

Effects of Polyurethane as Support Material for the Methanogenic Digester of a Two-Stage Anaerobic Wastewater Digestion System

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Abstract To increase the efficiency of a two-stage anaerobic wastewater digestion system, various polymers were added to the methanogenic reactor as supports. The addition of polyurethane addition (6%, w/v) to the methanogenic reactor facilitated the organic loading rate (2-day Hydraulic Retention Time), higher than that of the conventional methanogenic reactor (6-day HRT). During the operation of the polyurethane-added reactor, a significant decrease in the organic mass in the effluent (COD 5–6 kg/l) was achieved, compared to that of the conventional reactor (COD 15–20 kg/l). The methane gas production rate also improved about 3-fold in the polyurethane-added reactor. More biomass was found to accumulate in the polyurethane-liquid phase (volatile solid, 26–28 kg) than in the free-liquid phase (volatile solid, 5–7 kg/l) after 90 days of operation. A scaled-up experiment with a polyurethane-added 2.5-l reactor confirmed the previous results, and no adverse effects such as plugging or channeling due to decreased efficiency was observed even after 4 months of operation.

Key words: Two-stage anaerobic wastewater digestion system, polyurethane, hydraulic retention time (HRT), methanogenic reactor

Anaerobic fermentation is generally utilized as a pretreatment process for wastewater from the starch industry, alcohol fermentation industry, and agricultural use [3, 9, 13]. An anaerobic process in wastewater treatment has many advantages over an aerobic process in that 1) an anaerobic process does not require aeration to supply oxygen, thus less energy is required, 2) more than 90% of the organic materials in the effluent can be converted into useful gas for energy and only about 4% is accumulated as biomass, and 3) used sludge under anaerobic conditions can easily be stored for more than 1 yr and reused without any significant

activity loss [2, 4, 12, 14, 16]. In contrast, an anaerobic process has several drawbacks, since it depends on medium to slow rate fermentation by anaerobic microorganisms, which requires long hydraulic retention time (HRT) in a huge reactor [1, 5]. In an anaerobic process leading to methane production, high molecular weight macromolecules (carbohydrates, lipids, proteins) are first converted to low molecular weight organic acids that are then used as substrates for methanogenic bacteria. When compared with the acidogenic stage leading to the production of organic acids, the methanogenic stage is very slow and likely to be the late determining stage of an overall anaerobic wastewater treatment system [8, 15]. The improvement of wastewater treatment efficiency by separating the acidogenic phase from the methanogenic phase has been performed by many previous authors [6, 7, 10, 11, 17]. For high-rate methane fermentation, the retention of the methanogenic biomass in the methanogenic stage has shown to be essential.

Accordingly, the purpose of the current research is 1) to maintain a high level of biomass in a methanogenic stage reactor with the use of a support material and 2) to apply the process to a semi-continuous scaled-up reactor over an extended time period.

MATERIALS AND METHODS

Sludge Sampling and Acclimatization

Sludge was collected from the bed of local sewage water (Chegi-Chun and Sanggye-Dong, Seoul, Korea). The collected sludge was then acclimatized with alcohol fermentation wastewater (Dusan Brewery Co, Ie-Chun, Korea) for about 2 yr before use.

Wastewater

Wastewater from alcohol fermentation was collected and stored at 5°C before use. The pH of the wastewater was 3.7–4.0 and the COD was 45–55,000 ppm. The total solids,

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Table 1. Physical properties of polymers used as supports for the methanogenic reactor.

	Ceramic R12-165	Polyurethane	Nylon fabric	Polyethylene fabric	Nylon web
Total surface area (m ² /g)	31.49	N/A	N/A	N/A	N/A
Average pore diameter (mm)	0.04	0.30	N/A	N/A	N/A
Density (g/cm ³)	2.39	0.2	0.32	3.5	0.32

volatile solids, and suspended solids were about 45–55, 40–45, and 17–26 g/l, respectively.

Operation of Two-Stage Anaerobic Digestion System

The operation of the two-phase digestion system was performed under the conditions established by Park [15]. An organic acid producing reactor was operated at pH 6.0, 37°C, and 2-day HRT by replacing 25 ml of digested water with alcohol fermentation wastewater. The effluent from the organic acid producing reactor was used as the substrate for the methanogenic stage reactor, which was operated at pH 7.0 and 37°C. Acclimatized sludge (50ml) from each stage was transferred to 120-ml bottles, under nitrogen flushing. The bottle was capped with a rubber-stopper and sealed with a plastic cap with a hole in the center. The produced gas was measured using a glass syringe. In a scaled-up test, 1 l methanogenic sludge was used in a 2.5-l bottle and the gas produced was measured by substituting the gas with a saturated NaCl solution.

Support Materials

The ceramic R12-165 was a gift from Kagoshima University (Kagoshima, Japan). The polyurethane, nylon fabric, polyethylene fabric, and nylon web were purchased from a local market. The polymer supports at 3% (w/v) were added, then the ceramic R12-165 was added to the top of the sludge surface. The physical properties of the support materials are compared in Table 1.

Analysis of Effluents

The COD, total solids, volatile solids, and suspended solids were determined by the standard methods of the American Public Health Association. For organic acid quantification, the supernatants of each reactor were separated by centrifugation at 10,000 rpm for 5 min and oxalic acid was added to make a final concentration of 0.03 M. A 1 µl sample was injected into a gas chromatography (model GC-14A, Shimadzu, Japan) with flame ionization detector. A Glass column (ID 3.2 mm×3 m) packed with a carbopack (B-DDDA 80/120 4% CW20 M) was used. The column temperature, injection temperature, and detector temperature were maintained at 175, 200, and 200°C, respectively.

Composition of Gas

The gas collected with a glass syringe (1 ml) was analyzed by a gas chromatography (model GC-14A, Shimadzu, Japan) with a thermal conductivity detector (TCD). A stainless

steel column (ID 3 mm×3 m) packed with active carbon was used. The column temperature, injection temperature, and detector temperature were set at 90, 120, and 120°C, respectively.

RESULTS AND DISCUSSION

Addition of Support Polymers and Wastewater Treatment Efficiency

The effect of various support polymers on gas production was examined and a two-phase digestion system was carried out as described in Materials and Methods. With the addition of the supports in the methanogenic reactor operated with a 5-day HRT, a significant increase in the wastewater treatment efficiency was observed with all the supports (Fig. 1), while the most significant improvement on gas production was observed in the polyurethane-added reactor. Gijzen and Kansime [7] earlier reported similar finding with glucose solution as a substrate for anaerobic sludge. This was attributed to the highly porous structure of the polyurethane, which facilitated dense and rapid colonization of the methanogenic bacteria.

Effect of Polyurethane Level and Surface Area on Gas Production

The increase of methane production rate was proportional up to 6% (w/v) of polyurethane, and higher levels (9,

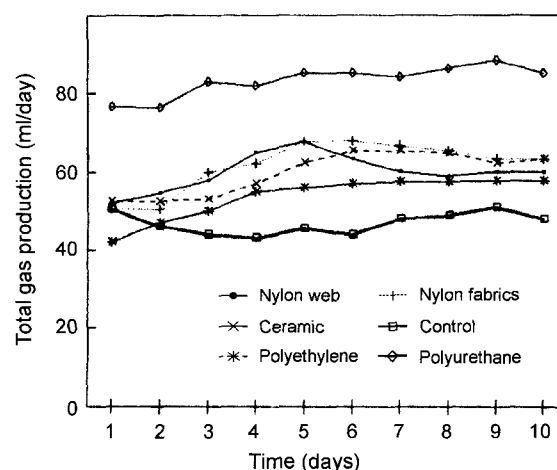


Fig. 1. Effect of added support materials in methanogenic reactor. HRT (hydraulic retention time) was controlled at 5 days and the support materials were added to 3% (w/w).

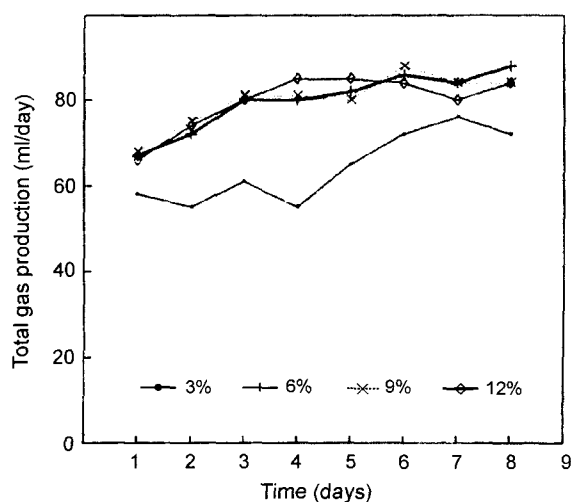


Fig. 2. Effect of added polyurethane level (w/v) on gas production of methanogenic reactor.

12%, w/v) of polyurethane addition did not result in any additional improvement on gas production (Fig. 2). It is highly likely that most of the liquid phase was already absorbed by polyurethane at the level of about 6%, therefore, any additional increase in the polyurethane concentration had no effect on increasing the reaction efficiency. Moreover, at a high level of polyurethane addition, substrate exchange was very difficult. This poor mixing of wastewater in the system could cause a decrease in the digestion efficiency when applied to a scaled-up continuous system.

To facilitate the mixing and penetration of the substrate into the polyurethane, the surface area of the polyurethane was increased by reducing the polyurethane volume by 1/2 or 1/4 before it was added to the reactor. The size reduction of the polyurethane did not result in any significant improvement of gas production rate (data not shown). This means that, at a polyurethane level of 6%, the clogging of polyurethane by the suspended solids was not significant and the liquid phase flow was adequate to provide sufficient substrate for methane fermentation.

Loading Rate Increase with Polyurethane-Added Methanogenic Reactor

In the case of a methanogenic reactor without support material, a decrease in the HRT of up to 6 days resulted in an increase in the gas production. However, the operation of the methanogenic reactor for an HRT less than 4 days resulted in a drastic increase in COD in the effluent, accompanied by a decreased gas production (data not shown). A methanogenic reactor with 6% polyurethane was subjected to a stepwise organic loading rate increase of up to 30 kg COD/m³/day (Fig. 3) by increasing the level of replacing wastewater. For the experiment, the methanogenic reactor capacity was increased to 2.5 l (working volume 1 l). The maximum gas production rate and COD removal

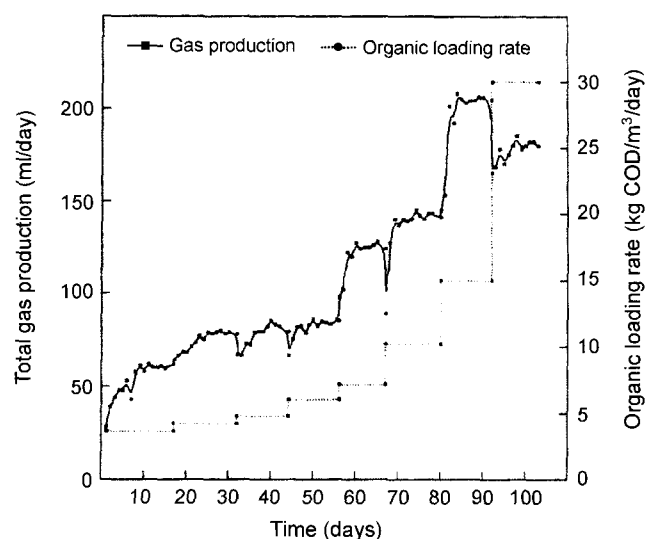


Fig. 3. Organic loading rate increase and gas production during operation of 6% (w/v) polyurethane-added methanogenic reactor.

efficiency were observed with an HRT of 2 days. When the loading rate was increased to 1 day, the gas production rate (Fig. 3) and COD removal in the effluent decreased (20,000–22,000 ppm). With an HRT of up to 2 days, the addition of polyurethane to the reactor facilitated a longer sludge retention time (SRT) and increased the wastewater treatment efficiency. Operation with an increased organic loading rate at an HRT of 1 day seemed to lead to the dilution of the active biomass and accumulation of undigested substrate compounds in the reactor. The gas production rate, methane content, and COD level in the effluent with a 2-days HRT operation are summarized in Table 2 and compared with a conventional two-phase digestion system operated with a 6-days HRT.

Biomass Accumulation in Reactor

The biomass accumulation in the reactor was monitored by measuring the volatile solid (VS) content in the polyurethane. During 90 days of operation with a methanogenic reactor

Table 2. Effects of polyurethane addition as support for methanogenic reactor in a two-phase anaerobic digestion system.

	Conventional system	Polyurethane system
HRT (days)	6 days	2 days
Methane production rate (l/l/day)*	1.0	3.2
Methane content in gas (%)	68	78
COD (g/l)	15–20	5.0–6.0
Total solid (g/l)	12.5	8.9
Volatile solid (g/l)	8.5	6.9
Residual organic acid (g/l)	0.4–0.5	0–0.2

*The methane production rate was calculated by multiplying the produced gas and methane content in the gas and dividing the working volume of the reactor.

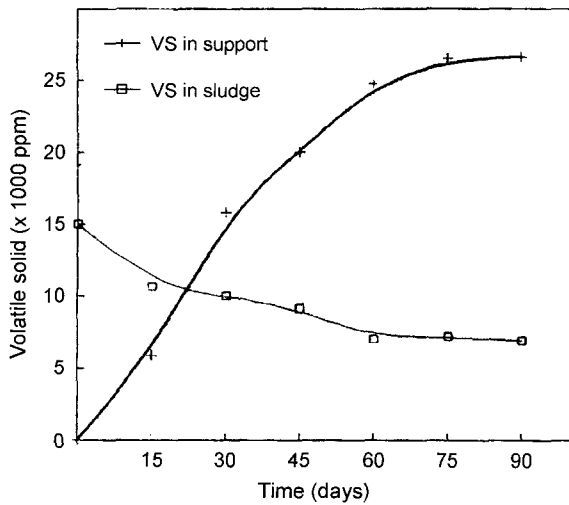


Fig. 4. Changes in volatile solids (VS) contents in support and aqueous phase of polyurethane-added (6%, w/v) methanogenic reactor.

containing 6% (w/v) polyurethane with a 6-days HRT (Fig. 4), the biomass level in polyurethane was exponentially increased with time up to 75 days, whereas the biomass in the effluent level slightly decreased with time up to 60–70 days. After 90 days of operation, the biomass in the polyurethane was about 26,000–27,000 ppm, which was about 4 times higher than the biomass content in the liquid phase at about 6,000–7,000 ppm. The biomass accumulation in both the polyurethane and the liquid phase reached a plateau (Fig. 4) after about 90 days of operation.

Operation of Polyurethane-Added Methanogenic Reactor During a Prolonged Period of Time

During 14 months of operation with added polyurethane, a large-scale methanogenic reactor (working volume 1 l) exhibited no adverse effects, such as plugging or channeling due to decreased efficiency, therefore, no cleaning of the reactor or support material exchange were required. In the scaled-up test, the average gas production rate and COD level in the effluent were 3.2 l/day and 5,000–6,000 ppm, respectively, thus confirming the previous results.

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