Development of a new type of anaerobic digestion process equipped with the function of nitrogen removal

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Abstract In order to develop a new type of anaerobic digestion process equipped with a nitrogen removal function, denitrification of nitrate nitrogen (NO_3-N) in anaerobic acidogenesis of organic fraction of municipal waste (OFMSW) was investigated by two semi-continuous reactors. Reactor 1 and Reactor 2 were fed by 3% and 7% of solids concentration of synthetic garbage, respectively. Generation of nitrogen gas (N_2) and ammonium nitrogen (NH_4-N) was simultaneously observed in the low load of nitrate (NO_3-N) (below 0.68g NO_3-N/L). In Reactor 1, ammonium nitrogen generation decreased as the addition of nitrate increased. Finally, the increase of the addition of nitrate resulted in the increase of acetic acid production.

Keywords Anaerobic acidogenesis; COD/NO_3-N ratio; denitrification; nitrogen removal; total solids concentration

Introduction

In recent years, global environmental problems have increased, and anaerobic digestion process has been rising in importance from the standpoint of recovery and preservation of energy resources. Anaerobic digestion has a unique advantage to produce methane gas. However, it has a disadvantage of producing ammonium nitrogen as the result of anaerobic degradation of protein and a high concentration of ammonium nitrogen is contained in the supernatant from the digestion tank. Much methanol is demanded for the removal of ammonium nitrogen in the biological nitrification-denitrification process. It is necessary to develop a new type of anaerobic digestion process equipped with ammonium nitrogen removal in order to save the amount of methanol used for denitrification in the supernatant treatment process.

In this study, the effects of nitrate on acidogenesis in anaerobic digestion were investigated to develop a new type of anaerobic digestion process equipped with the function of nitrogen removal by semi-continuous experiments using synthetic garbage as the substrate. It was assumed that most of the ammonium nitrogen in the supernatant was nitrified to nitrate and returned to acidogenic or methanogenic reactors in this study. The above-mentioned objectives were investigated based on the following three kinds of experimental results.

Nitrogen removal function of acidogenesis (Goo *et al.*, 2001)

Both acidogenesis and denitrification were observed in an acidogenic reactor of two-phase anaerobic digestion fed with synthetic substrate containing glucose and nitrate. The digestion temperature was 35 °C. KNO_3 was added to the reactor as nitrate nitrogen (NO_3-N). The acidogenic reactor to which nitrate was not added completely consumed glucose. However, the glucose degradation rate decreased as the COD/NO_3^--N ratio of the substrate

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decreased. When nitrate was added to the acidogenic reactor, the accumulation of nitrite was not observed under the low COD/NO_3^--N ratio. Based on nitrogen balance, the conversion ratios on influent nitrogen to nitrogen gas at COD/NO_3^--N ratios of 50, 30, 15, 9, 6 and 3 were 10.3, 14.2, 16.2, 21, 56.6 and 25.9%, respectively. The highest conversion ratio of nitrogen gas was also observed at the COD/NO_3^--N ratio of 6. Based on COD balance, the ratio of denitrifying bacterial biomass to influent COD was increased as the COD/NO_3^--N ratio in the substrate decreased from 9 to 3.

Nitrogen removal function of methanogenesis (Goo *et al.*, 2002)

In the methanogenic reactor to which nitrate was not fed, 59.5% of influent COD was converted to methane. On the other hand, the conversion efficiency decreased to 24.2% as the COD/NO_3^--N ratio of the substrate decreased to 6. Based on the COD balance, each ratio of NH_4^+-N and NO_2^--N to influent COD increased as the COD/NO_3^--N ratio of the substrate decreased. The highest conversion ratio of nitrate to nitrogen gas was observed at the COD/NO_3^--N ratio of 9. The oxidation reduction potential (ORP) of the reactor contents was maintained between –179 mV and –106 mV if the COD/NO_3^--N ratio were higher than 6, however, the ORP became extremely high level of +429 mV as the COD/NO_3^- ratio decreased from 6 to 3. The growth yields of mixed cultures of methanogenic and denitrifying bacteria were very close when the COD/NO_3^--N ratio of the substrate fed to those cultures was higher than 6.

Removal of nitrogen in anaerobic acidogenesis of organic fraction of municipal waste (OFMSW) by batch experiment (Figure 1)

For the application of the above-mentioned experimental results to a practical organic waste, the removal of nitrate in anaerobic acidogenesis of organic fraction of municipal waste (OFMSW) was investigated by batch and continuous experiments. The reason why nitrified supernatant was returned to the acidogenic reactor for denitrification was as follows. It is known that the optimum range of ORP, –60 mV to –220 mV, for biological denitrification is the almost the same as for acidogenesis. Moreover, acidogenesis is stable to the change in environmental factors such as pH, temperature and accumulation of volatile fatty acids, comparing with methanogenesis, and plenty of organic materials are prepared for denitrification in an acidogenic reactor. KNO_3 was added to the reactor as nitrate nitrogen (NO_3^--N). The batch experiment was conducted to investigate the influences of OFMSW concentrations and COD/NO_3^--N on denitrification in acidogenesis at 35 °C. A vial of 120 ml volume was used as the batch reactor, and 50 ml of seed sludge and 30 ml of OFMSW were added to the vial. It was observed that the nitrogen gas production increased as the total solid concentration and the COD/NO_3^--N ratio decreased. The

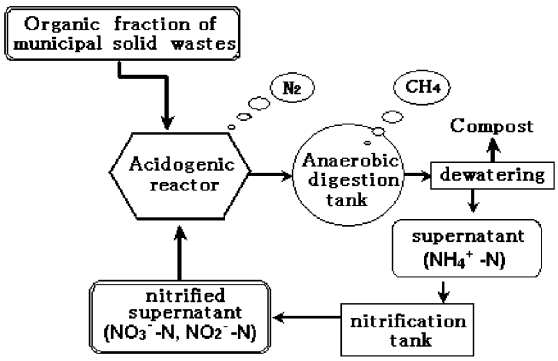

Figure 1 Anaerobic digestion process with nitrogen removal function

most nitrogen gas production was obtained at the COD/NO_3^--N ratio of 4, and total gas productions were 142 mL/gVSS and 107 mL/gVSS, respectively, in the reactors with the total solids of 3% and 5%. At the ratios of 9 and 15, conversion efficiency of NO_3^--N to nitrogen gas became higher, and ammonium nitrogen accumulated in the reactor. More than 70% of NO_3^--N was removed as the total solid concentration decreased and COD/NO_3^--N ratio increased and high percentage of NO_3^--N remained in the reactor at 10% of total solids concentration.

Materials and methods

Experimental apparatus and condition

The synthetic garbage used in this study was composed of vegetables, fruits, meat, fish, rice, and tea grounds, as shown in Table 1, which was selected based on the typical component of the organic fraction of municipal solid wastes (OFMSW) in Japan. They were shredded and mixed in a blender and then adjusted to 15.9% of TS by adding tap water.

Two semi-continuous reactors of 3L capacity with 2.5L working volume were used in the present study. Reactors 1 and 2 were fed by 3% and 7% of solids concentration of synthetic garbage, respectively. Figure 2 illustrates the scheme of the experimental apparatus. The reactors were installed in a temperature-controlled chamber maintained at 35 ± 1 °C. The reactors were stirred by four sheets of stroke paddle. In order to measure the volume of gas production, the reactor was connected to a gas collection cylinder placed in an acidic saturated salt solution of NaCl with 2% sulfuric acid. The reactors were operated at HRT of 2 days. The synthetic garbage was prepared daily and stored in a substrate reservoir maintained at 4 ± 1 °C. The contents of the substrate tank were continuously stirred with a magnetic stirrer. The substrate was injected into the reactor twice a day. The seed sludge was obtained from the mesophilic digestion tank in the Sendai municipal sewage treatment plant. The inoculum was acclimatized to 3% of solid concentration of synthetic garbage for more than one month. Table 2 shows the detailed experimental conditions.

Table 1 The composition of synthetic garbage used in this study

Food group	Materials	Weight	
		g	Wt(%)
Vegetables	Cabbage	130	41
	Carrot	130	
	Potato	130	
Fruit	Banana (skin)	120	25
	Orange (peel)	120	
Meat and fish	Meat (beef and pork)	80	16
	Fish (salmon)	80	
	Eggshell	30	3
Staple foods	Rice	100	11
Taste drinks	Tea grounds	30	3
Total		950	100

Table 2 Summary of the experimental condition

TS (%)			3						5		
COD (g/L)			34.2(17.1g COD/L/day)						90.6(45.3g COD/L/day)		
COD/NO_3–N	Blank	100	75	50	25	15	Blank	100	75	50	25
NO_3–N (g/L)	0	0.34	0.46	0.68	1.37	2.28	0	0.91	1.21	1.82	3.62
NO_3–N load rate (g NO_3–N /day)	0	0.17	0.23	0.34	0.68	1.14	0	0.45	0.60	0.91	1.81
pH	6.0 ± 01			6.8 ± 0.2			6.0 ± 0.1			6.8 ± 0.2	

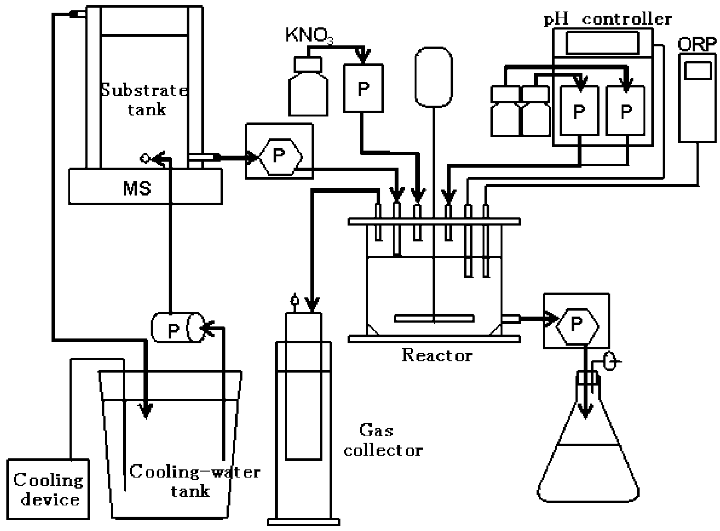

Figure 2 Schematics of the experimental apparatus

Analytical method

The percentage of N_2O in the gas was determined using a gas chromatograph (Shimadzu GC-14B) equipped with an electron capture detector (ECD) and a 3 m column packed with Porapak Q (80/100 mesh). The operational temperatures at the injection port, the column oven and detector were 60, 80 and 340 °C, respectively. N_2 was used as the carrier gas at a flow rate of 26.3 mL/min. The percentage of N_2 in the gas was analyzed using a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and a 2 m stainless column packed with Porapak T (50/80 mesh). The operational temperatures at the injection port, the column oven and detector were 100, 70 and 100 °C, respectively. The concentrations of volatile fatty acids (VFAs) were determined using a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector (FID) and a 2 m glass column packed with Unisole F-200 (30/60 mesh). The operational temperatures at the injection port, the column oven and the detector were 180, 165 and 180 °C, respectively. Helium was used as the carrier gas for the determinations of N_2 and VFAs at a flow rate of 30 mL/min. NH_4^+ concentration was determined using an ionic chromatograph (Shimadzu) with a Shimadzu Shim Pack IC-C3 column at 40 °C. The IC was equipped with a conductivity detector (COD 6A). The mobile phase consisted of 2.5 mmol oxalic acid dehydrated at a flow rate of 1.2 mL/min. NO_2^- and NO_3^- concentration was determined using a second IC of the same model with a Shim Pack IC-A3 column at 40 °C. The IC was equipped with a conductivity detector (COD 6A). The mobile phase consisted of 8.0 mmol p-hydroxybenzoic acid and 3.2 mmol Bis-Tris at a flow rate of 1.2 mL/min.

Results and discussion

Operational characteristics

Figure 3 shows the time course of total and nitrogen gas production rates in Reactor 1 to which 3% of garbage was fed for 200 days since the experiment started and Figure 4 shows those in Reactor 2 to which 7% of garbage was fed for 120 days. Here, the concentration of nitrate was increased in steps. Nitrogen gas production rates in Reactor 1 to which nitrate was added with COD/NO_3^--N ratios of blank, 100, 75, 50, 25 and 15, were 94.7, 87.3, 208, 337, 671 and 924 mL/L/day, respectively. Nitrogen gas production rates in Reactor 2 to which nitrate was added with COD/NO_3^--N ratios of blank, 100, 75, 50, 25 and 15, were 234, 175, 420, 498 and 304 mL/L/day, respectively. Nitrogen production increased as the concentration added to the reactor increased, but it rapidly decreased with COD/NO_3^--N ratio of 50.

Effects of COD/NO_3^--N ratio on VFA production

Figures 5 and 6 show the effects of nitrate addition on volatile fatty acids (VFA) production in Reactors 1 and 2, respectively. Acetic acid production remarkably increased as the amount of nitrate added to the reactor increased. Goo *et al.* (2001) also reported that nitrate addition promoted acetic acid production in the continuous experiments.

Acidogenic fermentation experiment was conducted using glucose as the substrate. In Reactor 1 in Figure 5, acetic acid and propionic acid rapidly decreased when nitrate was added with the concentrations of above 0.68 g NO_3^--N/L. Rustrian *et al.* (1997) reported that the cause of little production of VFA in addition with low COD/NO_3^--N ratio was not due to the suppression of VFA production, but due to the suppression of the consumption of nitrate by newly grown denitrifying bacteria and that the addition of high concentration of nitrate did not suppress the VFA production.

In Reactor 2 in Figure 6, acetic acid production stopped temporarily as the nitrate concentration added to the reactor increased, and when COD/NO_3^--N ratio increased by 25 (3.62 g NO_3^--N/L), volatile fatty acids except acetic acid rapidly decreased and only high concentration (15.5 g/L) of acetic acid was detected and 253 mg NO_3^--N/L of nitrate remained in the reactor. It is considered that acetic acid is the carbon source suitable for denitrifying bacteria as an electron donor (Akunna *et al.*, 1993), but much acetate suppressed denitrification action while much nitrate promoted acetic acid production.

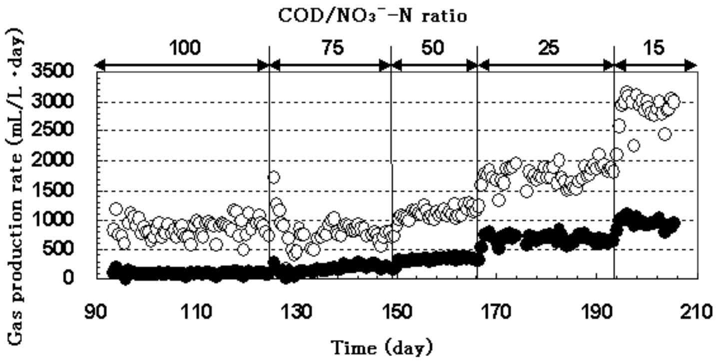

Figure 3 The time course of total and nitrogen gas production rates in Reactor 1 (○ total gas, ● N_2 gas)

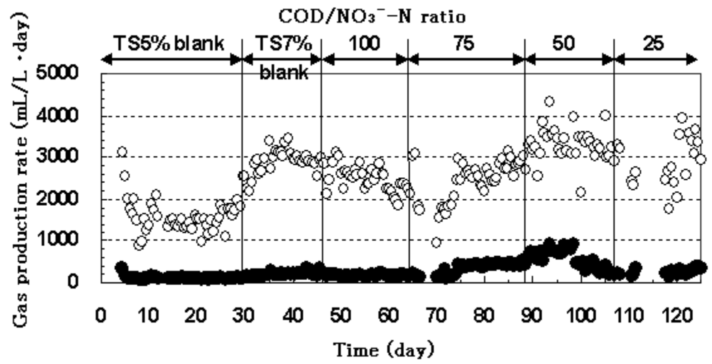

Figure 4 The time course of total and nitrogen gas production rates in Reactor 2 (○ total gas, ● N_2 gas)

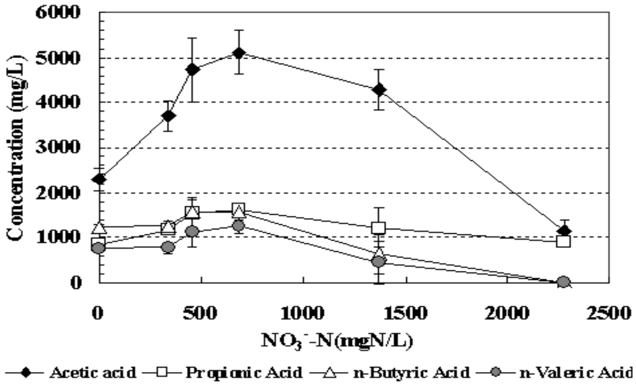

Figure 5 Effects of nitrate addition on VFAs production in Reactor 1

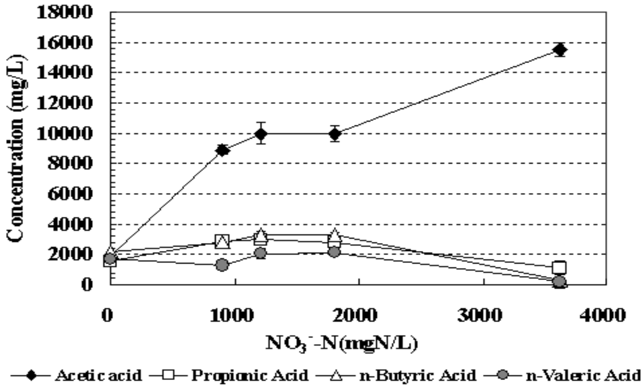

Figure 6 Effects of nitrate addition on VFAs production in Reactor 2

The behaviour of nitrogen composition

In order to investigate the behaviour of the change in nitrate added to the reactor, the percentages of gaseous, organic and inorganic nitrogen were calculated. The changes in nitrogen compositions in Reactors 1 and 2 are shown in Figures 7 and 8, respectively. In Reactor 1, nitrogen gas and ammonium nitrogen production stood somewhat high when the concentration of nitrate added to the reactor was in the low range and the COD/NO_3^--N ratio was above 50. In Reactor 2, the percentages of the conversion of nitrate to nitrogen gas were very low, 10%, on the other hand, those of the conversion of it to ammonium nitrogen and nitrous oxide (N_2O) were high. In Reactor 2, the acidogenic fermentation of garbage with high total solids concentration was promoted by the addition of nitrate, and the produced acetic acid suppressed denitrification and the nitrate reduction was exceeded. It is

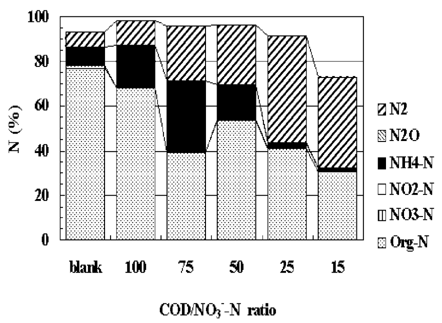

Figure 7 Nitrogen mass balance in Reactor 1

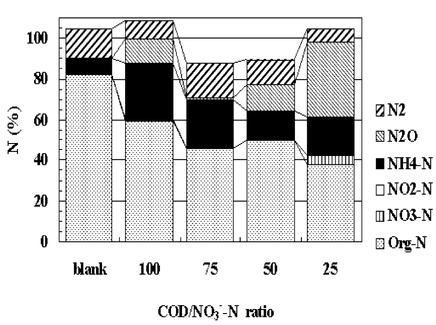

Figure 8 Nitrogen mass balance in Reactor 2

considered that the nitrate reduction (denitrification) was suppressed and high concentration of intermediate metabolite was produced, as the amount of nitrate added to the reactor increased.

Conclusions

In this study, the effects of COD/NO_3^--N ratio in the substrate on denitrification and acid-producing actions were investigated by semi-continuous experiments using the substrates with two kinds of total solids concentration of garbage.

The following conclusions can be drawn:

1) In Reactor 1, nitrogen gas production increased as the COD/NO_3^--N ratio increased.

2) In Reactor 1, denitrification and nitrate reduction actions occurred simultaneously when COD/NO_3^--N ratio was above 50. When COD/NO_3^--N ratio was less than 25, denitrification action was exceeded and nitrate was completely removed.

3) Production of volatile fatty acids and the metabolites of acidogenic fermentation were promoted as the concentration of nitrate fed to the reactor increased.

4) In Reactor 2, much acetic acid produced and nitrate added to the reactor was utilized either for the reduction to ammonium nitrogen or for the production of intermediate substances.

In short, the nitrate nitrogen added to the reactor was mostly utilized for the denitrifying reaction in anaerobic acidogenesis of OFMSW as total solid concentration and COD/NO_3^--N ratio decreased. These experimental results indicate the possibility of development of a new type of anaerobic digestion system equipped with the function of nitrogen removal.

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