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Mineral Requirements for Mesophilic and Thermophilic Anaerobic Digestion of Organic Solid Waste

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ABSTRACT: Anaerobic digestion of organic solid waste (OSW) from kitchen was conducted in completely stirred tank reactors (CSTRs) under both mesophilic and thermophilic conditions. The lab-scale reactors were fed with the OSW containing 10% of total solids (TS) at a hydraulic retention time (HRT) of 30 days (3.0-3.5 g-TS/L/d of volumetric loading rate). Both mesophilic and thermophilic reactors exhibited process failure due to severe acidification. A restoration of methane yield based on the volatile solids (VS) of the OSW added was observed after the addition of minerals (Ni, Co, and Fe) in the mesophilic reactor but not in the thermophilic reactor, suggesting that the requirement for minerals is higher in thermophilic anaerobic digestion than in mesophilic digestion. It is suggested that, among those minerals, Ni is the most important for anaerobic digestion of the OSW.

Key words: Anaerobic digestion, Organic solid waste, Methane yield, Mineral requirement

INTRODUCTION

Anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) has widely spread in this decade (Cecchi et al., 1988; Baere, 2000) because this technology is thought to be within the philosophy of sustainability. The energy recovered from anaerobic digestion of OFMSW is renewable and the effluent can be returned to the agricultural land, recovering the remaining organic matter and nutrients. Until the present day, various novel processes, such as Biocel (Brummeler et al., 1992 & 2000), BTA (Kubler & Schertler 1994), Dranco (Six & Baere 1992), Kompogas (Wellinger et al., 1993), Valorga (Laclos et al., 1997; Saint-Joly et al., 2000), and so forth, have been developed and employed for anaerobic digestion of OFMSW, especially in western European countries.

In Japan, trends in anaerobic waste treatment have been summarized with regard to five practical fields, namely, municipal wastewater and sludge, collected night soil, small scale domestic wastewater, animal waste, and industrial wastewater (Mikami *et al.*, 1997). Recently however Japanese solid waste management is being influenced by the European trend, and anaerobic digestion of OFMSW such as kitchen garbage and food processing waste from restaurants, retail stores, factories, and so forth is getting much attention.

Organic solid waste (OSW) from kitchen accounts for 30-40% (in v/v) of municipal solid waste in Japan, and has a high water content of approximately 80% (Li *et al.*, 1998). Therefore, supplementary fuel is necessary for treatment by direct incineration, resulting in considerable energy consumption and high operation cost. Furthermore, incineration facilities are not especially welcome in urban areas.

From this background, we consider that anaerobic technology is most suitable for the promotion of recycling and maximum recovery of the components of kitchen OSW. In the present study, the anaerobic digestibility of model kitchen OSW simulating Japanese standard composition was examined with regard to mineral

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requirements under mesophilic and thermophilic conditions.

MATERIALS & METHODS

The OSW used in this study was made by simulating Japanese standard composition according to Li *et al.*, (1998) that consists of, in % w/w, apple (10%), grapefruit (rind, 5%), orange (rind, 5%), banana (rind, 10%), cabbage (12%), potato (12%), carrot (12%), ground meat (5%), fish (5%), egg (4%), polished rice (10%), bread (5%), Japanese noodle (2.5%), and Chinese noodle (2.5%). Materials were chopped in a food processor and passed through a 2.8 mm sieve, then mixed homogenously and stored at 4°C. The OSW was diluted to 10% of TS with tap water when used (pH; 4.5-5.0). The ratio of VS per TS of the OSW was 0.95.

Methane yield based on the VS of the OSW added was estimated by a batch experiment using 120mL vial bottles. Mesophilically digested sewage sludge (final concentration of 7.6g-dry solids/L in vial), phosphate buffer (pH=7.0, 0.05M in vial) sodium sulfide (250mg/L in vial), minerals (Harada et al., 1994), resazurin (1mg/L in vial), and the OSW (1%-TS in vial) were added to the vials under an oxygen-free nitrogen atmosphere. Total volume of the mixed liquor was adjusted to 50 mL. The bottles were cultivated in a water bath, which was shaken at 120 strokes per min and kept at 37 °C, for a period of 28 days. Vials without the OSW were also cultivated as a control. The methane yield was calculated according to the difference of produced methane gas between bottles with and without the OSW.

Two CSTRs with working volume of 4.0 L were used in a continuous experiment. The reactors were placed in water baths kept at 37 °C and 55 °C, respectively. The evolved biogas was circulated in order to agitate the sludge mixture. The reactors were fed with 10%-TS of the kitchen OSW by fill-and-draw method at 1- or 2-day intervals. Mesophilically-digested sewage sludge obtained from Nagaoka sewage treatment plant, Japan, was employed as seed sludge for the mesophilic reactor; while thermophilically digested sludge from Morigasaki water treatment center, Japan, was used in the thermophilic reactor (initial concentration was adjusted at 20g/L). In this study, the thermophilic and mesophilic experimental runs were referred as Run 1 and Run 2, respectively. Both reactors started accepting minerals (5.2mg-Fe as FeCl₂4H₂O, 0.04mg-Ni as NiCl₂6H₂O, and 0.16mg-Co as CoCl₂6H₂O per liter of the OSW) on the 65th day. After Runs 1 and 2 were completed, another thermophilic reactor was started up by feeding the OSW containing the above amount of additional minerals from the beginning (Run 3).

Biobas composition was determined with a gas chromatograph (Shimazu 8AIT) equipped with a thermal conductivity detector. The column used was Molecular Sieve 5A 60/80 mesh (1500mm x 3mm ID). Argon was used as the carrier gas at a column pressure of 100kPA. The gas volume was determined by a wet-test gas meter. Volatile fatty acids (VFAs) were analyzed by a gas chromatograph (Shimazu 8APF) equipped with a flame ionization detector. A glass column with FAL-M 25% 80/100 mesh on Chromosorb (1500mm x 3mm ID) was used. Nitrogen was used as the carrier gas at a column pressure of 100kPA. Multi-mineral analysis of garbage and anaerobic sludge was carried out by an emission spectrometry system (Hewlett Packard 4500 series) with inductivity coupled plasma (ICP). The samples for ICP determination were degraded in a microwave oven (CEM MARS 5). Other chemical analyses were carried out according to Japan Sewage Works Association standards (JSWA 1997) unless otherwise stated.

RESULTS & DISCUSSION

A methane yield of 0.39 liter of CH_4 per g-VS of OSW added (L- CH_4 /g-VS added) was obtained from the batch experiment (Fig.1). calculated by subtracting methane production of the control bottles from that of the bottles containing the OSW. The methane yield was almost twice as great as that reported in previous studies for anaerobic digestion of actual OFMSW (around 0.2 L- CH_4 /g-VS added) (Cecchi *et al.*, 1991 & 1992). This is due to the fact that actual OFMSW contains less biodegradable and nonbiodegradable components such as yard waste (branches, leaves, and grass), paper waste (News paper, office paper and coated and uncoated



Fig. 1. Methane production from the model kitchen organic solid waste (shadow square: organic solid waste; black circle: control)

boards), plastics, and inert materials (Chynoweth and Pullammanappallil 1996; Mata-Alvarez et al., 1990). In this study, the methane yield obtained from the batch experiment was used as an index for the following continuous experiment. The performance of Runs 1 and 2 with respect to TS load and methane yield is given in Fig. 2. The reactors were started up at 30 days of HRT and 3.0-3.5 g-TS/L/d of volumetric loading rate. The methane yields in each experimental run in the steady state (during the 10-40th day) were, on average, 0.30 L-CH₄/g VS added for Run 1, and 0.38 L-CH₄/g-VS added for Run 2, respectively. The reactor under mesophilic conditions (Run 2) showed a methane yield nearly comparable to that obtained from the batch experiment. However, only 77% of the index value was observed in the thermophilic reactor (Run 1). The methane yields in each experimental run started decreasing gradually on the 40th day and sharply declined on the 51st day.

Fig. 3. shows the time course of total VFA in terms of chemical oxygen demand (COD) and pH of the sludge drawn from the Run 1 and Run 2 reactors. From Figs 2 and 3. it is evident that the increase in total VFA, decrease in pH and

deterioration of methane yield started simultaneously on the 40th day in both experimental runs. The addition of bicarbonate (3000-5000 mg/ L as NaHCO₃) was made during the 58-77th day in order to increase pH, but no significant restoration of the process was observed.

Generally, the critical concentration of ammonium nitrogen needed to inhibit nonacclimatized anaerobic sludge is reported at around 2000-2500 mg-N/L (Lay et al., 1998; Parkin et al., 1983). In this study, ammonium nitrogen concentrations in the sludge of Runs 1 and 2 reactors were kept under 2000 mg-N/L (780-1400 mg-N/L, data not shown) for whole experimental period. This indicates that the process failure caused by the acidification was not due to ammonia inhibition. Several researchers have reported that the addition of minerals contributed to improving process performance of anaerobic treatment of industrial wastewaters (Kida et al., 1991; Takashima et al., 1989) or OFMSW (Li et al., 1998). Consequently, we started adding minerals such as Ni, Co, and Fe from the 65th day to investigate whether the acidification was caused by the lack of these minerals.



Fig. 2. Time course of TS load (A) and methane production (B) in Run 1 and 2 (shadow square: Run 1; empty circle: Run 2; a: duration of bicarbonate addition; b: duration of mineral addition)



Fig. 3. Time course of pH (A) and total VFA-COD (B) in Run 1 and Run 2 (shadow square: Run 1; empty circle: Run 2)

In Run 2, after the addition of minerals, the methane yield dramatically increased up to around 0.8-1.0 L-CH₄/g-VS added, which was two times greater than the index value obtained from the batch experiment (Fig. 2). This phenomenon is attributed to the fact that the undigested OSW accumulated in the reactor during low methane yield phase came to be digested after the addition of minerals. Therefore, the TS load of Run 2 was further lowered to 0.8-0.9g-TS/L/d (HRT=120 days) in order to digest the accumulated OSW, and then increased stepwise to 3.0-3.5 g-TS/L/d (HRT=30 days). As a result, after the 116th day, a stable methane yield of 0.35 L-CH₄/g-VS added, on average, could be achieved (Fig. 2b). However, 10000 mg-COD/L of total VFA, on average, was observed during the steady state after acidification (Fig.3b).

On the other hand, the reactor under thermophilic conditions (Run 1) showed no increase of the methane yield after the addition of minerals, and acidification still progressed, resulting in a total VFA of up to 26000 mg-COD/L in the sludge at the termination of the experiment (the 97th day). The fact that the methane yield was restored after the addition of minerals in the mesophilic digestion but not in the thermophilic digestion suggested that the requirement for minerals is higher in thermophilic anaerobic digestion than in mesophilic digestion. Another thermophilic reactor was started up after Runs 1 and 2 were completed, which was fed with the OSW containing the additional minerals from the beginning (Run 3). In Run 3, no acidification occurred during whole experimental period of more than 80 days (HRT, 30 days; TS load, 3.25 g-TS/ L/d, on average). The methane yield of Run 3 was 0.38 L-CH₄/g-VS added, on average: comparable to that obtained in the steady state before acidification in Run 2.

COD balance in each experimental run

Table 1 summarizes the methane yields in each experimental run. In the thermophilic experiments, the methane yield in the steady state before acidification in Run 1 was 0.30 L-CH₄/g-VS added while 0.38 L-CH₄/g-VS added was obtained in Run 3. Fig. 4 shows the COD balance in each experimental run. Comparing residual COD of Run 1 with Run 3, degradation of OSW in Run 3 was superior to that in Run 1, suggesting that the addition of minerals influenced the efficiency of methane conversion of the OSW. Under mesophilic conditions (Run 2), the methane yield in the steady state before and after acidification was 0.38, and 0.35 L-CH₄/g-VS added, respectively. Judging from the COD balance in Run 2 before and after acidification (Fig. 4). this is obviously due to the accumulation of VFAs after the acidification.

Table 2 summarizes the concentrations of minerals such as Ni, Co, and Fe in the OSW and the seed sludge for Run 1 and Run 2 reactors. Compared with the seed sludge, the OSW contained an extremely small amount of minerals. According to a report of trace elements in foods in Japan (Suzuki and Tanushi, 1993), the foods used in this study contain no Co, and only grape fruit and polished rice contain a small amount of Ni (2.2 ¼g/kg for grape fruit and 2.72.2 ¼g/kg for polished rice), well corresponding to the results in Table 2. The changes in Ni and Co concentrations in Run 1 and Run 2 sludge with time are simply calculated by following equation using the data given in Table 2.

 $C_{I} = (C_{I-1} \times (V-D) + X \times D)/V$

 C_{I} : mineral concentrations in sludge after I th sampling time.

 C_{I-1} : mineral concentrations in sludge after (I-1) th sampling time.

Experimental run	Run 1 (55°C)	Run 2	(37°C)	Run 3 (55 °C)
	Steady state before a cidific ation	Steady state before a cidification	Steady state after acidification	28 🛶 79th day
Methane yield	0.30	0.38	0.35	0.38
(L - CH4/g-VS)	(0.05)	(0.03)	(0.02)	(0.04)

Table 1. Summary of experimental results

Uemura, Sh.



Fig. 4. COD balance in each experimental run (White: COD of recovered methane, shadow: COD of drawn sludge except for VFA, black: COD of VFA)

Table 2.	Composition	of Ni,	Co, and Fe in kitch	en waste and s	seed sludge (in mg/L)
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M in erals	O SW	Seed sludge for Run 1 (ther mop hilic)	Seed sludge for Run 2 (mesophilic)
Ni	ND	0.220	0.133
Co	ND	3.49	3.52
Fe	38.9	896	817

0‰ND: Not Detectable

V: reactor volume.

D: volume of drawn sludge (equals volume of OSW added).

X: mineral concentrations in the OSW.

The concentrations of Ni and Co in the kitchen OSW were given as 0 mg/L until the 64th day and 0.04 mg/l of Ni and 0.16 mg/l of Co after the addition of minerals. The result of Run 2 is given in Fig. 5 as representative data. The concentration of Fe and Co still tended to decrease after the addition of minerals in Run 2. With respect to Ni, the concentration was 0.032 mg/L just before the acidification and 0.022 mg/L at the beginning of the sharp depletion of the methane yield. Afterward, the Ni concentration increased from 0.016 mg/L on the 65th day to 0.033 mg/L on the termination of the experiment. Thus, in Run 2, although the Co and Fe concentrations continued to decrease after the addition of minerals, the concentration of Ni increased and the methane yield restored, indicating that Ni is the most important

among the three minerals used in this study. This result implies that process failure caused by a shortage of minerals might occur in long-term treatment by anaerobic digestion of Japanese standard kitchen OSW without additional minerals.

CONCLUSION

The following conclusions can be drawn from this study:

(1) Both mesophilic and thermophilic reactors fed with kitchen OSW containing no additional minerals such as Ni, Co, and Fe, exhibited process failure due to severe acidification.

(2) Methane yield was restored after the addition of minerals in mesophilic but not in thermophilic, suggesting that the requirement for minerals is higher in thermophilic anaerobic digestion than in mesophilic digestion.

(3) No acidification occurred in the thermophilic reactor fed with the OSW which contained additional minerals from the beginning.



Fig. 5. Changes of Ni and Co in sludge mixed liquor in Run 2 (Shadow square: Ni, black circle: Co, arrow a: start of acidification (the 40th day); arrow b: start of methane depletion (the 51st day); arrow c: start of mineral addition (the 65 day)

(4) It was suggested that Ni is the most important for anaerobic digestion of kitchen OSW among the three minerals.

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