MAXIMUM COD LOADING CAPACITY IN UASB REACTORS AT 37°C

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ABSTRACT: The maximum capacity chemical oxygen demand (COD) loading in upflow anaerobic sludge blanket (UASB) reactors is evaluated using three 8.5 L reactors and high-strength synthetic wastewaters composed of milk and sucrose at 37°C. The study was conducted over a wide-range COD loading rate (18–260 $g \cdot L^{-1} \cdot day^{-1}$), by varying hydraulic retention time (HRT) (1.8–10 hr) and COD levels in wastewater (6,000–20,000 mg/L). At COD loading rates of up to 160 $g \cdot L^{-1} \cdot day^{-1}$, which corresponded to HRT of 1.8 h and COD of 12,000 mg/L in the wastewater, the process removed 94–98% of soluble COD and 75–90% of total COD. At rates higher than 160 $g \cdot L^{-1} \cdot day^{-1}$, the efficiency of COD removal deteriorated because of sludge disintegration and washout resulting from vigorous mixing by the biogas produced. The capability of volatile suspended solids (VSS) to convert COD to methane increased with COD loading; it reached the maximum of 1.7 g methane COD per gram VSS per day at the COD loading of 100 $g \cdot L^{-1} \cdot day^{-1}$, corresponding to the food-to-microorganism (F/M) ratio of 3 g COD per gram VSS per day. Characteristics of the sludge granules, effluent, and biogas are also discussed.

INTRODUCTION

Since the introduction of the anaerobic filter (Young and McCarty 1969), anaerobic process has grown into an advanced technology for the treatment of high-strength wastewaters. This has been due to the appreciable research and development efforts by many engineers and microbiologists, resulting in the evolution of advanced reactor designs (Speech 1983), and a better understanding of the anaerobic microbiology (Zehnder 1988). A basic concept of advanced anaerobic treatment design is to retain the active biomass within the reactor. As a result, reactors can be operated at increased biological solids retention time (SRT) and increased biomass concentration without increasing the hydraulic retention time (HRT). Among these designs, the upflow anaerobic sludge blanket (UASB) (Lettinga et al. 1980; Fang et al. 1990; Lettinga and Hulshoff Pol 1991) and the anaerobic filter (Suidan et al. 1983; Young and Young 1991) have been successfully commercialized; hundreds of full-scale systems have been installed worldwide. Others, such as expanded/fluidized bed (Switzenbaum and Jewell 1980; Jewell et al. 1981, Sutton and Li 1983; Wang et al. 1986; Iza 1991) and downflow stationary fixed film (Kennedy and Droste 1985, 1991), are still in the development stage and have so far only limited commercial success (Hickey et al. 1991).

The maximum organic loading capacity of anaerobic reactors has received much concern from researchers conducting kinetic modeling, as well as engineers developing reactor design. Much of the research done in the past

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focused on the development of the active biomass and the quantification of biomass activity (Owen 1979; Ney et al. 1990; Gorris et al. 1988; Fox and Suidan 1990) to aid the design of different reactors. The loading rate of anaerobic processes—unlike that of the aerobic processes, often limited by the oxygen transfer from the gas to liquid phase—is limited by the quantity of the active biomass that can be retained in the reactor and the effective contact between the biomass and the substrate.

The maximum volumetric loading rate for an anaerobic reactor depends on a number of parameters, such as reactor design, wastewater characteristics, biomass settleability and activity, etc. In practical design, a rate of 10 g $\mathrm{COD \cdot L^{-1} \cdot day^{-1}}$ has been commonly used for high-strength wastewater. On the other hand, Henze and Harremoes (1983) estimated the maximum COD removal rate per unit biomass as about 2 g of COD per gram of volatile suspended solids (VSS) per day. Their estimate was based on a thorough review of literature on experimental and operational data followed by modeling analysis for a combined culture of methanogenic and acetogenic microorganisms.

The present study, conducted for over 200 days, evaluated the maximum COD loading capacity of UASB reactors and the maximum COD-removal efficiency for a unit biomass. The results were compared with those estimated by Henze and Harremoes (1983). Experiments were conducted in three identical UASB reactors, in which the biomass, quantified by the VSS concentration, could be accurately measured. High-strength, synthetic wastewater composed of milk, sucrose, and other nutrients was used. The present paper also discusses the characteristics of the sludge granules, mixed liquor, and biogas.

EXPERIMENTAL

Three identical UASB systems were operated in parallel. A process flow diagram is illustrated in Fig. 1. Each reactor was 8.5 L in volume and had an internal diameter of 104 mm and a height of 1,000 mm. Seven evenly distributed sampling ports were installed over the height of the column. On top of each reactor was a gas-liquid-solid (GLS) separator with an internal diameter of 144 mm and a height of 300 mm, making a filled volume of 5 L. All the reactors were installed in a constant temperature environmental chamber at 37°C, the optimal temperature for mesophilic microorganisms. Volumetric loadings in this study were based on the reactor volume alone, excluding volume of the GLS separator.

Table 1 summarizes the formulation of the synthetic wastewater. The carbon was provided by the milk powder and sucrose, whereas the nitrogen and phosphorus were provided by the ammonium chloride and potassium phosphates, in addition to any in the milk. The alkalinity was supplemented by sodium bicarbonate. In addition, trace elements, such as sulfur, magnesium, cobalt, copper, nickel, molybdenum, manganese, boron, iron, etc. were also provided. Only 70% of the total COD in the synthetic wastewater was in soluble form; the remaining 30% was from the insoluble constituents, i.e. proteins and lipids, of the milk. The synthetic wastewater was prepared each day and stored in a 500 L feed tank maintained at 4°C. Mixing was provided by a submersible pump. Three variable-speed pumps fed the wastewater through a preheater into the reactors, forcing an equal volume of supernatant out of the effluent line.

The analytical procedures for all tests were as outlined in the *Standard Methods for the Examination of Water and Wastewater* (1985), unless spec-

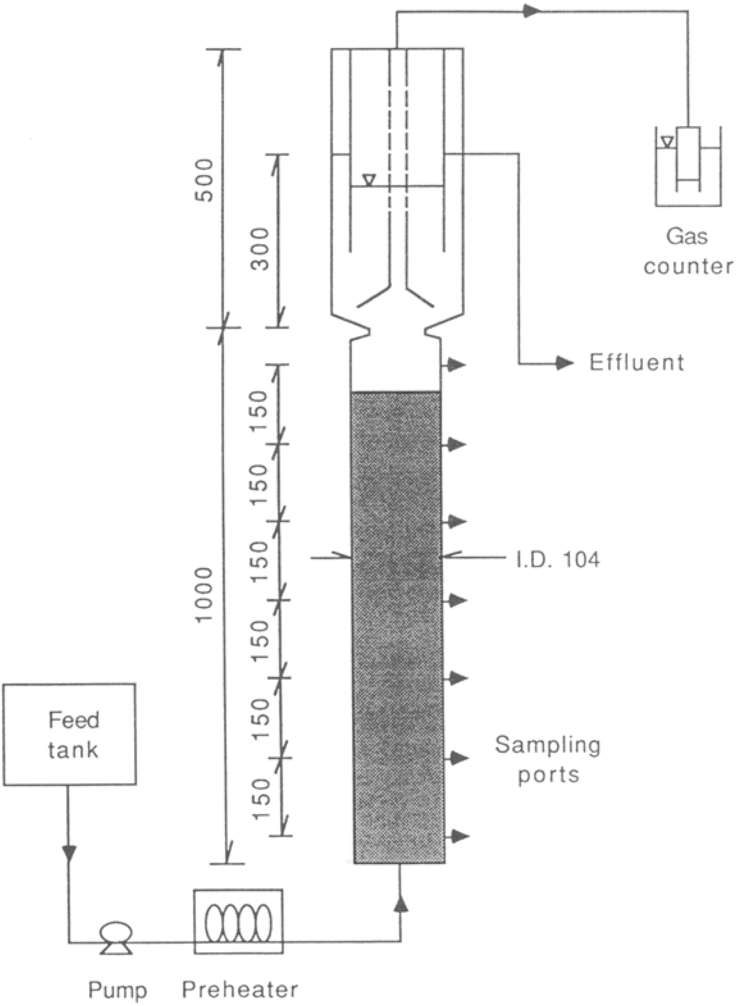

FIG. 1. Process Flow Diagram and UASB Reactor Design (dimensions in mm)

ified otherwise. The biogas production rate, which was measured by wet-type gas meters based on the design of Mosey and Matthews (1982), and the pH of the effluent were measured daily throughout the experiment. During the acclimation period, COD, total organic carbon (TOC), and volatile fatty acids (VFA) of the effluents were measured weekly. The total suspended solids (TSS) and volatile suspended solids (VSS) concentrations in various heights of the reactors were monitored biweekly. To ensure representative mixed liquor samples were taken, each sampling line was flushed with 5 mL of mixed liquor, before a 20 mL sample was taken for analysis.

The reactors were seeded with 6.5 L of digester sludge (1.0% VSS and 1.3% TSS) taken from the anaerobic digester of Shatin Wastewater Treat-

TABLE 1. Formulation of Substrates for each Gram of Chemical Oxygen Demand (COD) in Wastewater

Constituents (1)	Milligrams per gram of COD (2)
Sodium bicarbonate	1,000
Dry milk powder	390
Sucrose	390
Ammonium chloride	260
Magnesium sulfate (7 H_2O)	128.66
Potassium monohydrogen phosphate	75
Sodium citrate	67.91
Calcium chloride	52.10
Potassium dihydrogen phosphate	30.00
Nickel sulfate (7 H_2O)	16.00
Ferric chloride (6 H_2O)	12.45
Manganese(II) chloride (4 H_2O)	2.22
Zinc chloride	1.26
Cobalt chloride (2 H_2O)	1.10
Ammonium molybdate (4 H_2O)	0.80
Copper(II) chloride (2 H_2O)	0.65
Sodium borate (10 H_2O)	0.44

ment Works, Hong Kong. The initial COD loading to the reactor was 1 $g \cdot L^{-1} \cdot day^{-1}$ with a HRT of 12 h and a wastewater COD concentration of 500 mg/L. When the COD removal efficiency reached 80%, the organic loading of the reactor was increased stepwise by about 50%. The VFA concentrations were also closely monitored to ensure that the acetic acid concentration did not exceed 500 mg/L before the COD loading was increased. Throughout the study, the pH in the reactors was rather constant (7.1–7.8), because of the chemical buffers in the wastewater.

At each loading condition, each reactor was closely monitored until a steady state was reached. Steady state was assumed attained when the COD of the effluent and the biogas production rate were constant (within 1%) for three consecutive days. The parameters which were measured for three consecutive days included the COD, pH, and VFA of effluent, and the biogas production rate. Other data, such as TSS and VSS profiles, total Kjeldahl nitrogen (TKN), ammonia-nitrogen (NH_3-N), and alkalinity were obtained from samples once at the end of each steady-state condition. The effluent was acidified to pH 5 with concentrated sulfuric acid and purged with nitrogen at a flow rate of 100 mL/min for 15 min to remove the H_2S before COD analyses (Wang 1984). Soluble COD was obtained by filtering the sample through glass-fiber filter paper (Whatman GF/C) before the aforementioned procedures.

A gas chromatograph (GC) (Hewlett Packard model 5890A) was used to measure the composition of low molecular weight VFA (from acetic to heptoic acid) in the effluent and the composition of the biogas. For fatty-acid analyses, the GC was equipped with a 10 m × 0.53 mm HP-FFAP fused-silica capillary column and a flame ionization detector (FID), using helium as the carrier gas. Injector and detector temperatures were 200°C and 250°C, respectively. The fluid sample was filtered through a 0.45 μm membrane filter and acidified to pH 3 with concentrated phosphoric acid prior to injecting into the column using the fast-injection technique. The initial temperature of the column was 80°C for 5 min followed with a ramp of 10°C/min and a final temperature of 130°C for 4 min. Volatile fatty acid standards (Supelco, Inc., Bellefonte, Pa.) were used for the calibration of the FID.

For biogas analyses, the same GC was equipped with a thermal conductivity detector and a 2 m × 2 mm inside diameter (ID) stainless-steel column packed with Porapak N (80–100 mesh). Injector and detector temperatures were kept at 130°C while column temperature was 50°C.

RESULTS

Using the aforementioned procedures, the three reactors were acclimated fully in 70 days. At a low COD loading of 6 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$, the reactor was operated at a near-complete-mix mode. Constant levels of COD were observed for samples taken from the sampling ports at the 200 mm and higher levels. At a COD loading of 15 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$ and HRT of 8 h, all the reactors removed over 97% of soluble COD from the wastewater with 5,000 mg/L of COD. The COD and acetic acid concentration in the effluents were about 130 mg/L and 50 mg/L, respectively. The first granule in the UASB reactor was observed at day 16. The height of the sludge bed dropped to the minimum of 280 mm on day 47. It then gradually increased after day 61, as shown in Fig. 2. Fig. 2 also shows, as reported by Hulshoff Pol (1989), that during acclimation, the sludge concentration at the bottom of the reactor increased even though the height of the sludge bed decreased. After day 78, the reactor was filled with sludge granules; but no sludge blanket zone was observed. The three reactors were operated at a COD loading rate of 20 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$ (at an HRT of 8 h and influent COD of 6,500 mg/L) for an extended period, to ensure sludges in all reactors were identically conditioned prior to the subsequent loading tests.

Table 2 summarizes the conditions of the loading tests for each reactor. In addition, it also lists the pH, the methane content in the biogas, and concentrations of acetic, propionic, and *n*-butyric acids in the effluent. During these tests, each reactor was operated with wastewater containing various levels of COD, from 6,000 to 20,000 mg/L, and HRT from 1.8 h to 10 h. This represented a gradual increase of COD loading rate, over a wide range of 18–260 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$. The experimental program was terminated after 205 days when the reactors, at the time using wastewater with 20,000 mg/L of COD, experienced serious sludge washout at the high COD loading rates of 160–260 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$.

During the acclimation period, poor-settling sludge flocs were washed out from the reactor, while those with better settleability were retained, gradually forming a distinct sludge bed, as illustrated in Fig. 2. Biomass (about 1.0% concentration) was initially uniformly distributed along the 1,000 mm bed [Fig. 2(*a*)]. On day 61, the sludge bed was reduced to the 500 mm level with an average VSS of 1.9% [Fig. 2(*c*)]. From day 71 to day 158, the reactor was operated at a COD loading of 20 $\mathrm{g \cdot L^{-1} \cdot day^{-1}}$. During this period, the quantity of sludge steadily increased, requiring periodic wasting of sludge in order to maintain the bed at the 900 mm level. On day 158, the average VSS level in the sludge bed was 2.66% [Fig. 2(*e*)]. At the last stage of the study, the reactors produced large amount of biogas (47–73 $\mathrm{L \cdot L^{-1} \cdot day^{-1}}$) when they were operated at the COD loading of 160–260 $\mathrm{g\ COD \cdot L^{-1} \cdot day^{-1}}$, using wastewater with 20,000 mg/L of COD. During this period, the height of the sludge bed was drastically reduced [Fig. 2(*g*)] as a result of the vigorous mixing caused by the gas produced.

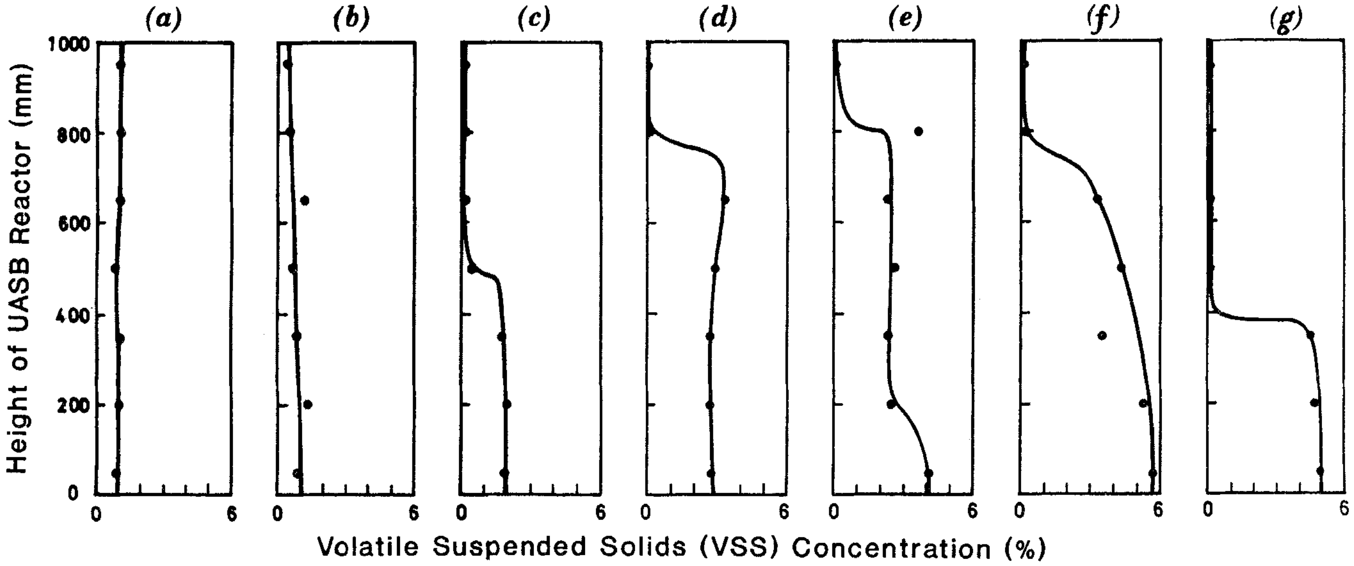

FIG. 2. Profile of VSS Throughout Study: (*a*) Day 4; (*b*) Day 26, (*c*) Day 61; (*d*) Day 105; (e) Day 158; (*f*) Day 179; (*g*) Day 204

TABLE 2. Operational Parameters, Characteristics of Effluents and Methane Content in Biogases under Steady-State Conditions

COD in wastewater (mg/L) (1)	HRT (h) (2)	COD loading ($g \cdot L^{-1} \cdot day^{-1}$) (3)	pH (4)	Acetic acid (mg/L) (5)	Propionic acid (mg/L) (6)	*n*-Butyric acid (mg/L) (7)	Methane content (%) (8)	Reactor (9)
6,000	8.0	18	7.1	29	17	5	63	A
6,000	6.0	24	7.5	31	11	2	63	B
6,000	4.5	32	7.1	29	22	4	63	C
8,900	10.0	21	7.4	38	20	5	59	A
8,900	8.0	27	7.8	25	8	2	59	B
8,900	6.0	36	7.4	40	30	6	57	C
13,000	9.0	35	7.4	40	21	6	52	A
13,000	7.0	45	7.3	31	18	5	52	B
13,000	5.5	57	7.5	45	37	8	51	C
6,300	2.8	54	7.5	26	24	3	50	A
6,300	1.8	84	7.5	62	88	3	49	B
6,300	1.8	83	7.1	58	97	4	49	C
12,000	2.8	100	7.4	77	248	11	47	A
12,000	2.2	130	7.3	91	193	7	48	B
12,000	1.8	160	7.4	101	354	13	46	C
20,000	3.0	160	7.1	520	3,200	24	30	A
20,000	2.3	210	7.1	850	2,500	29	29	B
20,000	1.8	260	7.0	860	3,000	14	27	C

At the bottom of the sludge bed, the VSS concentration increased from the initial 1.0% to 5.0–5.7% near the end of the study period, while the TSS increased from 1.3% to 18.4%. Fig. 3 illustrates the profile of VSS/TSS ratio along the sludge bed over the test period. At the bed bottom, the VSS/TSS ratio was reduced from the initial 0.72 to about 0.27 at the end. The drastic decrease of VSS/TSS ratio in the sludge after day 158 was due to increased calcium precipitation, as the calcium, alkalinity, and phosphate levels increased in the wastewater.

The high calcium content in the sludge granules at the bed bottom was observed by using the X-ray energy dispersive spectrometer under a scanning electron microscope (SEM). The high calcium content of sludge granules was also observed in other large scale reactors (Dolfing 1987). It is likely that the calcium content in the sludge could have a positive effect on the sludge settleability.

Sludge granules, which were taken when the reactors were operated for 30 days at the COD loading of 20 $g \cdot L^{-1} \cdot day^{-1}$, were examined under a scanning electronic microscope, the Cambridge Stereoscan 150. Prior to SEM examinations, granules had to be fixed by soaking in a 4% glutaldehyde aqueous solution for 2 h; sliced in half after being frozen in liquid nitrogen; dehydrated with a series of water/ethanol solutions, followed by another series of ethanol/carbon dioxide solutions at the critical point of carbon dioxide; and finally coated with gold-palladium. Figs. 4–7 illustrate the anaerobic microorganisms in the sludge granules.

A granule of about 1 mm diameter (Fig. 4) was sliced in half, exposing its dense skin layer, which had a thickness of about 20–30 μm, and its loosely packed interior (Fig. 5). The interior was predominantly populated by bamboo-shaped Methanothrix-like microorganisms (Fig. 6) and Methanococcus-like microorganisms. On the other hand, the granule surface and the dense skin layer had a diverse morphology (Fig. 7), consisting of cocci, rods, filaments, and spirochetes, similar to the observation by MacLeod et al. (1990). Methanosarcina, a methanogen capable of forming methane from both acetic acid and hydrogen, was not observed in the sludge granules.

Fig. 8 illustrates that, although the efficiency of COD removal decreased as the COD loading rate increased as expected, the UASB reactors overall were very effective in removing soluble COD from the synthetic wastewater. When treating wastewater with 12,000 mg/L or less of total COD, they consistently removed 96–98% of soluble COD when operated at COD loading of 18–84 $g \cdot L^{-1} \cdot day^{-1}$, and removed 94–96% of soluble COD at 100–160 $g \cdot L^{-1} \cdot day^{-1}$. However, when the wastewater with 20,000 mg/L of COD was treated at COD loading rates of 160–260 $g \cdot L^{-1} \cdot day^{-1}$, a large quantity of biogas was produced, creating a vigorous mixing condition at the top of the reactor. As a result, a large amount of the granular sludge was disintegrated and washed out of the reactor, and the experiment had to be stopped after three days. During this period, only about 70% of soluble COD in wastewater was being removed, due to the reduced concentration of sludge granules in the reactors. While both reactors were operated at the same COD loading of 160 $g \cdot L^{-1} \cdot day^{-1}$, reactor A had severe sludge washout when fed with wastewater containing 20,000 mg/L of COD, but reactor C operated smoothly without sludge washout when fed with wastewater containing 12,000 mg/L of COD. The reason for these results is not clear. Both reactors had similar VSS/TSS profiles, which seems to indicate that the granules in both reactors should have had similar degrees of settleability.

Suspended solids in the synthetic wastewater were mainly composed of

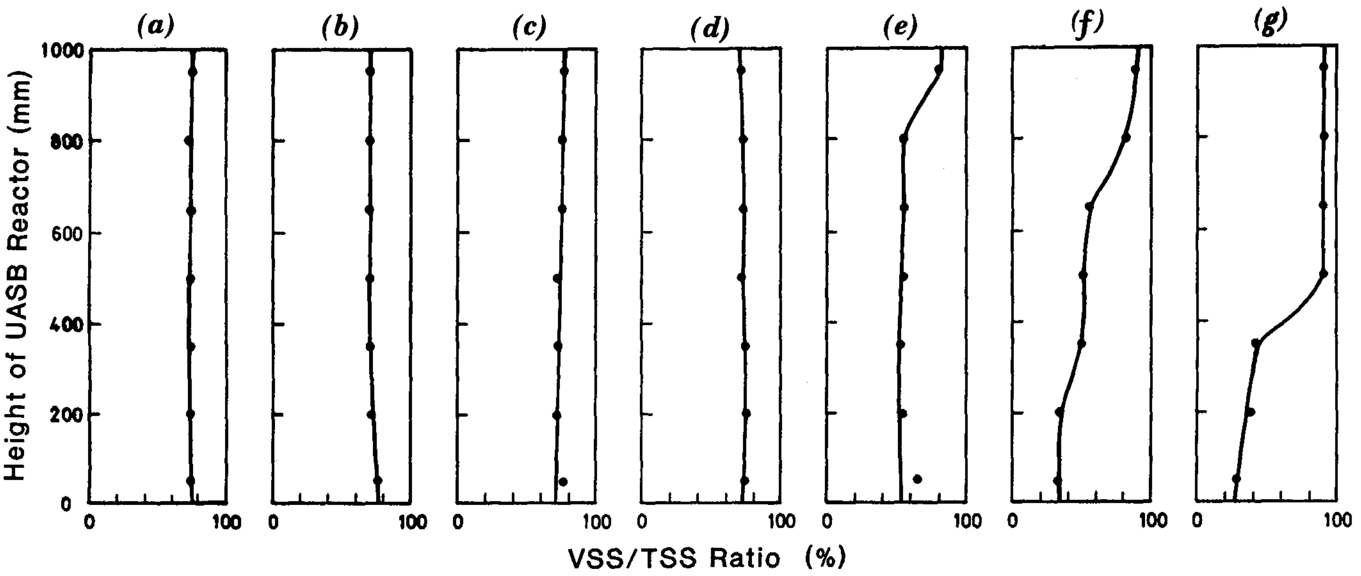

FIG. 3. Profile of VSS/TSS Ratio Throughout Study: (*a*) Day 4; (*b*) Day 26; (*c*) Day 61; (*d*) Day 105; (*e*) Day 158; (*f*) Day 179; (*g*) Day 204

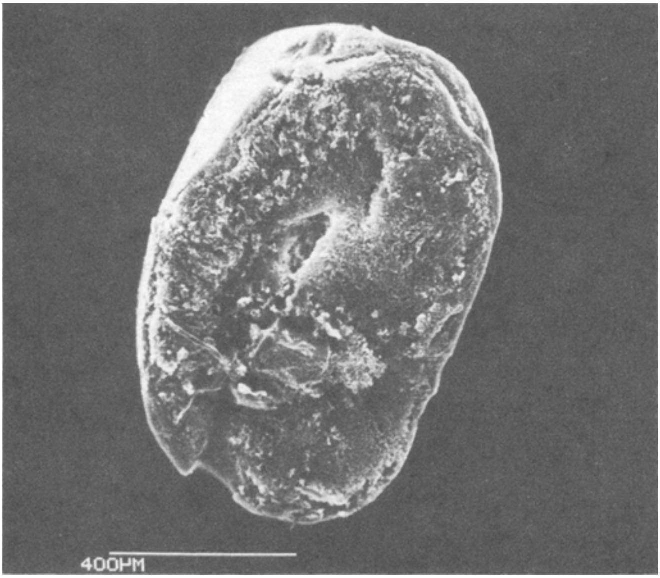

FIG. 4. SEM Picture of Typical Sludge Granules

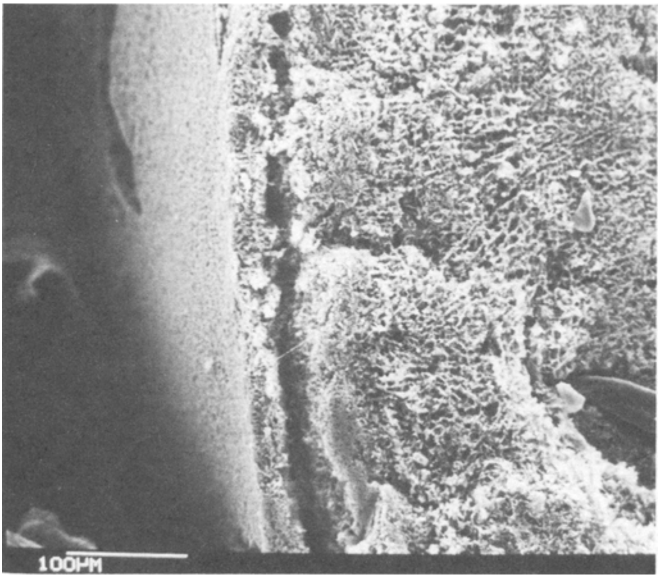

FIG. 5. SEM Picture of Skin Layer of Sludge Granule

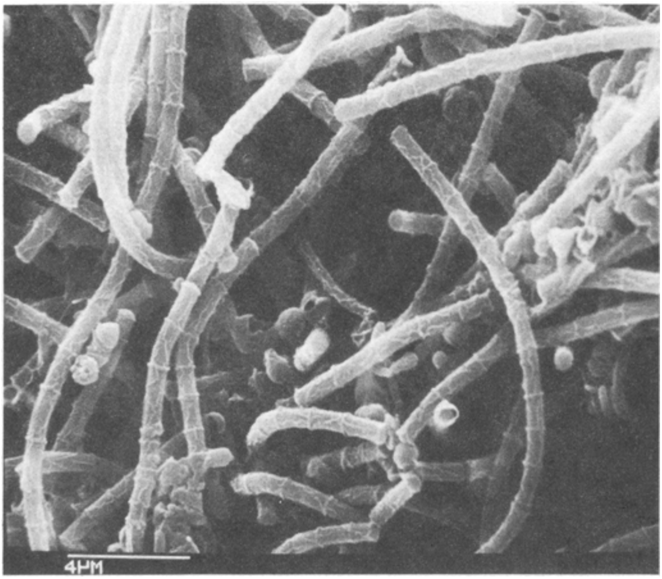

FIG. 6. SEM Picture of Methanothrix-like Microorganisms at Interior of Sludge Granule

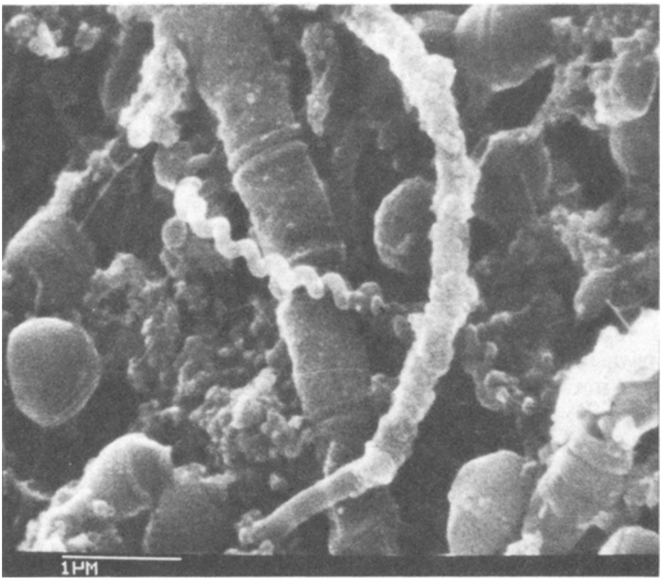

FIG. 7. SEM Picture of Diverse Morphology at Dense Surface of Sludge Granule

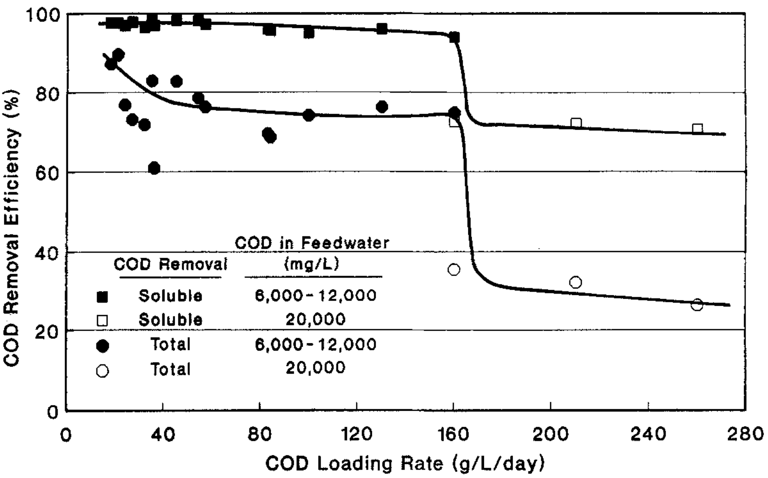

FIG. 8. Removal of COD from Wastewater at Various COD Loading Conditions

proteins and lipids, which had to be hydrolyzed into simpler molecules prior to being degraded by the acetogenic microorganisms. The hydrolysis is often the rate-limiting step for their anaerobic degradation, as reported by (Gossett and Besler 1982; Morris 1983). The removal efficiency of total COD (i.e. soluble plus insoluble) decreased as the COD loading increased, as also shown in Fig. 8. Removal decreased from about 90% at 20–30 g·L^{-1}·day^{-1} to 75% at 160 g·L^{-1}·day^{-1}. Furthermore, suspended solids could cause formation of scum (Lettinga and Hulshoff Pol 1991) in the UASB reactors. During the later stage of the present study, scum had to be removed nearly weekly. The solid contents and the corresponding COD in the scum were not measured. However, a COD balance for all the 18 runs shows that, on average, 88.3% of the wastewater COD was accounted for by the methane produced and the COD in the effluent. Biomass produced and scum accumulated in the reactors probably accounted for the remaining 11.7% of the wastewater COD.

As the COD loading increased, the production of biogas increased as expected. However, Table 2 shows that the methane concentration in the biogas decreased as the COD loading increased. The rate of methane production for a unit reactor volume versus COD loading is illustrated in Fig. 9. A maximum methane production rate of about 25.5 L·L^{-1}·day^{-1} was observed at COD loading of 130 g·L^{-1}·day^{-1}. When the carbonaceous matters in wastewater were converted to methane and emitted into the vapor space, COD in the wastewater was reduced. Each gram of methane emitted corresponded to four grams of COD removal. The amount of methane production at COD loading higher than 130 g·L^{-1}·day^{-1} was limited by the amount of active biomass.

Fig. 10 illustrates that the specific methane (expressed in COD) production rate increased with the COD loading rate, until it reached the maximum value of 1.7 g methane COD per gram VSS per day for COD loading rate of 100 g·L^{-1}·day^{-1} or higher. Fig. 11 illustrates the specific methane production rate as a function of food-to-microorganism (F/M) ratio. It shows that at a low F/M ratio of 0.6 g COD per gram VSS per day, the specific methane production rate was 0.5 g methane COD per gram VSS per day,

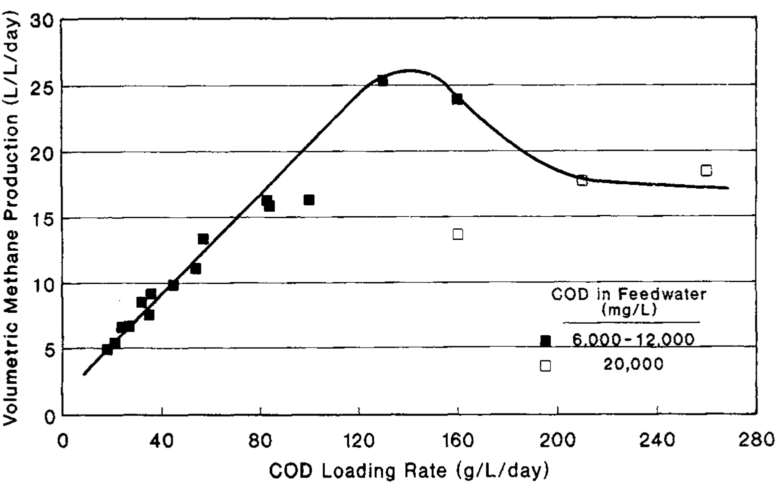

FIG. 9. Volumetric Methane Production Rate at Various COD Loading Conditions

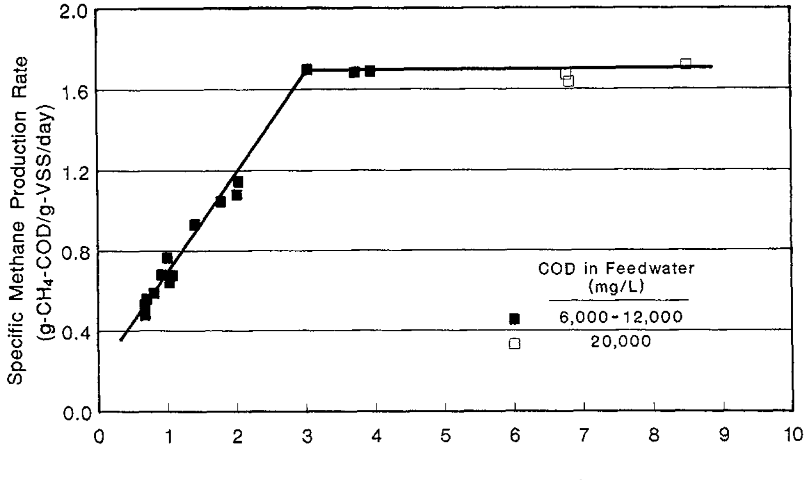

FIG. 10. Specific Methane Production Rate at Various COD Loading Rates

i.e. 83% of COD in wastewater was converted to methane. Since only 70% of the COD in wastewater was in soluble form, this result showed that a substantial fraction of the insoluble COD was converted to methane at the low F/M ratio. The specific methane production rate increased linearly with the F/M ratio, until it reached the maximum of 1.7 g methane COD per gram VSS per day at the F/M ratio of 3 g COD per gram VSS per day. The slope of the linear section in Fig. 11 is 0.53 g methane COD per gram COD. This means that, as the F/M ratio increased from 0.6 to 3.0 g COD per gram VSS per day, only 53% of the incremental COD in the wastewater was converted to methane. Thus, a substantial fraction of the insoluble COD in wastewater was not removed for F/M ratio higher than 0.6 g COD

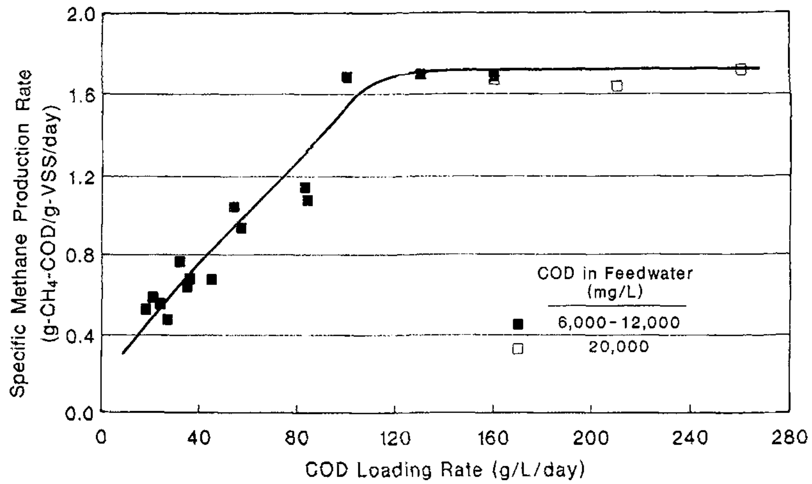

FIG. 11. Specific Methane Production Rate at Various Food-to-Microorganisms (F/M) Ratios

per gram VSS per day. This could likely be due to the short HRT conditions in this study, which limited the hydrolysis of the insoluble solids.

The specific methane production rate consistently remained at the maximum level of 1.7 g methane COD per gram VSS per day when the F/M ratio was increased from 3 to 8 g COD per gram VSS per day. It shows that the methanogenic bacteria reached their maximum capacity at 3 g COD per gram VSS per day, or 100 g COD$\cdot$L$^{-1}\cdot$day^{-1}. Beyond this loading rate, methanogenic reaction became the rate-limiting step. Henze and Harremoes (1983) estimated that the maximum COD removal rate for a 100% active biomass as about 2 g COD per gram VSS per day; their estimate was based on a thorough review of literature on experimental and operational data followed by modeling analysis for combined culture of methane-producing and acid-producing bacteria. Assuming only 50% of biomass was active, they estimated that the practical COD removal rate would be 1 g COD per gram VSS per day. However, results from this study showed that the maximum COD conversion to methane was consistently 1.7 g COD per gram VSS per day over wide ranges of F/M ratio and COD loading rate.

It is known that the biogas composition depends mainly on the nature of the substrates. GC analysis showed that the biogas was consistently composed of 98–99% of methane and carbon dioxide, with nitrogen making up the balance. Concentration of hydrogen in the biogas was not measured. Gujer and Zehnder (1983) estimated that degradation of lipids would produce biogas containing about 67–74% methane, but only 50–58% methane for proteins and about 50% for carbohydrates. In the present study, the methane concentration was about 63% at COD loading of 18–30 g$\cdot$L$^{-1}\cdot$day^{-1}, and was gradually decreased to 46% at 160 g$\cdot$L$^{-1}\cdot$day^{-1}. When the COD in wastewater further increased to 20,000 mg/L at COD loadings of 160–260 g$\cdot$L$^{-1}\cdot$day^{-1}, the methane concentration was drastically reduced to as low as 28%. The initial decrease of methane concentration was probably because, as the COD loading increased, the biomass preferentially biodegraded the more soluble carbohydrates and proteins, instead of the more complex lipids. The drastic decrease of methane concentration in biogas at higher loadings was because the methanogenic reaction had become the rate-limiting step, as evidenced by the accumulation of VFA in the effluent.

Table 2 shows that the VFA concentrations in the effluents were consistently low when the reactors were operated at low COD loading rates. At 100 g COD $\cdot$ L^{-1} $\cdot$ day^{-1} or less, concentrations of acetic and propionic acids were observed below 60 mg/L and 100 mg/L, respectively. Low VFA concentrations indicated that methanogenic reaction was not the rate-limiting step at these conditions. Acetic acid concentration at 200 mg/L or less favored the growth of the methanothrix rather than the methanosarcina-like microorganisms (Hulshoff Pol 1989; Gujer and Zehnder 1983); this was evidenced by the absence of the latter in the sludge granules.

At COD loadings of 100–160 g $\cdot$ L^{-1} $\cdot$ day^{-1}, as methanogenic bacteria reached their maximum capacity, the concentration of acetic and propionic acids approached 100 mg/L and 350 mg/L, respectively. As COD loading further increased to 160–260 g $\cdot$ L^{-1} $\cdot$ day^{-1}, the concentration of acetic and propionic acids increased drastically to more than 500 mg/L and 2,500 mg/L, respectively. The accumulation of VFA at COD loadings of 100–260 g $\cdot$ L^{-1} $\cdot$ day^{-1}, i.e. at F/M ratios of 3–8 g COD per gram VSS per day, indicated that methanogenic reaction had become the rate-limiting step, as also reflected by the aforementioned decrease of methane in the biogas.

It appears that there is no report in the literature indicating that a UASB reactor could be operated at a COD loading as high as 160 g $\cdot$ L^{-1} $\cdot$ day^{-1}. Such a high COD loading was now accomplished in the present study. This could be attributed to a number of reasons, including the easy-to-biodegrade characteristics of the synthetic wastewater, the balanced nutrients, the systematic acclimation strategy used during the start-up, and so forth. As a result, a highly active biomass with good settleability was generated and retained in the reactors. It has been reported that small anaerobic reactors could be operated at a COD loading of 206 g $\cdot$ L^{-1} $\cdot$ day^{-1}. Aivasidis and his coworker (Aivasidis 1985; Aivasidis and Wandrey 1988) used an uncommon design in their study, in which biomass was immobilized in sintered glass. It appears that a feedwater containing low levels of suspended solids was used to prevent clogging of the sintered glass. The COD removal in their study was 78%. Application of such a design for large-scale operation, however, remains to be seen.

CONCLUSIONS

This experimental study examined the maximum capability of COD removal by the UASB process at 37°C using a synthetic wastewater containing 30% insoluble COD. The total COD ranged from 6,000 to 20,000 mg/L, whereas the HRT varied from 1.8 h to 10 h. Based on the results and discussion in the previous section, the following conclusions have been reached.

For the synthetic wastewater used in this study with COD of 12,000 mg/L or less, COD loading rate was an important operating parameter that affected the COD removal. At a COD loading of 160 g $\cdot$ L^{-1} $\cdot$ day^{-};^{1}, the UASB reactors effectively removed 94% of soluble COD and 75% of total COD from the synthetic wastewater. Such a high COD loading was accomplished probably due to the easy-to-biodegrade characteristics of the wastewater, the balanced nutrients, and the systematic acclimation strategies during the start-up.

For the synthetic wastewater used in this study with COD of 20,000 mg/L and a COD loading higher than 160 g $\cdot$ L^{-1} $\cdot$ day^{-1}, the COD removal capacity of the UASB reactors drastically declined. Large quantities of sludge were disintegrated and washed out, as a result of the vigorous mixing caused by the biogas generated.

At a F/M ratio of 3 g COD per gram VSS per day, corresponding to a COD loading of 100 $g \cdot L^{-1} \cdot day^{-1}$, methanogenic microorganisms reached their maximum capacity; each gram of VSS converted 1.7 g/day of COD to methane. At higher F/M ratios of 3–8 g COD per gram VSS per day, or COD loadings of 100–260 $g \cdot L^{-1} \cdot day^{-1}$, methanogenic process gradually became the rate-limiting step, as reflected by the increase of acetic and propionic acid concentrations in the effluent and the decrease of methane in the biogas.

Sludge granules calcified as a result of the high calcium, alkalinity, and phosphate levels in wastewater. At the end of the present study, sludge granules at the reactor bottom had a VSS/TSS ratio as low as 0.27. However, the bioactivity per unit VSS remained unchanged.

The interior of the sludge granules were predominantly composed of methanothrix-like and methanococcus-like microorganisms, whereas the surface and the skin layer of the granules had a much more diverse morphology.

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