0273-2289/02/98-100/0753/$13.00

Mass Production of Methane from Food Wastes with Concomitant Wastewater Treatment

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Abstract

We developed a process for production of methane at a pilot scale. This process consists of three stages. The first stage is a semianaerobic hydrolysis/acidogenic step in which organic wastes are converted to various sugars, amino acids, and volatile fatty acids (VFAs). Operation temperature and pH were 45°C, and 5.0–5.5, respectively. Hydraulic retention time (HRT) was 2 d. To remove the putrid odor and to enhance the hydrolysis of organic wastes, a mixture of bacteria isolated from landfill soil was inoculated into the reactor. Total chemical oxygen demand (tCOD) and biological oxygen demand (BOD) were 36,000 mg/L and 40,000 mg/L, respectively. The second stage was an anaerobic acidogenic process, which can produce large amount of VFAs including acetate, propionate, butyrate, valerate, and caproate. Operation temperature and pH were 35°C, and 5.0–5.5, respectively. HRT was 2 d. The third stage was a strictly anaerobic methane fermentation step producing methane and carbon dioxide from VFAs. The working volume of upflow anaerobic sludge blanket (UASB) type reactor was 1200 L, and operation temperature and pH were 41°C, and 7.7–7.9, respectively. HRT was 12 d. Seventy two percent of methane at maximum was generated and the yield was 0.45–0.50 m^3/kgVS of food wastes. Through the process, 88% of tCOD and 95% of BOD were removed. The wastewater was treated with the biological aerobic and anaerobic filters immobilized with heterotrophic and autotrophic nitrifying and denitrifying bacteria.

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Ninety percent of total nitrogen (T-N) was removed by this treatment. The residual T-N and total phosphorous (T-P) were removed by the algal periphyton treatment system. The final concentrations of nitrogen and phosphorous in the drain water were 53 and 7 mg/L, respectively.

Index Entries: Anaerobic digestion; volatile fatty acids; methane; biological filter; algal periphyton treatment system.

Introduction

Disposal of food wastes has become a major concern in Korea. From the year 2004, sanitary landfills will be prohibited by the environmental law due to the putrefaction and leachate of food wastes. Therefore, a few alternative treatment techniques have been suggested. For example, techniques converting food wastes to fermented fertilizer, foodstuff for animals, and compost have been developed. However, it has been realized that the reuse of food wastes has a practical limitation due to the nutritional imbalance and salts.

Anaerobic digestion is an alternative method to digest food wastes and to produce methane that can be used as a renewable energy source. It has long been used for the stabilization of wastewater sludges. However, recently, it has been applied to other fields through a better understanding of the microbiology of this process and improved reactor designs. The important advantage of anaerobic digestion over aerobic processes is that 50% of organic carbon is converted to biomass under aerobic conditions, whereas only 5% is converted into biomass under anaerobic conditions, as regards cell yields. The net amount of cells produced per metric ton of chemical oxygen demand (COD) destroyed is 20–150 Kg in anaerobic digestion, as compared to 400–600 Kg in aerobic digestion *(1)*.

Generally two types of processes for anaerobic digestion have been developed. In a conventional single-stage process, both acid and methane could be produced simultaneously by the acidogenic and methanogenic bacteria, respectively, so it is difficult to maintain optimal conditions for fermentation. Moreover, fermentation stability tends to be lowered by changes in influent properties. However, a two-stage digestion can provide optimal conditions for the process and allow operation at much higher loading rates and shorter hydraulic retention times (HRTs) *(2)*. In this system, syntrophic bacteria grow well even with excessive amounts of organic compounds because hydrogen is maintained at low levels *(3)*. Therefore, the two-stage anaerobic system has been studied intensively.

One of the significant problems with high-solids anaerobic digestion is volatile fatty acid (VFA) accumulation that leads to severe retardation of the methanogenesis process. The high VFA accumulation with a concomitant pH depression to 4 led to cessation of hydrolytic and acidfication reactions presumably due to end-product inhibition of fermentative acidogens. Syntrophic and acetoclastic methanogenic activities were also severely inhibited under the sour digestion conditions *(4)*. An innovative

process resolving this problem was the leach-bed two-phase anaerobic digestion process *(5)*. Although this process could be operated successfully, methane fermentation was virtually inhibited under the extreme sour-digestion condition.

A modified three-stage process that can produce methane effectively from easily biodegradable food wastes has been developed in this laboratory *(6)*. This system consisted of three stages: a semianaerobic hydrolysis/ acidogenic stage, a strictly anaerobic acidogenic stage, and a strictly anaerobic methanogenic stage. The separate reactor system efficiently reduced the HRT by increasing the rates of hydrolysis, acidogenesis, and methanogenesis without affecting the pH and showed high methane yield. These advantages were very important in the economical aspect because the reactor volume could be reduced to a small scale.

We report here the composition and operational conditions of a pilot-scale (total 2500 L) three-stage methane fermentation process. For practical use, we also developed a wastewater treatment system consisting of both biological filter system and algal periphyton treatment system to remove COD, total nitrogen (T-N), and total phosphorus (T-P) of the final effluent to satisfy the "Permissible Pollutant Discharge Standard of Wastewater" in Korea.

Materials and Methods

Design and Operation Conditions of Pilot Scale Three-Stage System

A three-stage methane fermentation system was developed to a pilot scale on the basis of the bench-scale system *(6)* which was modified from the two-phase digestion system designed by Ghosh and Pohland *(7)* (Fig. 1). It consisted of a semianaerobic hydrolysis/acidogenic process, an anaerobic acidogenic process, and a strictly anaerobic methanogenic process. The primary continuous stirred-tank reactor (CSTR) type of semianaerobic digester was designed for rapid hydrolysis and acid production from food wastes at a working volume of 200 L. Mixed household food wastes with high total solid (TS) contents were crushed to small particles (3–5 mm) and fed to the digester. The fluid was stirred at 180 rpm, and 1 vvm of air was applied to the bottom of reactor. Food wastes were hydrolyzed semianaerobically because of the unbalanced diffusion of oxygen in the reactor. To remove non-degradable materials, a drain valve (i.e., $\varnothing = 20$ cm) was made at the center of the bottom of the reactor. Operation temperature was adjusted to 45°C because a putrid smell was generated at 37°C by the putrefactive bacteria. The pH was controlled to 5.0–5.5 with a finally treated drain wastewater of pH 8.8–9.2. After 2 d digestion, 100 L of hydrolyzed acid-containing solution was transferred to the bottom of secondary UASB type digester with a 200 L working volume. In this reactor, a large amount of VFA was produced for 2 d at a mesophilic temperature (35°C). *Clostridium butyricum* was inoculated to improve the production of acids such as acetic and butyric acid. One hundred liter of acid effluent was fed to the bottom

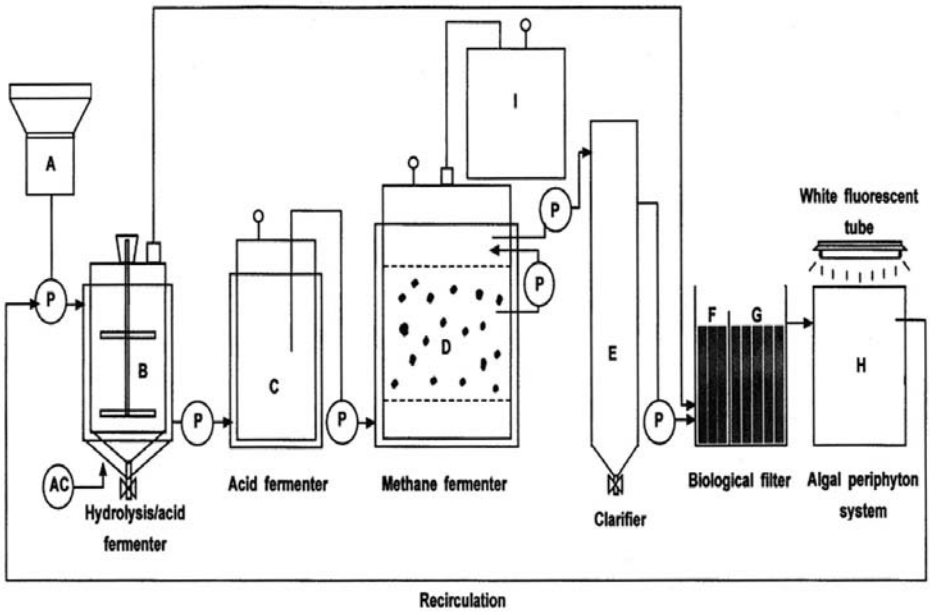

Fig 1. Schematic diagram of a pilot scale three-stage methane fermentation system consisting of a CSTR hydrolysis/acidogenic reactor and two UASB reactors for acidogenic and methanogenic processes. A, crusher; B, hydrolysis/acid reactor; C, acid reactor; D, immobilized-bed methane reactor; E, clarifier; F, aerobic biological filter chamber; G, anaerobic biological filter chamber; H, algal periphyton chamber; I, gas reservoir tank; P, pump; AC, air compressor.

of UASB type methanogenic reactor. The working volume and operation temperature were 1200 L and 41°C, respectively. Methane fermentation was performed using methanogenic bacteria. Round form ceramic biofilters (∅ = 3 cm) were used as packing materials. The digesters were equipped with heat exchangers, gas meters, flame traps, and gas vents.

Design and Operation Conditions of Wastewater Treatment System

To remove residual COD, T-N, and T-P contained in the effluent derived from the methane digester, additional wastewater treatment processes have been developed (Fig. 1). One hundred liters of effluent were transferred to the sedimentation tank (∅ = 0.4 m, h = 2.0 m) where solid fractions were precipitated and the supernatant was applied to the aerobic biological filter chamber (100 L) containing immobilized nitrifying bacteria, which convert ammonia to nitric acid. One vvm of air was applied to the chamber. One day after, 100 L of effluent were moved to the anaerobic immobilized biological filter chamber (200 L) to remove nitrogen by denitrifying bacteria. The filters were made of polyvinyl chloride bars (length = 1 m) and the surface was swelled so that they have a high ratio of surface area to volume. To immobilize microorganisms, filters were submerged into the wastewater for 30 d. Unpleasant gas blew off from the primary

digester and was transferred to the aerobic biological filter chamber to remove odor.

However, the wastewater still contained high concentration of T-N, and a more advanced process was required to reduce it. Algal periphyton treatment systems used periphyton to take up nitrogen and phosphorus dissolved in the wastewater. Initial algal density has been shown to be important for their activities and reduction of nutrients. Lau et al. *(8)* reported that initial algal density of 1×10^7 cells/mL seemed to be more beneficial for achievement of a satisfactory nutrient level within 7 d. In this study, algal cells were inoculated at $7–8 \times 10^6$/mL into the wastewater containing 200 mg/L T-N and incubated for 4 d at 25°C with illumination of 7000 lux.

Microorganisms

In the primary semianaerobic hydrolysis process, a mixture of moderate thermophilic bacteria (at least 100 strains including *Bacillus* sp., *Lactobacillus* sp., *Actinomycetes* sp., photosynthetic bacteria, yeast) isolated from many landfill soil samples were introduced for the rapid hydrolysis of carbohydrates, proteins, fats, chitins, and pectins. *C. butyricum* (NCIB 7423) was inoculated in the secondary acidogenic process for the mass production of VFA, especially acetic and butyric acids. In case of methanogenic process, cow manure and anaerobic methane-generating landfill soil were supplied to the reactor. Nitrifying and denitrifying bacteria used in the biological filters were prepared from the activated sludge. Algae, *Selenastrum capricornutum* and *Chlorella* sp., were used in the algal periphyton treatment systems.

Analytical Methods

The following parameters were determined: TS, volatile solids (VS), tCOD, soluble COD (sCOD), BOD, and pH. T-N, ammonia (NH_4-N), nitric acid (NO_3-N), and T-P concentrations were also monitored. These parameters were analyzed by the methods described in the ref. *9*. COD was measured by the closed reflux, colorimetric method using $K_2Cr_2O_7$, and BOD was calculated from the difference between initial and final dissolved oxygen of sample in the airtight Winkler bottle. Total VFAs (tVFAs) were determined by gas chromatographic system (HP 5890A). Analytical conditions were as follows: FFAP capillary column (Hewlett Packard, 0.2 mm × 25 m) temperature, 150°C; injector temperature, 200°C; detector (flame ionization) temperature, 250°C; H_2 flow, 30 mL/min; air flow, 317 mL/min; column head pressure, 100 kPa. The composition of food wastes was analyzed by Elemental Analyzer (model 240C; Perkin-Elmer). The amount of gas produced from the digesters was monitored by a wet gas meter (W-NK-5; Shinagawa), and the gas composition was analyzed by a gas chromatography (GC-14B; Shimadzu) using a packed column (Haysep D, 100/120 mesh, 1/8 in. × 10 ft; Alltech). Temperatures for column, injector, and detector (thermal conductivity) were 150, 200, and 220°C, respectively.

Results and Discussion

Operation and Changes in Chemical Properties of Digestive Fluid

A three-stage process for pilot scale production of methane was operated as a stepwise system. Because of high TS (17–18%), food wastes were mixed with water at a ratio of 1:1 (v/v), then 100 L of the mixture was fed to the primary digester. The mixture was stirred at 180 rpm and hydrolyzed by a combination of aerobic and anaerobic bacteria for 2 d at 45°C. It was postulated that 2 d of HRT was enough to digest the waste in the primary digester. tCOD, sCOD, and BOD of the hydrolysate were 36,000, 23,000, and 40,000 mg/L, respectively (Fig. 2). At the same time, VFAs produced were continuously monitored through the fermentation process. In this step, the main VFA was acetic acid, whereas trace amounts of propionic, butyric, and caproic acids were produced (Fig. 3). Consequently, it seemed that the easily degradable polymers were hydrolyzed rapidly to oligomers or monomers by the aerobic bacteria, and they were simultaneously further converted to the acids by anaerobic bacteria. Although the initial pH was adjusted to 6.5, it decreased to 3.8 as acids were produced during the fermentation. The pH should be maintained at 5.0–5.5, because syntrophic and acetogenic activities were severely inhibited under sour digestion conditions *(4, 10–11)*. Therefore, mixing of acid hydrolysate with alkalic effluent (pH 8.8–9.2) derived from the finally treated drain wastewater was an efficient way to resolve the problem, and then more acid could be produced continuously.

When the primary digester was operated at 30°C, unpleasant odor was generated by the putrefactive bacteria contaminated from food wastes. However, the odor disappeared after the temperature was elevated to 45°C,because the bacteria cannot grow at the moderately high temperature.

After the hydrolysate was moved to the secondary digester, acid fermentation was carried out for 2 d. The products still showed high values of tCOD, sCOD, and BOD (Fig. 2), but more than two times large amounts of VFAs were produced (Fig. 3). It indicates that a significant amount of the biodegradable materials from food wastes is digested sufficiently and converted to VFAs and carbon dioxide without removal of organic wastes in large amounts. As shown in Table 1, the gas produced from acidogenic digester was mainly carbon dioxide.

While the acid effluent was injected to the methane digester, pH was adjusted to 5.0–5.5 with 5 N NaOH to relieve the acid impact on the methanogenic bacteria, because the methane fermentation virtually stopped under extreme sour conditions. While acid effluents resided for 12 d in the methane digester, tCOD, sCOD, and BOD decreased dramatically (Fig. 2). Removal rates of tCOD, sCOD, and BOD through the pilot-scale three-stage process were 88%, 87%, and 95%, respectively. This indicates that the digestion capability of the pilot-scale system is almost the same as that of bench scale, which has already been recognized as an effective and time-saving process for the disposal of food wastes with a high TS content *(6)*.

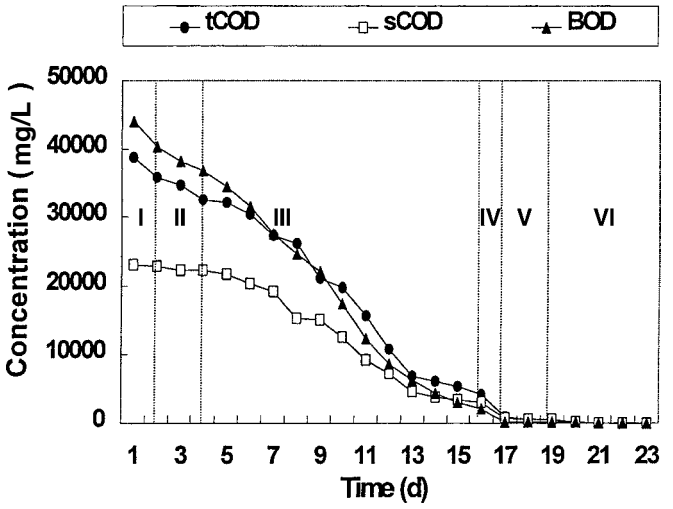

Fig. 2. Reduction of tCOD, sCOD, and BOD during the full digestion processes. I, semi-anaerobic hydrolysis/acidogenic process; II, anaerobic acidogenic process; III, anaerobic methanogenic process; IV, aerobic biological filter; V, anaerobic biological filter; VI, algal periphyton system.

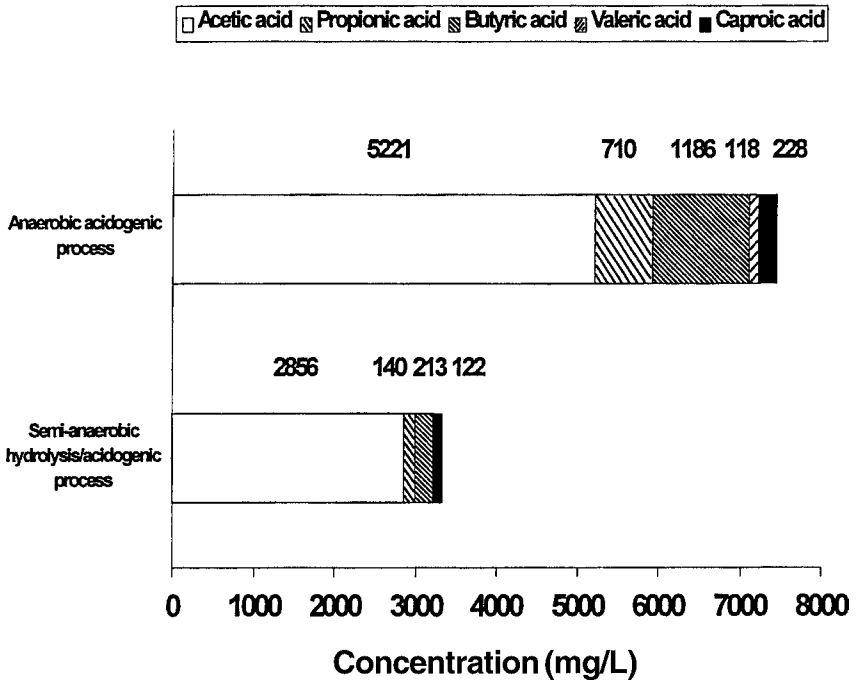

Fig. 3. VFA production from the primary semi-anaerobic hydrolysis/acidogenic process and the secondary anaerobic acidogenic process.

Table 1
Operational Conditions and Performance of Pilot Scale Three-Stage Methane Fermentation System

Parameter	First stage	Second stage	Third stage	Biological filter		
				Aerobic	Anaerobic	Algal periphyton
HRT (d)	2	2	12	1	2	4
Loading (kg VS/[m^3d])	104.4–105	60.4–61.2	54.9–55.4	5.7–6.0	1.8–1.9	1.7–1.8
pH	5.0–5.5	5.0–5.5	7.6–7.9	8.4–8.8	8.8–9.2	8.8–9.2
Temperature (°C)	45	35	41	35	35	25
T-N (mg/L)	5040	4496	4104	1124	500	53
NH3-N (mg/L)	181	203	1945	73	65	5
NO3-N (mg/L)	163	180	60	26	31	19
T-P (mg/L)	780	673	120	42	30	7
COD (mg/L)						
tCOD	35947	34625	4232	881	510	—
sCOD	22965	22244	3020	820	490	73
BOD (mg/L)	40268	35234	2046	246	161	21
Gas yield (m^3/kg VS)	—	—	0.65–0.70	—	—	
Gas composition(%)						
CH_4	—	9	72	—	—	—
CO_2	—	91	28	—	—	—
Methane yield (m^3/kg VS)	—	—	0.45–0.50	—	—	—
Volatile acids (mg/L)						
Acetic	2856	5221	385			
Propionic	140	710	0			
Butyric	213	1186	0	—	—	—
Valeric	0	118	0			
Caproic	122	228	0			
Total	3331	7463	385	—	—	—

VFAs and Methane Production

In the primary digestion process, 3331 mg/L of tVFA was produced (Fig. 3). Although acetic acid (86%) was the favored product, propionic, butyric, and caproic acids were produced in a small amount. In the secondary acidogenic process, the concentration of tVFA increased to 7463 mg/L, and acetic (5221 mg/L), propionic (710 mg/L), butyric (1186 mg/L), valeric (118 mg/L), and caproic acids (228 mg/L) were produced (Fig. 3). For the rapid acetoclastic reaction, acetic acid had an advantage to be cleaved to methane easily. Therefore, it seemed that the semianaerobic system was more effective than the strict anaerobic system in producing acetic acids.

Biogas could be accumulated in the methane reactor. The total gas yield in the methane fermentation system was 0.65–0.70 m^3/kg VS. Methane, carbon dioxide, ammonia, and hydrogen sulfide were detected. Seventy two percent of the total gas produced was methane and the yield was 0.45–0.50 m^3/kg VS (Table 1). Total gas and methane yield showed similar values compared to those of other work *(11–14)*. The most important parameters of the normal operation for the rapid digestion were particle size of wastes, pH, loading rate, and volume rate between acid and methane digester.

Wastewater Treatment

Although more than 85% of tCOD, sCOD, and BOD were removed through the three-stage process, the wastewater still contained high concentrations of them (Fig. 2). Moreover, only 19% T-N was removed through the process (Table 1). In case of NH_3-N, the concentration increased up to 1945 mg/L through the anaerobic methanogenic process. Therefore, additional wastewater treatment system was required because these concentrations were too high to be drained out. Aerobic and anaerobic biological filter systems have been developed. The biological filters were immobilized with nitrifying and denitrifying bacteria together with heterotrophic bacteria to degrade residual organic wastes in the wastewater. Through the process, T-N and NH_3-N concentrations decreased to 500 and 65 mg/L, respectively, and BOD reduced to 21 mg/L. Removal rates of T-N, T-P, and BOD were 90, 98, and 99.9%, respectively.

Since they were not further decomposed in the biological filter systems, an alternative method, algal periphyton system, was adopted. This system was very effective for wastewater containing low concentrations of T-N and T-P. *S. capricornutum* grew faster than *Chlorella* sp. under the condition that T-N concentrations are below than 500 mg/L. When they were inoculated to the wastewater having higher concentrations of T-N, they died slowly after 7 d. The optimum concentration of T-N for growth was 150 mg/L (Fig. 4A and B). At the same time, T-N removal rate of *S. capricornutum* was also higher than that of *Chlorella* sp., and it reached 53% within 4 d (Fig. 5A and B). When 3.00 mg/L of Mg^{2+} and 1.44 mg/L of Ca^{2+} were added to the wastewater (initial T-N concentration, 150 mg/L)

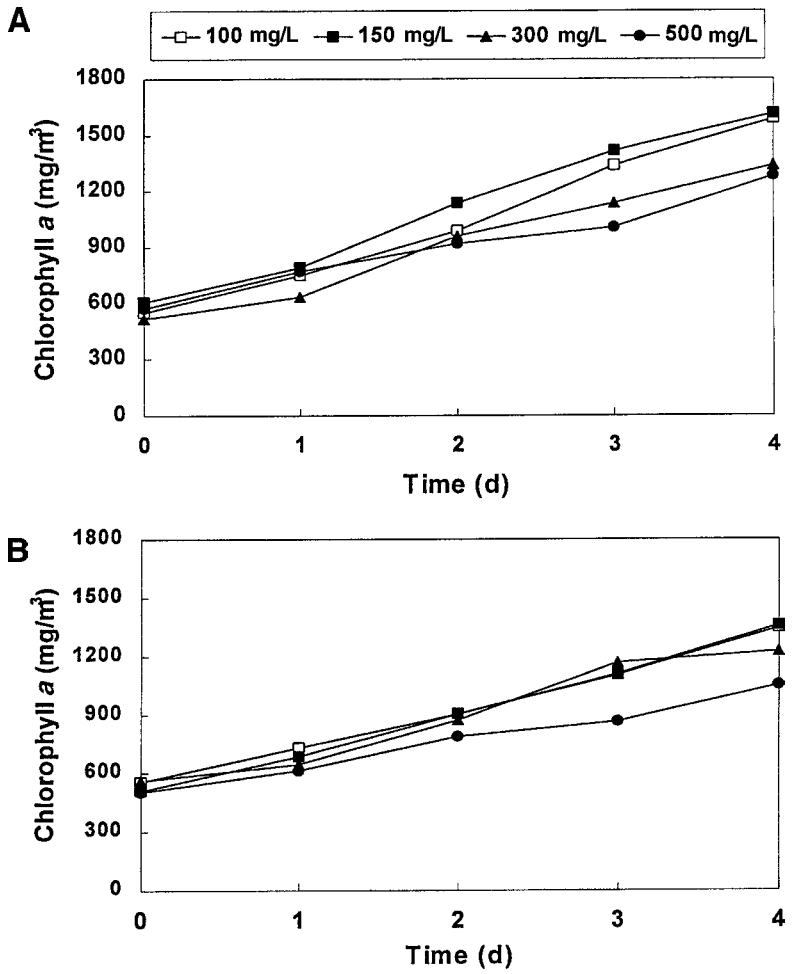

Fig. 4. Comparison of growth of *S. capricornutum* **(A)** with *Chlorella* sp. **(B)** in wastewaters containing various concentrations of T-N.

and incubated for 4 d, the removal efficiency of T-N increased and the final T-N concentration was 53 mg/L (Fig. 6). Consequently, the final effluent could maintain low concentrations of COD, BOD, T-N, and T-P, and satisfy the "Permissible Pollutant Discharge Standard of Wastewater" in Korea (Table 1). The permitted concentrations of COD, BOD, T-N, and T-P in the wastewater derived from the industrial complexes are 40, 30, 60, and 8 mg/L, respectively.

After all, three-stage methane fermentation process has more advantages than the conventional two-stage process: first, food wastes are hydrolyzed rapidly in the semianaerobic condition and HRT is reduced dramatically; second, nondegraded materials can be easily removed through a hole at the bottom of the semianaerobic reactor; third, pH of the primary and secondary reactors can be easily controlled by the addition

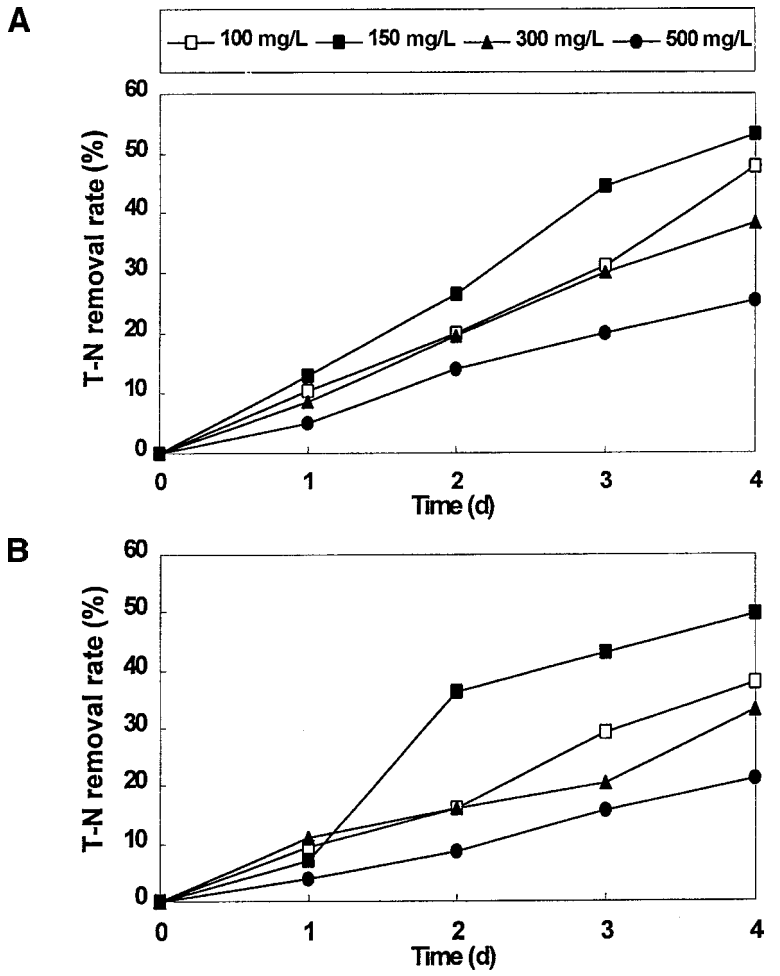

Fig. 5. Comparison of nitrogen removal rates of *S. capricornutum* **(A)** with *Chlorella* sp. **(B)** in wastewaters containing various concentrations of T-N.

of alkalic final effluent from algal periphyton process and more methane can be produced.

Conclusion

1. The pilot scale methane fermentation system developed in this study was an effective system to digest food wastes and to produce methane. Methane yield was 0.45–0.50 m^3/kg VS of food wastes. The removal efficiency of tCOD and BOD were 88 and 95%, respectively.
2. Wastewater eluted from the above system was further treated both with biological aerobic/anaerobic filter system and algal periphyton system. The remaining concentrations of COD, BOD, T-N, and T-P were 73, 21, 53, and 7 mg/L, respectively.

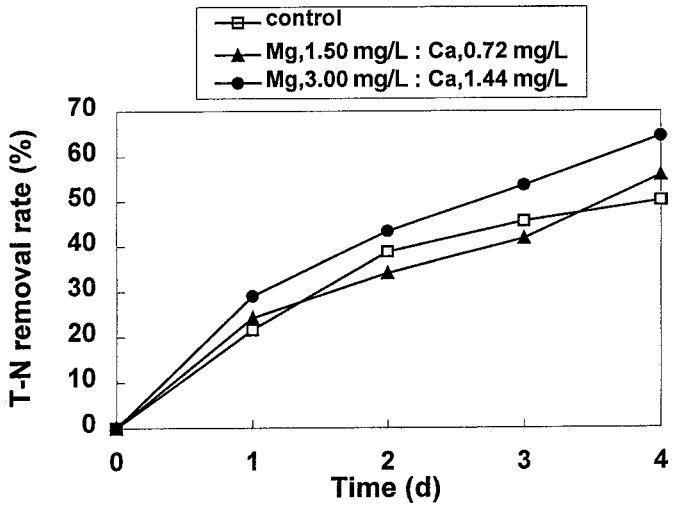

Fig. 6. Effect of Mg^{2+} and Ca^{2+} on the removal of nitrogen by *S. capricornutum* in wastewater containing 150 mg/L of T-N.

Acknowledgment

This work was supported by the ERC Grants from Ministry of Science and Technology in Korea and KOSEF (Korea Science and Engineering Foundation) in the year of 2000.

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