

FEASIBILITY FOR APPLICATION OF METHANOGENESIS/DENITRIFICATION PROCESS TO MUNICIPAL LEACHATE TREATMENT

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Abstract : Two different processes such as the methanogenesis only process and the simultaneous methanogenesis/denitrification process were used in the single anaerobic reactor, and were compared by observing organic removal, biogas production, and its composition. Denitrification and methanogenesis were successfully occurred in a single anaerobic reactor of the anaerobic-aerobic system for treating leachate. In the methanogenesis only process, the maximum organic removal rate was 2.5 kg COD/m³/day while it was 1.6 kg COD/m³/day in the methanogenesis/denitrification process. Denitrification efficiency reached to approximately 100% in methanogenesis/denitrification process. The biogas compositions in methanogenesis/denitrification process were CH₄ of 71%, CO₂ of 25%, and N₂ of 4%, while its compositions in methanogenesis only process were CH₄ of 63%, CO₂ of 28%, and N₂ of 9%. The biogas production rates of methanogenesis only process and methanogenesis/denitrification process were 20 to 28 L/day and 7 to 13 L/day, respectively. The methanogenesis/denitrification process was presented as a feasible process in the anaerobic-aerobic system constructed for treating organic and nitrogen compounds in the leachate.

Key Words : methanogenesis, denitrification, anaerobic-aerobic system, gas production

INTRODUCTION

In Korea, an anaerobic reactor has been constructed for treating high-loading organic compounds discharged from young landfill site. The chemical compositions of leachate from landfills differ markedly depending on the type of waste deposited and the age of the landfill. Also the compositions of leachate are changed according to stabilized degree of the landfill site. Stabilized leachate contains relatively low concentrations of degradable carbon compounds

with relatively high concentrations of ammonia.¹⁾ Generally, the concentrations of leachate discharged from a municipal landfill site are COD of 40,000 to 50,000 mg/L, BOD₅ of 25,000 to 30,000 mg/L, and NH₄⁺-N of 2,500 to 3,000 mg/L so that the existed wastewater treatment plants have limitations to properly remove NH₄⁺-N as well as organic compounds.²⁾ Also, strong inhibition and toxic effects might be occurred during a biological nitrogen treatment in a high concentration of NH₄⁺-N.³⁾ However, 2 to 3 years later after the completion of landfill, the organic concentration in leachate has been dramatically decreased into 9,800 mg/L while the nitrogen concentration has been

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relatively maintained stable showing about 2,000 mg/L.²⁾ Therefore, this research has focused on utilizing anaerobic reactor more effectively removing nitrogen as well as organic for give specific duration of test.

Figure 1 shows the temporal profiles of BOD₅ and T-N in leachate produced from the landfill site Pusan, Korea with a elapsed time.²⁾ Conventionally, an anaerobic reactor has been mostly installed in leachate treatment process for treating high-loading organic compounds discharged from young landfill area. In the mean time, organic concentration has been decreased rapidly during 2 to 3 years so that the expensive anaerobic reactor designed for removal of high organic concentration was no longer effectively operated. Sometimes, the designing for leachate treatment process is designed based on average BOD₅ concentration of 10,000 mg/L for 2 to 5 years.⁴⁾ In this case, young leachate containing high loading of nitrogen and organic compounds are not efficiently treated resulting in possible serious problems around the vicinity of a landfill.⁵⁾

A methanogenesis/denitrification process has been proposed in a single reactor.⁶⁻⁸⁾ It was generally considered to occur in preference to methanogenesis, as long as in the presence of nitrate or nitrite.⁹⁾

In this research, the anaerobic-aerobic system

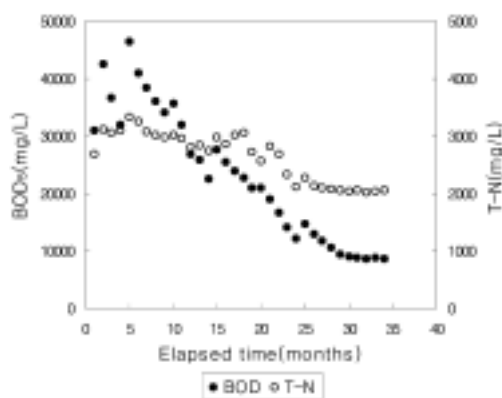


Figure 1. The profiles of BOD₅ and T-N concentrations in leachate with regard to landfill age.

was applied for treatment of leachate produced from the municipal landfill site. Two different processes; the methanogenesis only process and the simultaneous methanogenesis/denitrification process were operated by with recycling and without recycling in the anaerobic reactor, respectively, they were compared by observing organic removal, denitrification capacity, biogas formation, and its composition.

MATERIALS AND METHODS

Experimental Apparatus

Figure 2 shows the experimental arrangement. The reactor consisted of up-flow anaerobic biofilm reactor (V=20L) with additional four stages of an activated sludge reactor (V=40L). The up-flow anaerobic reactor was constructed of stainless steel and was 112 cm long from influent port to effluent port in 15 cm in diameter. The temperature of the reactor was maintained to 36±1°C using a thermal wire. The inner cycle was adjusted to allow adequate mixing through the anaerobic reactor. The 70% of the anaerobic reactor volume was packed with the media (SARAN-1000, Japan) to obtain a sufficient biomass concentration for enhancing the maximum removal efficiency in the reactor. The upper part of the reactor was designed for separation of gas, liquid, and solid.

The experiments were performed when it was considered that biofilm was enough developed in the anaerobic reactor that was filled with the leachate during three months for microbial attachment of the media. The aerobic reactor was divided into four sections to provide better mixing and was operated in the temperature of 20±2°C. The sludge in the clarifier was recycled to the aerobic reactor with 100% of a recycle ratio. Three hundreds percent of the effluent from the aerobic reactor was also recycled into the anaerobic reactor for denitrification.

The composition of leachate

The leachate discharged from the Kyungjoo city municipal waste landfill site was collected bi-weekly and preserved at 4°C in a refrigerator.

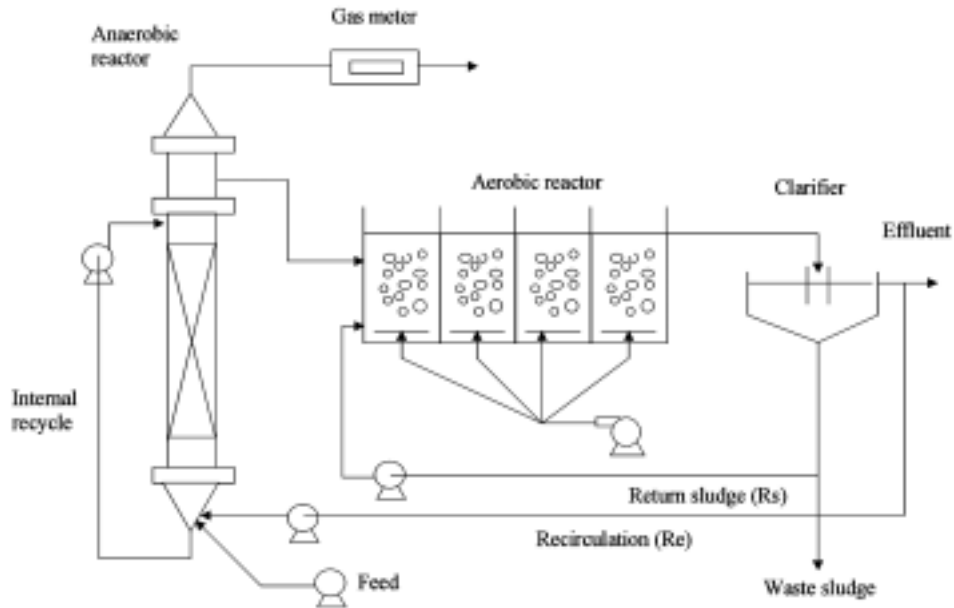


Figure 2. Schematic diagram of lab scale reactors.

Table 1. Characteristics of Kyungjoo City municipal wastes landfill leachate

(unit : mg/L)

Item	Range	Average	Item	Range	Average
pH	7.2 ~ 7.6	7.3	As	ND~0.406	0.226
TSS	1,860 ~ 2,520	2400	Cd	0.018~0.023	0.02
CODCr	21,300~26,940	24,400	Cr	0.44~5.25	2.4
BOD5	9,250~11,650	10,800	Cu	0.51~0.95	0.78
TKN	1,708~1,932	1,766	Fe	52.8~103	76.4
NH ₄ ⁺ -N	1,635~1,810	1,682	Pb	0.28~0.96	0.72
Alkalinity	5,800~7,640	6,700	Mn	11.7~19.2	16.4
T-P	29.5~32.7	31.2	Ni	0.038~0.404	0.16
SO ₄ ⁻	105~182	162	Se	ND	ND
Cl ⁻	2,600~4,200	3,160	Zn	1.3~3.82	2.76

Kyungjoo-city leachate inflow into the holding tank was discerned by two different sources in terms of a transient landfill and completed landfill areas. The leachate from transient landfill was used for experiments and its characteristics are shown in Table 1. The COD/BOD₅ and C/N ratio were 0.44 and 14, respectively suggesting that the leachate contained sufficient organic compounds for denitrification.

Operating Condition

The anaerobic reactor was operated with two different conditions; only methanogenesis process

and methanogenesis/denitrification process (Table 2). The organic removal efficiency, the biogas production, and the variation of gas composition were observed in both operating conditions to investigate which process was more dominantly involved in. The young leachate influent was diluted with tap water (1:1 ratio) with organic loading of 2.7 kg COD/m³/day in the anaerobic reactor, and the nitrogen loading of 0.26 kg NH₄⁺-N/m³/day in the aerobic reactor. The supernatant in the settling tank was returned to the anaerobic reactor at 3Q.

Table 2. Operating conditions

Parameters		Methanogenesis Only	Methanogenesis & Denitrification
HRT	Anaerobic	4 day	
	Aerobic	8 day	
COD loading rate		2.7 kg COD _C /m ³ /day	
Remarks		Leachate : 50%, tap water : 50%	
Recirculation		0 %	300 %

Analytical Methods

Temperature, pH, DO, SS, COD, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N and alkalinity in the leachate and the reactors were monitored a week. BOD₅ was obtained by Winkler-Azid method and DO probe (YSI 58, Korea), and pH was also measured by pH meter (Orion 420A). COD, NH₄⁺-N, and TKN were determined by open reflux method, potassium permanganate method, Nessler Method, and semi-micro-Kjeldahl method, respectively. NO₂⁻-N and NO₃⁻-N were analyzed using Ion Chromatography (Water 432, USA). T-P and heavy metals were observed by stannous chloride method and ICP-AES, respectively.

RESULTS AND DISCUSSIONS

Higher Organic Removal Rate in Methanogenesis Process

In the anaerobic reactor for methanogenesis only employed, the influent concentrations, the effluent concentration from the anaerobic, and the final effluent from the aerobic reactor were 10,000 to 11,000 mg COD/L, 1,000 to 1,500 mg COD/L, and 100 to 400 mg COD/L, respectively. Initially, the effluent COD from the anaerobic reactor was increased to 2500 mg COD/L until the operation period of 14 days, afterward it was decreased to 1000 mg COD/L that was the similar COD as in methanogenesis/denitrification. Even the ratios of BOD/ COD of leachate was 0.44, COD removal efficiency of anaerobic reactor was above 85% because the non-biodegradable COD was converted into the biodegradable COD during 4 days HRT in the anaerobic reactor. Also the dilution effects of the recycle flow for denitrification caused the

better efficiency in methanogenesis/denitrification. During whole period of experiment, the final effluent COD was maintained relatively constant as 320±30 mg COD/L. The final effluent BOD₅ was nearly zero in both operating conditions suggesting that compositions of COD represented non-biodegradable materials.

Figure 3 shows that COD profiles in the anaerobic-aerobic system at different operating conditions for only methanogenesis and methanogenesis/denitrification. In the case of methanogenesis/denitrification, reduction of HRT (Hydraulic Retention Time) into 1/4 responding to recycle flow (3Q) gave the dilution effect enhancing the removal efficiency of 85 to 91%. Based on calculation of removal rate excluding the dilution effect, the COD removal rate were 1.6 kg COD/m³/day and 2.5 kg COD/m³/day in methanogenesis/denitrification and methanogenesis, respectively. However, the overall COD removal rate was similar because of additional COD removal in the aerobic reactor of methanogenesis/denitrification process. It was suggested that decreased HRT in the anaerobic reactor caused

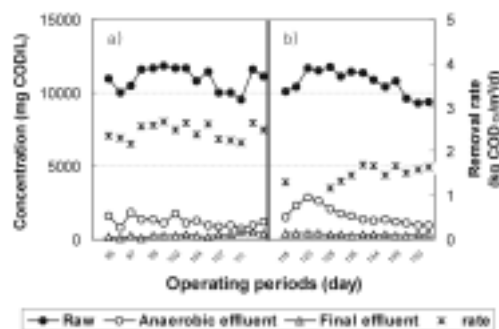


Figure 3. COD profiles in the anaerobic-aerobic system ; a) Methanogenesis only b) Methanogenesis/Denitrification.

to slow down the reaction rate and enhance organic removal by denitrification of $\text{NO}_x\text{-N}$.

Enhanced Nitrification Rate in Methanogenesis/Denitrification

In methanogenesis only, there was no significant difference between influent and effluent $\text{NH}_4^+\text{-N}$ concentration. The influent and effluent concentration were 800 to 1,100 mg $\text{NH}_4^+\text{-N/L}$ and 780 to 1,070 mg $\text{NH}_4^+\text{-N/L}$, respectively, however; effluent $\text{NH}_4^+\text{-N}$ concentration in methanogenesis/denitrification was diminished 350 mg/L to 550 mg $\text{NH}_4^+\text{-N/L}$ due to the dilution effect. Considering the total performance of the anaerobic-aerobic system, the $\text{NH}_4^+\text{-N}$ concentrations of the final effluent in methanogenesis/denitrification was lower than that in only methanogenesis because recovered alkalinity during denitrification in the anaerobic reactor could enhance nitrification in the aerobic reactor. Only 80% of $\text{NH}_4^+\text{-N}$ in the influent was nitrified. The alkalinity was below 100 mg/L in the second stage of the aerobic reactor implying that nitrification was completed in the first stage of aerobic reactor. After 30 days operation, the addition of alkalinity could reduced $\text{NH}_4^+\text{-N}$ concentration of the effluent to below 20 mg $\text{NH}_4^+\text{-N/L}$ in equivalent to 97% nitrification accomplished.

Figure 4 shows the nitrogen profiles in the anaerobic-aerobic reactor using two type of processes in the anaerobic reactor; methanogenesis only process and methanogenesis/denitrification process. While most $\text{NO}_x\text{-N}$ was present as a form of $\text{NO}_3^-\text{-N}$ in methanogenesis only, $\text{NO}_2^-\text{-N}$ was accumulated even as nitrification efficiency was increased to 80% in methanogenesis/denitrification process. The addition of alkalinity providing for sufficient nitrification was expected to increase $\text{NO}_3^-\text{-N}$ significantly in the effluent. However, $\text{NO}_x\text{-N}$ concentration in final effluent was not exceeded to 220 mg/L which was limited from using recycle ratio of 3Q because sufficient organic concentration in leachate allowed complete denitrification. In the initial operation, 90% of $\text{NO}_x\text{-N}$ was present as

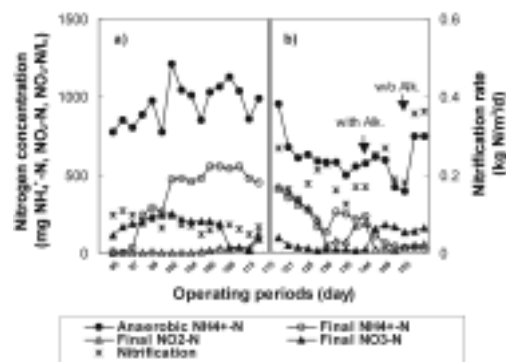


Figure 4. Nitrogen profiles in the anaerobic-aerobic system ; a) Only methanogenesis b) Methanogenesis/Denitrification.

the form of $\text{NO}_2^-\text{-N}$ and most $\text{NO}_2^-\text{-N}$ was nitrified to $\text{NO}_3^-\text{-N}$ by alkalinity addition. The main factors influenced on $\text{NO}_2^-\text{-N}$ accumulation were TKN loading, HRT, DO, product inhibition by heavy and nitric acid, and substrate inhibition by NH_3 . HRT and pH in the aerobic reactor were 8 days and 6.2 to 7.0, respectively. The dissolved oxygen concentration of above 6.0 was maintained to supply enough oxygen for nitrification. NH_3 concentration of 0.5 mg/L was not reached to inhibition concentration of 1 mg/L. It was considered that the deficiency of alkalinity and low pH caused insufficient nitrification resulting in the accumulation of $\text{NO}_2^-\text{-N}$. The alkalinity for nitrification was deficient in the initial operation so that the addition of alkalinity could improve nitrification and guaranty further sufficient nitrification even ceasing the alkalinity addition. The denitrification in methanogenesis/denitrification was occurred completely in a single anaerobic reactor.

Different Gas Composition Produced from Methanogenesis Only Process and Methanogenesis/Denitrification Process

Figure 5 shows the comparison of the methane production in the anaerobic reactor between only methanogenesis and methanogenesis/denitrification. In methanogenesis only, biogas formation was 20 to 28 L/day. In methanogenesis/denitrification, when the flow from the settling

tank was recycled to the anaerobic reactor with 3Q during the initial operation, biogas production was rapidly diminished to 7 L/day and then recovered to 13 L/day after 15 days.

Gas production rate was decreased in methanogenesis/denitrification process because of the reduction of COD removal rate compared to that in methanogenesis only process as shown Fig. 3.

The theoretical gas production was calculated assuming 0.5 m³ biogas per 1 kg COD removed.¹⁰⁾ In only methanogenesis, real gas formation was similar to theoretical value with 0.51 m³ biogas per 1 kg COD while in methanogenesis/denitrification, there was significant reduction over theoretical gas formation, suggesting that some portion of organic compounds

was utilized during denitrification. From the result, it was said that 3.05 g COD might be required for denitrification of 1 g NO_x-N.

Fig. 6 shows biogas composition of only methanogenesis process and methanogenesis/denitrification. For only methanogenesis process in anaerobic reactor, the biogas compositions were 71% of CH₄, 25% of CO₂, and 4% of N₂. Considering 65% of CH₄ was generally formed during organic removal, 71% of CH₄ was relatively high gas formation. It was explained that the most of leachate consisted of volatile fatty acids (VFA) would convert into CH₄ gas during methanogenesis.¹¹⁾ This agreed with the results of the research performed by others.^{12,13)} In comparison, gas compositions were 63% of CH₄, 28% of CO₂, and 9% of N₂ in methanogenesis/denitrification. It was considered that the increasing fraction of CO₂ and N₂ was ascribed to methanogenesis and denitrification simultaneously occurred in an anaerobic reactor.

CONCLUSION

For the advanced treatment of leachate from municipal waste landfill using anaerobic-aerobic system, the feasibility of application of simultaneous methanogenesis/denitrification process was investigated using the single anaerobic reactor. The result of this study was summarized as followings.

1. Even the COD removal rate of methanogenesis/denitrification process was less than in methanogenesis only, the total COD removal rate was similar because removal of residual COD in the following aerobic reactor.
2. Over 95 % of denitrification was occurred in methanogenesis/ denitrification process because of sufficient organic concentration in leachate. Nitrification was also completely performed and NO₂-N build-up was not observed.
3. Gas production and CH₄ fraction of gas in methanogenesis/ denitrification process was reduced from 20-28 L to 13 L and from 71%

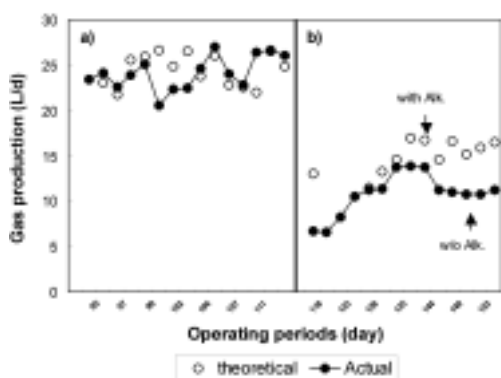


Figure 5. Gas production in anaerobic-aerobic system ; a) Only methanogenesis b) Methanogenesis/Denitrification.

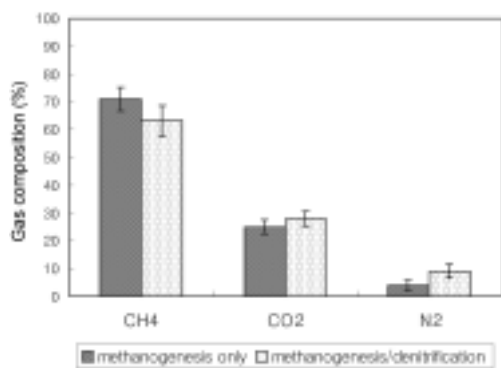


Figure 6. Comparison of gas composition between only methanogenesis process and methanogenesis/denitrification process.

to 63%, respectively, compared to those in methanogenesis only process.

4. Organic and nitrogen removal were sufficiently occurred in the single anaerobic reactor without separately anoxic reactor for denitrification.

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