Novel Anaerobic Two-Stage Process Producing Hydrogen as Well as Methane from Food Waste

Sun Kee Han*, Soo Youl Kwon, Dong Uk Park and Byong Jun Yoon

Department of Environmental Health, Korea National Open University, Seoul 110-791, Korea

Abstract

This study aimed to develop a novel anaerobic two-stage process converting food waste to H_2 and CH_4. The anaerobic two-stage process was devised by combining hydrogen fermentation with methane fermentation. At the high loading rate of 12.3 kg VS/m^3/d, it could remove 72.5% of VS and convert $VS_{removed}$ to H_2 (28.2%) and CH_4 (69.9%) on COD basis in 8 days.

Introduction

Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into H_2. The reactions involved in H_2 production are rapid and useful for treating large quantities of wastewater. Since they cannot utilize light energy, the decomposition of organic substrates is incomplete and volatile fatty acids (VFA) remain. Nevertheless, these reactions are still suitable as an initial step of H_2 production from waste, which is followed by methane fermentation.

The objective of this work was to optimize hydrogen fermentation and methane fermentation, and then to develop a novel anaerobic two-stage process producing H_2 as well as CH_4. This process could improve the economic feasibility of waste treatment.

Materials and Methods

Seed sludge

The seed sludge for hydrogen fermentation was taken from an anaerobic digester in a sewage treatment plant and boiled for 15 min to harvest anaerobic spore formers such as *Clostridium* sp. (van Ginkel *et al.*, 2001). Partially granulated sludge (8.5 L) obtained from an anaerobic plant treating brewery wastewater was used to seed the upflow anaerobic sludge blanket (UASB) reactor.

Feedstock

Food waste, collected from a dining hall, was fed into the reactor after separating out bones and shells. The bulk density, moisture content, VS/TS, Na^+ and C/N of the waste were 519.5 kg/m^3, 80.2%, 0.95, 0.8 g/L and 15.4, respectively. Food waste contained grains, vegetables and meats, of which composition was 61.1%, 29.7% and 9.2% on total solids (TS) basis. The wastewater from the hydrogen fermentation of food waste had a soluble COD of 3,104 mg/L, which consisted of VFA (1,891 mg COD/L) and alcohol (1,213 mg COD/L). The pH was about 6.7, and the alkalinity was about 2,158 mg/L as $CaCO_3$.

Experimental setup

Four leaching-bed reactors were operated for hydrogen fermentation. Each leaching-bed reactor was 3.9 L in working volume with an internal diameter of 0.15 m and a height of 0.22 m. The wastewater from four leaching-bed reactors were converted to CH_4 in a UASB reactor with a working volume of 40.0 L in working volume (lower part: 790 mm high by 200 mm ID; upper part: 400 mm high by 220 mm ID). The anaerobic two-stage process combining four leaching-bed reactors with a UASB reactor was operated at a temperature of 37°C.

Results and Discussion

Optimization of hydrogen fermentation

The first experiment (Reactors 1-4) was conducted to investigate the effect of initial *D* on H_2 fermentation of food waste. Reactor 1 showed low pH values (4.0-4.3) in the first two days. Since simple organic matters were rapidly acidified in initial stage, its low dilution rate (*D*) of 2.1 d^{-1} resulted in pH drop. Reactor 4 indicated high pH (6.2-7.5) over the operation period. At high *D* of 5.6 d^{-1}, microbial washout might be greater than microbial growth. Thus, the low concentration of biomass in the reactor led to the decrease of VFA production and the increase of pH. The maximum H_2 production was observed in Reactor 3. At *D* of 4.5 d^{-1}, the H_2 production of 58.1 L was the highest among the reactors. The optimum pH of 5.5 was maintained in the first two days (van Ginkel et al., 2001).

The theoretical COD (COD_{th}) of food waste was 412.6 g COD (that is, 375.1 g VS × 1.1 g COD/g VS), while the actual cumulative COD (COD_a) produced in hydrogen fermentation until day 7 were 212.3 (Reactor 1), 227.9 (Reactor 2), 239.2 (Reactor 3) and 221.4 g COD (Reactor 4). Thus, the maximum efficiency, obtained by dividing COD_a by COD_{th}, was 58.0% (Reactor 3) at initial *D* of 4.5 d^{-1}. The COD removed in Reactor 3 was converted to H_2 (10.1%), VFA (30.9%), and ethanol (17.0%).

Based on the results of the preceding experiment, initial *D* was kept at 4.5 d^{-1} in all the reactors in the first two days. The second experiment (Reactors 1-4) was performed to investigate the effect of *D* control on H_2 fermentation of food waste. In the first two days, pH and H_2 production were maintained in the range of 5.4-5.5 and 46-48 L/d, respectively. Although simple organic matters were rapidly degraded, pH drop did not occur at initial *D* of 4.5 d^{-1}. In Reactors 1 and 2, the reduction of simple organic matters caused the decrease of VFA production and the increase of pH after 2 days. H_2 production also slightly increased, as microbial proliferation was less than microbial loss by washout. However, the performance of Reactor 3 was dramatically improved by reducing *D* from 4.5 to 2.3 d^{-1}. The pH was maintained below 6.0 on day 3-6. H_2 production was the highest among the reactors, indicating that *D* control resulted in the enhanced degradation of slowly degradable matters. The environmental conditions became favorable to microbial growth by *D* shift.

The theoretical COD (COD_{th}) of food waste was 412.4 g COD (that is, 374.9 g VS × 1.1 g COD/g VS), and the actual cumulative COD (COD_a) produced in hydrogen fermentation until day 7 were 243.6 (Reactor 1), 271.1 (Reactor 2), 292.1 (Reactor 3) and 260.8 g COD (Reactor 4), respectively. Thus, the maximum efficiency, obtained by dividing COD_a by COD_{th}, was 70.8% (Reactor 3) at *D* control of 4.5-2.3 d^{-1}. The COD removed in Reactor 3 was converted to H_2 (19.3%), VFA (36.5%), and ethanol (15.0%).

Optimization of methane fermentation

In the first 235 days, the COD removal efficiency was consistently over 96% up to HRT of 0.24 d, which corresponded to the loading rate of 12.9 g COD/L/d and a food-to-microorganism (F/M) ratio of 0.61 g COD/g VSS/d. The biogas production rate increased with COD loading rates and reached the maximum of 216.0 L/d at 12.9 g COD/L/d. The maximum COD loading rate (12.9 g COD/L/d) was comparable to the maximum VFA-converting activity of 14.0 g COD/L/d in a UASB reactor fed with synthetic VFA wastewater (Fang et al., 1995) and the maximum ethanol-converting activity of 6.8 g COD/L/d in a UASB reactor fed with synthetic ethanol wastewater (Kato et al., 1997). Beyond this loading rate, the efficiency decreased as the loading rate increased. The COD removal efficiency was drastically reduced to about 73% at 0.20 d HRT (15.3 g COD/L/d), and to about 56% at 0.18 d HRT (16.8 g COD/L/d). The VSS concentration in the effluent also increased sharply to 255 mg/L at 15.3 g COD/L/d, and to 393 mg/L at 16.8 g COD/L/d. This indicated that the decrease of COD removal efficiency was due to sludge flotation and washout in the reactor, which resulted from short HRT of less than 0.24 d (5.8 h).

The specific methane production rate (SMPR) increased linearly with the specific substrate utilization rate (SSUR) with a slope of 0.93, until reaching the maximum of 0.55 g CH_4 COD/g VSS/d at the SSUR of 0.59 g COD/g VSS/d. The slope indicated that of all the COD removed, 93% was converted to CH_4 and the rest 7% was presumably converted to biomass. The SMA is an indicator for evaluating the methanogenic activity of the biomass under a condition in which the supply of substrate is not a limiting factor. This indicated that the VFA-degrading activity of granule was the highest for butyrate (1.01) and the lowest for propionate (0.59 g CH_4 COD/g VSS/d). Meanwhile, SEM observations demonstrated that typical granules were composed of *Methanosaeta*-like bamboo-shaped rods.

Development of a novel anaerobic two-stage process

From the experiments of H_2 fermentation and CH_4 fermentation, a novel anaerobic two-stage process was developed as shown in Fig. 1. This novel anaerobic two-stage process comprises two main parts: four leaching-bed reactors for H_2 recovery and a UASB reactor for CH_4 recovery. Four leaching-bed reactors are operated in a rotation mode with a two-day interval between degradation stages. Seed sludge (10% v/v) boiled for 15 min is inoculated into the reactor. After 6 h of acclimation, dilution water is delivered to a leaching-bed reactor. In initial stage, simple organic matters are likely to cause pH drop and product inhibition. Initial *D* (4.5

d^{-1}) is, therefore, maintained relatively highly to move produced VFA to the UASB reactor quickly. However, after 2 days, *D* is lowered from 4.5 to 2.3 d^{-1} for the enhanced degradation of cellulose and protein. Proper *D* control could make the environmental conditions favorable to microbial growth during hydrogen fermentation. A UASB reactor converts COD materials from the leaching-bed reactors to CH_4. Effluent from the UASB reactor recirculates through the leaching-bed reactors as dilution water.

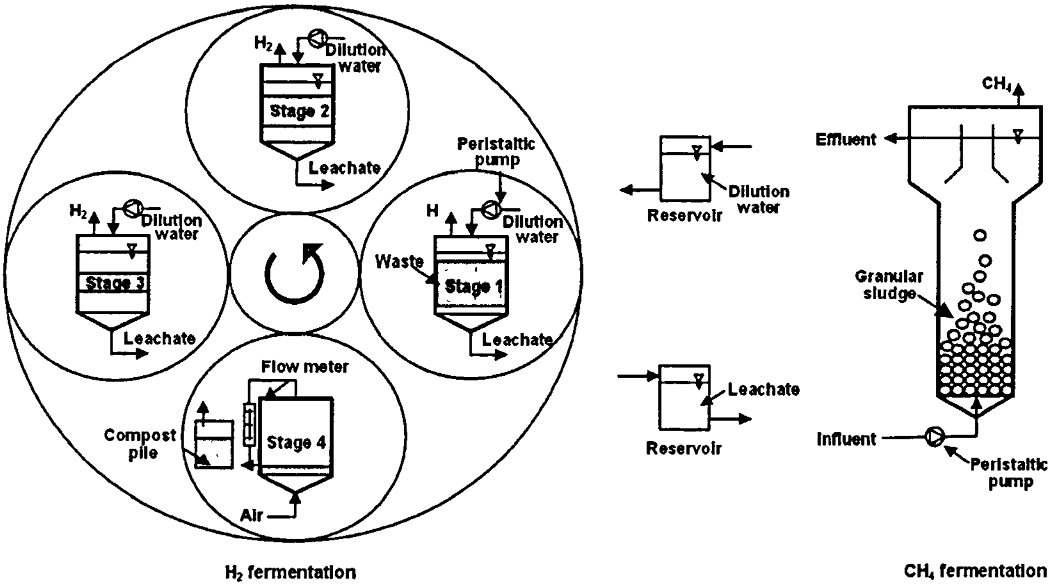

Fig. 1. Novel anaerobic two-stage process producing H_2 as well as CH_4.

The novel anaerobic two-stage process showed that, at the high loading rate of 12.3 kg $VS/m^3/d$, it could remove 72.5% of VS and convert $VS_{removed}$ to H_2 (28.2%) and CH_4 (69.9%) on COD basis in 8 days. H_2 gas production rate was 3.63 $m^3/m^3/d$, while CH_4 gas production rate was 1.75 $m^3/m^3/d$. The yield values of H_2 and CH_4 were 0.31 and 0.21 m^3/kg VS_{added}, respectively.

Conclusion

A novel anaerobic two-stage process producing H_2 as well as CH_4 from food waste was developed by combining H_2 fermentation with CH_4 fermentation. At the high VS loading rate of 12.3 $kg/m^3/d$, the anaerobic two-stage process removed 72.5% of VS and converted $VS_{removed}$ to hydrogen (28.2%) and methane (69.9%) on COD basis in 8 days. Its performance was stable, reliable and effective over the operation period.

References

Fang, H. H. P., Li, Y. Y. and Chui, H. K. : UASB treatment of wastewater with concentrated mixed VFA. *J Environ Eng, ASCE,* 121(2), 153-60, 1995.

Kato, M. T., Field, J. A. and Lettinga, G. : The anaerobic treatment of low strength wastewaters in UASB and EGSB reactors. *Water Sci Technol,* 6(6-7), 375-82, 1997.

Van Ginkel, S., Sung, S. and Lay, J.-J. : Biohydrogen production as a function of pH and substrate concentration. *Environ Sci Technol,* 35, 4726-4730, 2001.