

Effect of salinity on nitrous oxide emission in the biological nitrogen removal process for industrial wastewater

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Abstract

The effects of wastewater salinity on both nitrogen removal efficiency and N₂O emission rate were investigated in a single nitrification process, a single denitrification process and an anoxic–oxic activated sludge process. In the single nitrification process, by increasing the salt concentration from 1.0 to 2.0 wt%, the N₂O conversion ratio in the steady state increased by 2.2 times, from 0.22 to 0.48%. In the single denitrification process, a minimal change in the N₂O conversion ratio was observed in the steady state even when the salt concentration was increased from 3.0 to 5.0 wt%. From the results of the anoxic–oxic activated sludge process, it was found that a salt concentration increase from 1.6 to 3.0 wt% significantly increases the N₂O conversion ratio from 0.7 to 13%. It is suggested that an increase in salt concentration markedly influences N₂O emission both directly and indirectly via the inhibition of N₂O reductase activity. The indirect inhibition is due to the high concentration of dissolved oxygen which is transported from the oxalic tank to the anoxic tank through the circulated liquid. Thus, the salt concentration should be maintained below 3.0% to suppress N₂O emission in an anoxic–oxic activated sludge process.

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1. Introduction

The excess emission of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) causes climate changes that threaten the existence of numerous living things on Earth, including humans. Among these greenhouse gases, N₂O has attracted much attention because of its special characteristics, as follows: (1) the global warming potential per molecule of N₂O is about 300 times higher than that of CO₂; (2) the concentration of atmospheric N₂O is increasing at almost the same rate as that of atmospheric CO₂; (3) N₂O is a significant ozone-depleting gas [1–3].

Biological nitrogen removal processes have been used in various wastewater treatment plants to prevent the eutrophication of closed-water bodies. Moreover, it was reported that

N₂O is emitted in both nitrification and denitrification processes. The amounts of N₂O emitted in several treatment processes for domestic wastewater and night soil have already been estimated [4–6]. However, N₂O emission characteristics in treatment processes for industrial wastewater, which often contains a high nitrogen load, have been scarcely investigated.

Thus, it is necessary to study N₂O emission in the biological nitrogen removal process for industrial wastewater. In studies on domestic wastewater and night soil treatment processes, it was reported that operational factors such as pH, dissolved oxygen (DO), carbon/nitrogen (C/N) ratio, and nitrogen load, which directly influence nitrification or total nitrogen (T-N) removal ability, affect N₂O emission [5]. On the other hand, it was reported that industrial wastewater contains various inorganic compounds such as NaCl and Na₂SO₄ at high concentrations compared with domestic wastewater, and that such high salt concentrations influence nitrogen re-

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Table 1
Operational condition of single nitrification process

SRT (day)	100
HRT (day)	2
Sludge amount (mg l^{-1})	2500
Aeration volume (l min^{-1})	2
pH	7.0
Salt concentration (wt%)	1.0–2.0

removal efficiency [7–9]. Therefore, it is necessary to clarify the effects of salinity, as well as other operating and environmental conditions, on N_2O emission for the precise evaluation of N_2O emission in industrial wastewater treatment processes.

In this study, the effect of influent wastewater salinity on N_2O emission in a single nitrification or denitrification process was initially investigated. Industrial wastewater with high concentrations of ammonia, nitrate, and NaCl (as in the case of metal-refining wastewater) was utilized as an example. The effects of salinity on N_2O emission and nitrogen removal efficiency in a laboratory-scale anoxic–oxic activated sludge process were evaluated.

2. Materials and methods

2.1. Single nitrification or denitrification process

An oxic or anoxic activated sludge bioreactor was operated continuously by increasing the salt (NaCl) concentration.

In the nitrification experiment, a substrate composed of 2360 mg l^{-1} $(\text{NH}_4)_2\text{SO}_4$ (500 mg N l^{-1}), 22 mg l^{-1} KH_2PO_4 , 5 mg l^{-1} $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 5 mg l^{-1} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and NaHCO_3 (for pH control and as an inorganic carbon source) was continuously fed into the oxic tank (volume: 3.0 l) under the conditions shown in Table 1. Salt concentration was increased from 1.0 to 2.0 wt% on day 15 when the nitrification efficiency and N_2O conversion ratio reached a stable value.

In the denitrification experiment, a substrate composed of 2960 mg l^{-1} NaNO_3 (500 mg N l^{-1}), 1710 mg l^{-1} CH_3COONa , 6 ml l^{-1} CH_3COOH , 22 mg l^{-1} KH_2PO_4 , 5 mg l^{-1} $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 5 mg l^{-1} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was continuously fed into the anoxic tank (volume: 3.6 l) under the conditions shown in Table 2. Salt concentration was increased from 3.0 to 5.0 wt% on day 24 when the nitrogen removal efficiency and N_2O conversion ratio reached a stable value.

Table 2
Operational condition of single denitrification process

SRT (day)	21
HRT (day)	1.6
Sludge amount (mg l^{-1})	2500
Sludge return ratio	0.5
pH	7.0
Salt concentration (wt%)	3.0–5.0

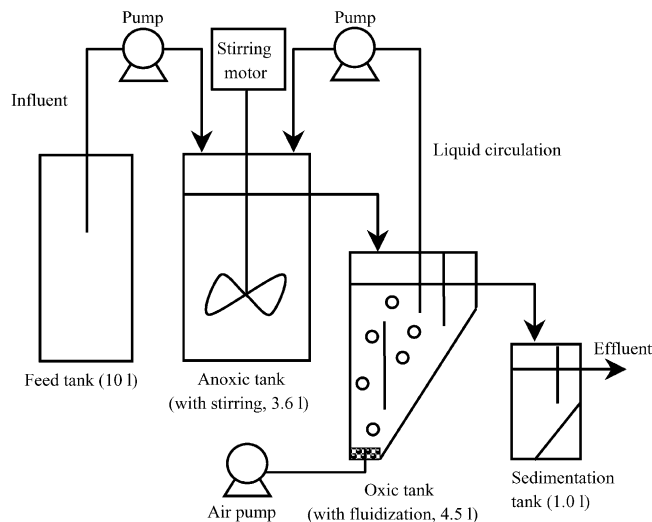


Fig. 1. Schematic diagram of anoxic–oxic activated sludge process.

2.2. Anoxic–oxic activated sludge process

An anoxic–oxic activated sludge process was operated continuously in a laboratory-scale bioreactor (anoxic tank volume: 3.6 l; oxic tank volume: 4.5 l). The salt concentration was increased to observe the salinity effect on N_2O emission and nitrogen removal efficiency. A schematic diagram of the experimental setup is shown in Fig. 1. Metal-refining wastewater containing 2590 mg l^{-1} $(\text{NH}_4)_2\text{SO}_4$ (550 mg N l^{-1}), 8590 mg l^{-1} NaNO_3 (1450 mg N l^{-1}), 10.25 ml l^{-1} CH_3COOH (3000 mg C l^{-1}), and 22 mg l^{-1} KH_2PO_4 was fed under the conditions shown in Table 3. Salt concentration was increased on day 49 (from 1.0 to 1.6 wt%) and day 192 (from 1.6 to 3.0 wt%), when the efficiencies of nitrification and nitrogen removal reached a stable value.

2.3. Gas sampling and analysis

To determine the N_2O conversion ratio, the concentrations of both N_2O emitted into the atmosphere and N_2O dissolved in the effluent water were measured. A gas-collecting chamber that covered the tank surface was used for collecting the N_2O emitted into the atmosphere. In the oxic tank, a portion of the aeration gas was collected directly into a gas-sampling bag through the chamber. In the anoxic tank, the gas-collecting chamber where the gas phase had been re-

Table 3
Operational condition of anoxic–oxic activated sludge process

DO (in the oxic tank) (mg l^{-1})	>2
SRT (day)	12
HRT (day)	3.6
Sludge amount (mg l^{-1})	2500
C/N ratio	2
Liquid circulation ratio	4
pH	7.5–8.5
Salt concentration (wt%)	1.0–3.0

placed by nitrogen was floated on the tank surface for 1 h. A portion of the gas phase in the chamber was then collected into a gas-sampling bag. On the other hand, the headspace method was used for collecting N_2O dissolved in the effluent water as follows: 30 ml of water and 30 ml of nitrogen gas were loaded into a 50-ml syringe, and 1 ml of 3000 mg l^{-1} $HgCl_2$ was added to reduce microbial activity. After shaking and standing for 1 h, the gas phase in the syringe was collected as the sample.

All gas samples were analyzed using a GC-ECD (GC-8A, Shimadzu Co., Kyoto, Japan), and N_2O was quantified according to the method of Kimochi et al. [10].

The N_2O emission rate from the oxic reactor, F_{oxic} , was calculated as follows:

$$F_{\text{oxic}} = \frac{Q\omega_{\text{air}}MP}{RTV_1} \quad (1)$$

where Q is the volumetric flow rate of aeration, ω_{air} the N_2O concentration in the aerated gases analyzed by GC-ECD, M the molecular weight of N_2O (44.02), P the atmospheric pressure (1.0 atm), R the gas constant ($0.082 \text{ l atm K}^{-1} \text{ mol}^{-1}$), T the temperature (K), and V_1 is the volume of the aeration reactor.

The N_2O emission rate from the anoxic reactor, F_{anoxic} , was calculated as follows:

$$F_{\text{anoxic}} = \frac{V_2\omega_{\text{air}}MP}{RTV_c \Delta t} \quad (2)$$

where V_2 is the head space volume of the anoxic reactor, ω_{air} the N_2O concentration of the head space, Δt the time between nitrogen gas replacement and gas sampling, and V_c is the volume of the gas-collecting chamber. All other symbols are the same as those in Eq. (1).

The dissolved N_2O concentration in a unit volume of the water sample, C_{N_2O} , was calculated as follows:

$$C_{N_2O} = \frac{(1 + \beta)\omega_{\text{dis}}MP}{RT} \quad (3)$$

where β is the Ostwald's solubility coefficient for N_2O and ω_{dis} is the N_2O concentration in the gas phase in the syringe.

The N_2O conversion ratio to the influent nitrogen, Y_{N_2O} , was calculated as follows:

$$Y_{N_2O} = \frac{F_{\text{oxic}} + F_{\text{anoxic}} + C_{N_2O}/\tau}{C_{T-N}/\tau} \quad (4)$$

where τ is the hydraulic residence time (HRT) of the total system and C_{T-N} is the total nitrogen concentration in the influent.

2.4. Water quality analysis

$NO_2^- - N$ and $NO_3^- - N$ concentrations were measured using an HPLC (column: IC-Anion-PW; Tosoh Co., Tokyo, Japan) with a UV detector (UV-8011; Tosoh Co.). Total organic carbon (TOC) concentration was measured using an automatic TOC analyzer (TOC-5000A; Shimadzu Co.).

$NH_4^+ - N$ concentration was measured using an automatic ion chromatograph (DX-120; Dionex, Osaka, Japan). All samples were filtered using glass filters (GF/C, Whatman, Springfield Mill, UK) before analysis.

3. Results and discussion

3.1. Influence of salt concentration on N_2O emission in single nitrification process

The time courses of N_2O conversion ratio and nitrification efficiency in a single nitrification process are shown in Fig. 2(a). Nitrification efficiency was maintained at more than 90% even after the salt concentration was increased from 1.0 to 2.0 wt%. In contrast, the average N_2O conversion ratio in the steady state increased by 2.2-fold, from 0.22 to 0.48%. Moreover, the magnified figure (Fig. 2(b)) for the time courses of N_2O conversion ratio and salt concentration after the salt concentration was increased to 2.0% clearly shows that the N_2O conversion ratio increased with increasing salt concentration. Since the sludge amount kept constant (2500 mg l^{-1}), it is suggested that increasing salt concentration increases N_2O production potential per unit nitrifying bacterial cell.

3.2. Influence of salt concentration on N_2O emission in single denitrification process

The time courses of N_2O conversion ratio and nitrogen removal efficiency in a single denitrification process are shown in Fig. 3(a). Nitrogen removal efficiency was maintained at

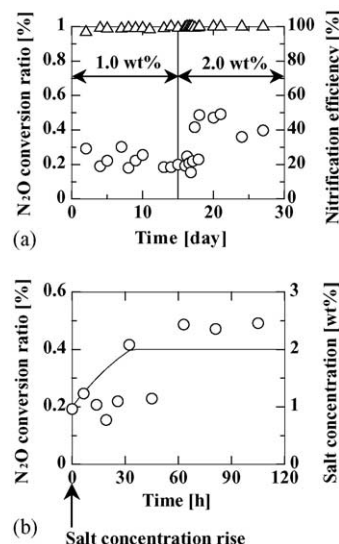


Fig. 2. Time courses of N_2O conversion ratio and nitrification efficiency (a) and magnified time courses of N_2O conversion ratio and simulated salt concentration after a salt concentration increase (b) in single nitrification process. (a) (○) N_2O conversion ratio, (△) nitrification efficiency and (b) (○) N_2O conversion ratio, (—) salt concentration.

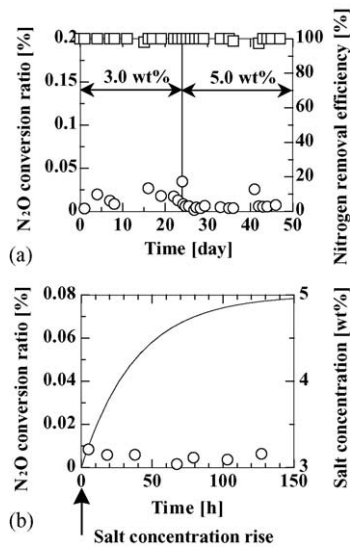


Fig. 3. Time courses of N_2O conversion ratio and nitrogen removal efficiency (a) and magnified time courses of N_2O conversion ratio and simulated salt concentration after a salt concentration increase (b) in single denitrification process. (a) (○) N_2O conversion ratio, (□) nitrogen removal efficiency and (b) (○) N_2O conversion ratio, (—) salt concentration.

more than 90% even after the salt concentration was increased from 3.0 to 5.0 wt%. The average N_2O conversion ratios were 0.018 and 0.0055% when the salt concentrations were 3.0 and 5.0 wt%, respectively. These results indicate that an increase in salt concentration has almost no influence on N_2O emission in a single denitrification process. Moreover, the magnified figure (Fig. 3(b)) for the time courses of N_2O conversion ratio and salt concentration after the salt concentration was increased to 5.0% also supports the notion that N_2O emission is independent of salt concentration (3.0–5.0%) in a single denitrification process.

3.3. Influence of salt concentration on N_2O emission in an anoxic–oxic continuous activated sludge process

Fig. 4 shows the time courses of TOC and $\text{NO}_x^- - \text{N}$ concentrations in the anoxic tank, and $\text{NH}_4^+ - \text{N}$ concentration in the oxic tank. Almost no change in water quality was observed in both tanks even after the salt concentration was increased from 1.0 to 1.6 wt%. However, when the salt concentration was increased from 1.6 to 3.0 wt%, $\text{NO}_3^- - \text{N}$ and TOC accumulated in the anoxic tank, while $\text{NH}_4^+ - \text{N}$ accumulated in the oxic tank. This showed that nitrification and denitrification efficiencies decreased due to the salt concentration change. Subsequently, $\text{NO}_3^- - \text{N}$ and TOC concentrations gradually decreased in the anoxic tank, and $\text{NO}_x^- - \text{N}$ was no longer detected on day 245. In contrast, no decrease in $\text{NH}_4^+ - \text{N}$ concentration was observed in the oxic tank. These results indicate that denitrification ability could recover completely even at a salt concentration of 3.0 wt%, but nitrification ability could not. On the other hand, the results obtained in the single denitrification process indicated that the salin-

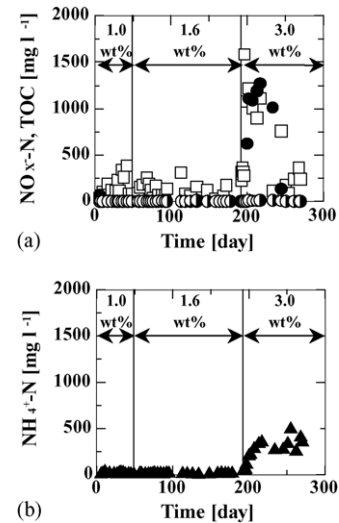


Fig. 4. Time courses of $\text{NO}_x^- - \text{N}$, $\text{NH}_4^+ - \text{N}$, and TOC concentrations in anoxic–oxic activated sludge process. (a) Anoxic tank and (b) oxic tank. (●) $\text{NO}_3^- - \text{N}$; (●) $\text{NO}_2^- - \text{N}$; (□) TOC; (▲) $\text{NH}_4^+ - \text{N}$.

ity as high as 5.0 wt% had almost no effect on denitrification ability (Fig. 3). Therefore, the temporal decrease in denitrification efficiency after switching to a salt concentration of 3.0 wt% was probably caused by a high DO concentration (0.5 mg l^{-1}) in the anoxic tank. When nitrification stopped due to the salt concentration increase, the circulated liquid from the oxic tank contained a relatively high DO.

Fig. 5 shows the time course of N_2O emission rate in the anoxic–oxic activated sludge process. By increasing the salt concentration from 1.0 to 1.6 wt%, the average N_2O emission rate in the steady state slightly increased in the oxic tank (from 1.9×10^{-3} to $8.6 \times 10^{-3} \text{ mg min}^{-1} \text{ l}^{-1}$), whereas that in the anoxic tank hardly changed. On the other hand, after the salt concentration was increased to 3.0 wt%, the average

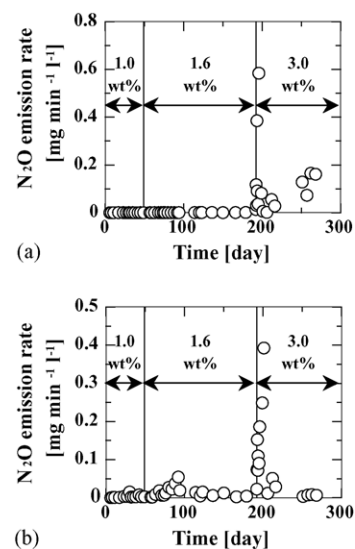


Fig. 5. Time course of N_2O emission rate in anoxic–oxic activated sludge process. (a) Anoxic tank and (b) oxic tank.

N_2O emission rate in the steady state in the anoxic tank increased to $0.13 \text{ mg min}^{-1} \text{ l}^{-1}$ (at around day 260), whereas that in the oxic tank, after a sharp peak (at around day 200), decreased to the same level ($0.64 \times 10^{-3} \text{ mg min}^{-1} \text{ l}^{-1}$) as that under the lower salinity condition. When nitrification stopped due to the salt concentration increase, N_2O was no longer emitted from the oxic tank, and at the same time, the circulated liquid from the oxic tank contained a relatively high DO. As a result, the DO concentration in the anoxic tank reached 0.5 mg l^{-1} , leading to constant N_2O emission in the anoxic tank (at around day 260). This result agrees with the reports that a high DO prevents the activity of N_2O reductase that catalyzes the reduction of N_2O into N_2 gas [11–15].

Fig. 6 shows the magnified time courses of N_2O emission rate and water quality immediately after the salt concentration was increased from 1.6 to 3.0 wt%. NH_4^+-N and NO_3^--N began to accumulate in the oxic and anoxic tanks at 90 and 180 h, respectively, after the salt concentration change. The observed differences in accumulation starting times between NH_4^+-N and NO_3^--N are due to the differences in the inhibitory factor to nitrification and denitrification: the former is directly inhibited by increase in salt concentration and the latter is inhibited by increase in DO due to the stop of nitrification.

N_2O emission rates in the anoxic and oxic tanks increased with increasing salt concentration until about 100 and 200 h, respectively, and then rapid decreases in N_2O emission rates were observed in both tanks (Fig. 6). These results demonstrate that N_2O emission in both oxic and anoxic tanks are completely suppressed when nitrification and denitrification

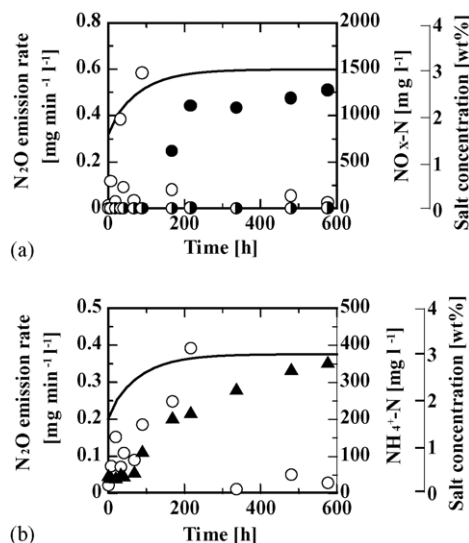


Fig. 6. Magnified time courses of N_2O emission rate, salt concentration, and NH_4^+-N or NO_3^--N concentration after a salt concentration increase in anoxic-oxic activated sludge process. (○) N_2O conversion ratio; (●) NO_3^--N ; (◐) NO_2^--N ; (▲) NH_4^+-N ; (—) salt concentration (simulated).

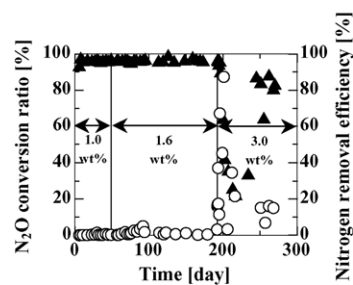


Fig. 7. Time courses of N_2O conversion ratio and nitrogen removal efficiency in anoxic-oxic activated sludge process. (○) N_2O conversion ratio and (▲) nitrogen removal efficiency.

efficiencies fall to quite low levels. In addition, considering that a high salinity such as 5.0 wt% in the synthesized wastewater had almost no effect on N_2O emission in the single denitrification process (Fig. 3), the transient accumulation of N_2O in the anoxic tank immediately after switching to a salt concentration of 3.0 wt% is supposedly ascribed to complex inhibition by high salinity and presence of heavy metals in the metal-refining wastewater. In fact, the actual wastewater used in this study contains heavy metals, such as Cu (0.24 mg l^{-1}), Mo (0.23 mg l^{-1}), Ni (0.44 mg l^{-1}), Pb (0.43 mg l^{-1}), and Zn (0.93 mg l^{-1}), most of which possibly inhibit activity of N_2O reductase and induce N_2O emission by the combined effects with a high salinity.

Fig. 7 shows the time courses of overall N_2O conversion ratio and total nitrogen removal efficiency in the anoxic-oxic activated sludge process. The average N_2O conversion ratios in the steady state were 0.2, 0.7, and 13%, at salt concentrations of 1.0, 1.6, and 3.0 wt%, respectively. By increasing the salt concentration from 1.6 to 3.0 wt%, N_2O conversion ratio increased sharply reaching a maximum of 90%. N_2O conversion ratio then decreased with decreasing nitrogen removal efficiency until day 245.

These results suggest that influent wastewater salinity has a direct influence on N_2O emission in the anoxic-oxic activated sludge process. In addition, when nitrification efficiency in the oxic tank decreases due to higher salt concentrations, secondary N_2O emission in the anoxic tank takes place (at around day 260). It is indicated that, in anoxic-oxic activated sludge process, nitrogen removal efficiency is subject to deteriorate and N_2O conversion ratio exhibit unexpectedly high at high salt concentrations, which are hardly observed in a single nitrification process or a single denitrification process. This is because inhibitory factors to enzyme activities are mixed by liquid circulation from the oxic tank to the anoxic tank.

In conclusion, in order to reduce N_2O emission in the biological nitrogen removal process for industrial wastewater, it is necessary to maintain the salt concentration at less than 3.0 wt%. In addition, some industrial wastewaters tend to contain heavy metals, some of which inhibit enzyme activity inducing N_2O emission even at low concentrations ($<1 \text{ mg l}^{-1}$)

owing to the combined effects with a high salinity. Therefore, heavy metals should be completely removed from such wastewaters prior to biological treatment.

4. Conclusions

In this study, the effect of salinity on N_2O emission in the biological nitrogen removal process for industrial wastewater was investigated. The following conclusions were drawn:

1. In a single nitrification process, a salt concentration increase from 1.0 to 2.0 wt% leads to a N_2O emission increase in the steady state. This could be due to an increase in the N_2O production potential per unit nitrifying bacterial cell.
2. In a single denitrification process, a salt concentration range from 3.0 to 5.0 wt% has almost no influence on N_2O emission in the steady state.
3. In an anoxic–oxic activated sludge process, after the salt concentration was increased to 3.0 wt%, nitrification and denitrification efficiencies decreased. After that, denitrification ability recovered, but nitrification ability did not. N_2O emission rates in the anoxic and oxic tanks transiently increased after the salt concentration was increased to 3.0 wt%. At the steady state, N_2O was no longer emitted from the oxic tank due to the stop of nitrification, whereas constant N_2O emission was observed in the anoxic tank. The transient decrease in denitrification efficiency and constant N_2O emission in the anoxic tank were due to a relatively high DO in the circulated liquid from the oxic tank to the anoxic tank, which was caused by insufficient nitrification in the oxic tank.
4. It is important to maintain a salt concentration below 3.0 wt% without any fluctuations if N_2O emission in the anoxic–oxic activated sludge process is to be suppressed.

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