Nitrogen removal from purified swine wastewater using biogas by semi-partitioned reactor

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Abstract

Nitrate and ammonium removal from purified swine wastewater using biogas and air was investigated in continuous reactor operation. A novel type of reactor, a semi-partitioned reactor (SPR), which enables a biological reaction using methane and oxygen in the water phase and discharges these unused gases separately, was operated with a varying gas supply rate. Successful removal of NO\textsubscript{3}\textsuperscript{−} and NH\textsubscript{4}\textsuperscript{+} was observed when biogas and air of 1 L/min was supplied to an SPR of 9 L water phase with a NO\textsubscript{3}\textsuperscript{−} and NH\textsubscript{4}\textsuperscript{+} removal rate of 0.10 g/L/day and 0.060 g/L/day, respectively. The original biogas contained an average of 77.2% methane, and the discharged biogas from the SPR contained an average of 76.9% of unused methane that was useable for energy like heat or electricity production. Methane was contained in the discharged air from the SPR at an average of 2.1%. When gas supply rates were raised to 2 L/min and the nitrogen load was increased, NO\textsubscript{3}\textsuperscript{−} concentration was decreased, but NO\textsubscript{2} accumulated in the reactor and the NO\textsubscript{3}\textsuperscript{−} and NH\textsubscript{4}\textsuperscript{+} removal activity declined. To recover the activity, lowering of the nitrogen load and the gas supply rate was needed. This study shows that the SPR enables nitrogen removal from purified swine wastewater using biogas under limited gas supply condition.
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1. Introduction

The processes for traditional nitrogen removal from wastewater consist principally of two sub-processes, nitrification and denitrification. In the nitrification process ammonium (NH\textsubscript{4}\textsuperscript{+}) is oxidized generally to nitrate (NO\textsubscript{3}\textsuperscript{−}) by autotrophic bacteria; in the subsequent denitrification process, NO\textsubscript{3}\textsuperscript{−} is reduced to dinitrogen gas (N\textsubscript{2}) by heterotrophic bacteria. The latter process requires electron donors like organic carbon sources for the heterotrophic microbial reaction. If wastewater is poor in organic carbon sources, carbon sources such as methanol have been supplemented, but doing so requires additional expense. It is reported that CH\textsubscript{4} is useable for the denitrification under circumstantially micro-aerobic conditions in the presence of CH\textsubscript{4} and O\textsubscript{2}. Denitrification using CH\textsubscript{4} has been experimentally applied to wastewaters that do not contain sufficient organic carbon for denitrification, such as landfill leachate (Werner and Kayser, 1991), nitrified municipal wastewater (Houbron et al., 1999), and ground water (Eisentraeger et al., 2001). Methane is present at high concentration in biogases produced in anaerobic waste treatment reactors and landfills, which would make it substantially less expensive to use than introduced chemicals. While use of CH\textsubscript{4} for denitrification would be advantageous at such sites from the point of view both of carbon source reuse and cost reduction, it has not yet been in actual use.

Methane use for NO\textsubscript{3}\textsuperscript{−} removal in the presence of CH\textsubscript{4} and O\textsubscript{2} has been investigated in the past. However, recently the simultaneous removal of NO\textsubscript{3}\textsuperscript{−} and NH\textsubscript{4}\textsuperscript{+} in the presence of CH\textsubscript{4} and O\textsubscript{2} has been reported in reactor operation and
batch incubation experiments on the lab-scale using artificial synthetic wastewaters (Khin and Annachhatre, 2004; Lee et al., 2001; Waki et al., 2002). It was supposed that nitrification, denitrification using methane oxidation intermediates and microbial assimilation result in simultaneous removal, although it was not fully elucidated. Both $\text{NO}_3^-$ and $\text{NH}_4^+$ are frequently contained in the wastewater targeted for nitrogen removal using $\text{CH}_4$ such as effluent from aerobic reactors treating animal wastewater, owing to the imperfect nitrification that occurs due to high and varying $N$ concentrations (Tanaka et al., 1999). Therefore, simultaneous removal of $\text{NO}_3^-$ and $\text{NH}_4^+$ would be necessary for practical application of nitrogen removal using $\text{CH}_4$. However, there are few studies with actual wastewater.

To carry out the $\text{NO}_3^-$ removal process using methane and oxygen, conventional laboratory-scale reactors such as activated sludge, trickling filter, and fluidized bed reactors are operated with a mixed supply of $\text{CH}_4$ and $\text{O}_2$ (Houbron et al., 1999; Thalasso et al., 2004; Werner and Kayser, 1991). Studies with these reactors targeting $\text{NO}_3^-$ removal have shown obvious $\text{NO}_3^-$ removal activity. However, these types of reactors are not suitable for full-scale implementation since their off-gas contains unused $\text{CH}_4$ mixed with $\text{O}_2$, which is difficult to reuse as fuel. Methane must be highly concentrated for use as fuel; e.g., more than 55% $\text{CH}_4$ for the generation of electricity. Moreover, the mixture becomes explosive if the concentration of $\text{CH}_4$ in air is 5–14%. The release of off-gas containing $\text{CH}_4$ into the atmosphere is also inappropriate because $\text{CH}_4$ is greenhouse gas with high global-warming potential. However, the novel semi-partitioned reactor (SPR) has been shown to work by subjecting $\text{CH}_4$ and $\text{O}_2$ to the water phase for microbial reaction, enabling the separate discharge of undissolved $\text{CH}_4$ and $\text{O}_2$ (Waki et al., 2005). In one lab-scale operation of the SPR, $\text{NO}_3^-$ was successfully removed from synthetic wastewater under supply of $\text{CH}_4/\text{CO}_2$ gas mixture and air (Waki et al., 2005). However, operation of the SPR with actual wastewater and actual biogas are indispensable for practical application. In this study, we examined the performance of the SPR removing $\text{NO}_3^-$ and $\text{NH}_4^+$ in purified swine wastewater, supplied only with air and actual biogas from the anaerobic treatment of swine wastewater.

2. Methods

2.1. Reactor operation

The semi-partitioned reactor (SPR) used in this experiment is shown in Fig. 1, and allows the mixing of dissolved $\text{CH}_4$ and $\text{O}_2$ gases in the liquid phase and discharge of unused these unused gases separately (Waki et al., 2005). It has a 9 L liquid phase and 3 L headspace. A partition completely divided the headspace of the SPR into two spaces, but only partially divided the liquid layer. At the effluent outlet of the reactor, a mesh sheet (opening less than 0.5 mm) was attached to prevent sludge washout. A sludge settling tank was set up downstream of the SPR. The SPR was stirred for 1 min every 3 h to mix the settled sludge in nooks. The sludge of the settling tank was

![Diagram of the semi-partitioned reactor (SPR) and process of methane-dependent denitrification treatment. Items marked “P” and “B” are pumps and blowers, respectively.](image-url)
2.2 Analytical method

Ten swine wastewater that was treated by the upflow anaerobic sludge blanket (UASB) reactor and then by a trickling filter (Tanaka et al., 2006) was used as the influent to the SPR with a hydraulic retention time of 2.1 days. Effluent from the trickling filter contained both NO$_3^-$ and NH$_4^+$ because nitrification was not complete. In order to increase the nitrogen load to SPR, NaNO$_3$ and NH$_4$Cl was added to the effluent from the trickling filter. Seed sludge collected from the actual activated sludge plant which treats livestock wastewater in the National Institute of Livestock and Grassland Science (Tsukuba, Japan) was added to the SPR and acclimatized for a total of six months, including an intermission for the winter season. The SPR was maintained at an average 31°C (range 29.6–35.1). To supply CH$_4$, biogas from the UASB reactor was supplied to the SPR with 1, 1.5 or 2 L/min. To supply O$_2$, air was supplied at the same rate as the biogas. $K_{L_a}$ of the diffuser was 7.7 L/h, 9.8 L/h, and 14.2 L/h at 30°C, for the air supply rates of 1 L/min, 1.5 L/min, and 2 L/min, respectively.

2.2.1 Nitrate removal in the SPR

The concentrations of NO$_3^-$, NO$_2^-$ and SO$_4^{2-}$ were measured by an ion exchange chromatograph (HIC-VP super, Shimadzu, Japan) with a column Shim-pack IC-A3 at a column temperature of 40°C with mobile phase 8 mM p-hydroxybenzoic acid, 3.2 mM bis-tris, and 50 mM Boric acid. The concentrations of NH$_4^+$ were measured by an ion exchange chromatograph (DX-120, Dionex, Japan) with column Ion Pac CS12A at Col. Temp. 35°C with mobile phase 20 mM methanesulfonic acid. BOD (20°C, 5 days) was determined by a pressure sensor method using BOD Track (Hach Co., USA), with a nitrification inhibitor. The DO concentration was determined by a dissolved-oxygen meter (DO-24 P TOA-DKK Co., Japan). The pH value was measured with a glass electrode (B-211, Horiba, Japan). The mixed liquor volatile suspended solid (MLVSS) was determined after drying the precipitates from the wastewater after washing them twice by centrifuging at 1000 g, and decanting and resuspending in deionized water at 105°C and 600°C.

The concentrations of CH$_4$ in the biogas and off-gases were measured by a thermal conductivity detector attached to a gas chromatograph (Model 802T, Ohokura Riken, Japan), as described by Yokoyama et al. (2007). N$_2$O was measured by an electron capture detector attached to a gas chromatograph (GC-14A, Shimadzu, Japan) with a column of Unibeadz C 60/80 mesh at column temperature 45°C with a carrier of 95% Ar and 5% CH$_4$. The concentrations of H$_2$S in the supplied gases and off-gases were measured with a detection tube and a gas sampler (Gas-tech, Japan).

3. Results

3.1 Nitrate removal in the SPR

Raw swine wastewater contains a high concentration of BOD and nitrogen compounds; however, as a result of anaerobic treatment followed by aerobic treatment of the trickling filter, almost all of the BOD was removed and NH$_4^+$ was partially nitrified to NO$_3^-$ (Tanaka et al., 1999, 2006). In the present study, effluent from the trickling filter reactor was used as influent to the SPR. The influent was a neutral pH at 6.9 (range 5.4–8.1), and the BOD concentration was as low as 21 (range 0–44) mg/L. At the first month of the experimental period in which biogas and air was supplied to the SPR at 1 L/min, the DO concentration in the reactor was as low as 0.1 (range 0–0.4) mg/L, and a decrease of NO$_3^-$ concentration was observed without NO$_2^-$ accumulation (Fig. 2). The average removal rate for NO$_2^{-3}$ was 0.10 ± 0.02 gN/L/day. To increase the removal activity, the gas supply rate was increased from 1 to 2 L/min on the 36th day. At first, the NO$_3^-$ removal activity increased, but when the nitrogen load was increased, NO$_3^-$ accumulated and NO$_2^-$ removal remained steady. Thus, the NO$_3^-$ removal activity declined (Fig. 2). At this gas condition, DO concentration in the reactor slightly increased to 0.6 (range 0.2–1.0) mg/L. When the nitrogen load lowered on the 74th day and the gas supply rate was lowered on the 102nd and 116th days, NO$_3^-$ accumulation and NO$_2^{-3}$ removal activity recovered. The last 36 days with the gas supply rate of 1 L/min, the NO$_2^{-3}$ removal rate was 0.10 ± 0.02 gN/L/day. In the same gas supply period, MLVSS in the reactor was an average 4300 mg/L, the BOD in the effluent was an average 110 mg/L, and the pH was 7.1.

3.2. Ammonium removal

During the first one month of the experimental period, in which biogas and air was supplied to the SPR with 1 L/min, a decrease of NH$_4^+$ concentration was observed with a removal rate of 0.046 ± 0.023 gN/L/day (Fig. 2). When the gas supply rate was increased from 1 to 2 L/min on the 36th day, the removal activity increased, but when the nitrogen load was increased, the removal declined. As the nitrogen load lowered again, NH$_4^+$ removal activity recovered. In the last 36 days with a gas supply rate of 1 L/min, the NH$_4^+$ removal rate was 0.060 ± 0.015 gN/L/day.

3.3 Methane gas separation

As shown in Fig. 3, the CH$_4$ concentration was almost constant. It averaged 77.2 (range, 71.6–80.4) % in the first experimental period with the gas supply side at 1 L/min. The off-gas CH$_4$ concentration from the biogas supply side
(cell A side) also stayed steady at 76.9 (range 70.2–81.2) %, while the off-gas from the air supply side (cell B side) contained a small concentration of CH₄ averaging 2.1 (range, 1.1–5.2) %, in that period. Gas compounds other than CH₄ in biogas and off-gas from the biogas supply side included CO₂, which was produced at anaerobic treatment, and N₂ and O₂, which were contaminants from the ambient air (data not shown). In many cases, N₂O, which is a greenhouse gas, is emitted in the biological nitrogen removal process, during both nitrification and denitrification. In our experiment, off-gas from the air supply side (cell B side) contained N₂O at an average concentration of 9.7 (range, 3.9–26.5) ppm in the first period. Off-gas from both the biogas side and the air side contained N₂O; the ratio of the loss as N₂O to total removed nitrogen was estimated about 1.2%, which was smaller than that observed in N₂O removal using a CH₄ experiment with artificial wastewater (5–13%) (Waki et al., 2005).

3.4. H₂S removal by the SPR

In many cases, biogas from anaerobic treatment contains a high concentration of H₂S. In our experiment, H₂S averaging 170 ppm with a 0–1000 ppm range was contained in the biogas (Fig. 4). However, it was removed to 0–31 ppm throughout the experiment by passing it through the SPR, probably due to the absorption of H₂S by liquid in the reactor. Some of the absorbed H₂S must have been oxidized to SO₂⁻, because the SO₂⁻ concentration was 15 mgS/L in the influent and increased to 61 mgS/L in the effluent (Fig. 4). The average H₂S removal rate and SO₂⁻ production was 0.043 ± 0.059 gS/L/day and 0.022 ± 0.015 gS/L/day, respectively.

4. Discussion

In this study we performed nitrogen removal from actual wastewater with biogas using the SPR. This method is applicable for an actual wastewater treatment facility, including anaerobic treatment and biogas energy use. In many actual livestock wastewater treatment processes, nitrified wastewater contains both NO₃⁻ and NH₄⁺ due to high and varying nitrogen concentrations. Therefore, in this study we used purified swine wastewater containing both NO₃⁻ and NH₄⁺. During the SPR operation with biogas and air supply with 1 L/min, both NO₃⁻ and NH₄⁺ markedly decreased (Fig. 2). The BOD concentration in the influent was too low to be used as a carbon source for the NO₃⁻ removal; e.g., it was estimated that no more than 7 mgN/L NO₃⁻ could be removed by ordinary denitrification using the BOD in the influent (21 mg/L) with a BOD/N ratio of 3. H₂S in biogas might be used as an electron donor for denitrification; however, it was not sufficient for the observed NO₃⁻ removal; e.g., hypothetically no more than an average of 51 mgN/L NO₃⁻ could be removed by denitrification using H₂S even if all of the removed H₂S was used for denitrification. Therefore, NO₃⁻ removal observed in this study was carried out with methane. In previous studies with artificial wastewater, the simultaneous removal of NO₃⁻ and NH₄⁺ in the presence of CH₄ and O₂ has been reported (Khin and Annachhatre, 2004; Lee et al., 2001; Waki et al., 2002). Our results showed that simultaneous removal is possible with actual wastewater and biogas.

In our study, the maximum inorganic nitrogen removal activity was observed under the condition supplying 1 L/min of CH₄ and O₂. At this condition, the specific inor-
Organic nitrogen removal rate was calculated as 1.65 mgN/gVSS/hr, and this value is higher than that from one experiment involving artificial wastewater containing NO\textsubscript{3} and NH\textsubscript{4}, 1.1 mgN/gVSS/hr (Khin and Annachhatre, 2004), but lower than that from another experiment involving artificial wastewater containing NO\textsubscript{3} and NH\textsubscript{4}, 2.5 mgN/gVSS/hr (Lee et al., 2001). In an experiment with artificial wastewater containing NO\textsubscript{3}, Waki et al. reported the importance of having a CH\textsubscript{4}/O\textsubscript{2} molar ratio in the supplied gas greater than 1.0 and a high supply rate of O\textsubscript{2} to have high NO\textsubscript{3} removal activity, (Waki et al., 2004). In our study, the CH\textsubscript{4}/O\textsubscript{2} gas supply ratio was 3.6, satisfying the greater-than-1.0 rule; however, the increase of the gas supply rate with a high nitrogen load caused NO\textsubscript{3} accumulation and a decrease of the NH\textsubscript{4} removal activity while NO\textsubscript{3} decrease was maintained. Too-high gas supply and nitrogen load conditions likely resulted in incomplete denitrification and inhibition of microbial activity for ammonium removal by the accumulated NO\textsubscript{3}. In practical application, improvement of reactor operating conditions would be required to prevent overly high nitrogen concentration in the reactor; this could be achieved, for example, by diluting the wastewater.

The SPR is advantageous for producing off-gas containing a high concentration of CH\textsubscript{4} because the bubbles of biogas and air can be collected separately by semi-partition...
(Waki et al., 2005). In the present study, the decrease of CH₄ concentration in off-gas from the biogas supply side was insignificant; therefore, the off-gas would be usable for the production of heat or electrical energy through combustion. In addition, desulfurization equipment is necessary in order to use biogas as an energy source, since H₂S is corrosive. For example, desulfurization facilities like chemical absorbents or bio-scrubbers are generally used for energy use of the biogas, in biogas plants. In the SPR operation, much of the H₂S in the biogas was removed by the reactor (Fig. 4), showing that the SPR could be used as desulfurization equipment.

In practical use of the reactor, the mass balance of CH₄ consumption to nitrogen removal is important. Although it could not be estimated in this study, as the off-gas volume could not be measured precisely, a ratio of about 7–8 of CH₄ consumption to inorganic nitrogen removal was observed for NO₃⁻ and NH₄⁺ removal in the previous study (Waki et al., 2002). When the ratio in the previous study was adopted, biogas produced in anaerobic wastewater treatment of low concentration of BOD and BOD/N ratio would be insufficient for nitrogen removal using CH₄. However, when wastes contain high concentrations of BOD with a high BOD/N ratio, and methane fermentation and then the first step post-treatment for the nitrogen removal using residual BOD is carried out, as in a proposed methane fermentation system for a swine slurry (Kataoka et al., 2002), nitrogen removal using CH₄ would be possible as a final treatment using some portion of the produced biogas. A precise estimation of the ratio in a continuous reactor would be required.

The off-gas from the air supply side contained a small but not negligible concentration of CH₄. Improvement to decrease the CH₄ exhaust might be required in view of the explosion risk, carbon source loss, and greenhouse effect of CH₄. The contamination of CH₄ in the off-gas from the air supply side must be attributed to gas transfer from dissolved CH₄ to bubbles in the air supply side, and the bubble transformation from the biogas supply side to the air supply side. The contamination of CH₄ due to the latter influence would be decreased by improvements in reactor construction like setting the diffuser on an end side wall and extension of the partition, when the reactor size of SPR is increased. The exact control of the biogas supply rate would also decrease the contamination of CH₄ by the former influence.

5. Conclusion

The results of this study demonstrated nitrogen removal from purified swine wastewater using biogas produced during anaerobic treatment. The SPR had a successful NO₃⁻ and NH₄⁺ removal and off-gas discharge ability that could be used as energy in a limited-gas condition. To apply nitrogen removal with CH₄ using the SPR, further study to improve the nitrogen removal rate avoiding NO₃⁻ accumulation, and estimation of the CH₄ consumed in the nitrogen removal is required.

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