., Findlay,

- B. M., McDonnell, T. and Gajda, C.: Kinetics of denitrification by *Pseudomonas fluorescens*: oxygen effects, Soil Biol. Biochem., 26 (7), 901-908 (1994).
- 15) Davis, K. J. P., Lloyd, D. and Boddy, L.: The effect of oxygen on denitrification in *Paracoccus denitrificans* and *Pseudomonas aeruginosa*, J. General Microbiol., 135, 2445-2451 (1989).
- 16) Shoun, H., Kim, D. H., Uchiyama, H. and Sugiyama, J.: Denitrification by fungi, FEMS Microbiol. Letters, 94, 277-282 (1992).
- 17) Robertson, L. A., Niel, E. W. J., Torremans, R. A. M. and Kuenen, J. G.: Simultaneous nitrification and denitrification in aerobic chemostat cultures of *Thiosphaera pantotropha*, Appl. Environ. Microbiol., 54, 2812-2818 (1988).
- 18) Hochstein, L., A., Betlach, M. and Kritikos, G.: The effect of oxygen on denitrification during steady-state growth of *Paracoccus halodenitrificans*, Arch. Microbiol., 137, 74-78 (1984).
- 19) Japan's Second National Communication under the United Nations Framework Convention on Climate Change (1997).
- 20) Kimochi, Y., Inamori, Y., Mizuochi, M., Xu, K. Q. and Matsumura, M.: Nitrogen Removal and N₂O Emission in a Full-scale Domestic Wastewater Treatment Plant with Intermittent Aeration, J. Ferment. Bioeng., (in press).
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