PERFORMANCE AND SLUDGE CHARACTERISTICS OF UASB PROCESS TREATING PROPIONATE-RICH WASTEWATER

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Abstract—UASB process consistently removed 97–99% of chemical oxygen demand (COD) in wastewater containing concentrated propionate at 37°C in 12 h for loading rates up to 23 g-COD/l·day. Of all the COD removed, 95% was converted to methane and the rest was converted to biomass with an average sludge yield of 0.040 g-VSS/g-COD. Each gram of propionate-degrading granules in the reactor had a daily maximum capacity of converting 0.60 g of COD into methane. The granules were densely packed but did not exhibit any patterned microstructure. A typical propionate-degrading granule was composed of microcolonies of *Methanothrix* and several syntrophic microcolonies with hydrogen-producing acetogens in juxtaposition with hydrogen-consuming *M. hungatei* and *Methanobrevibacter*-like bacteria.

Key words—granule, loading rate, methanogenic activity, microstructure, propionate, UASB, wastewater, yield

INTRODUCTION

Treating complex wastewater anaerobically in two phases (Pohland and Ghosh, 1971) has higher efficiency (Aoki and Kawase, 1991) and better resistance to shock load (Bull *et al.*, 1984) than in the conventional single-phase treatment. In the first phase, complex pollutants are degraded by the fermentative and acidogenic bacteria into volatile fatty acids (VFA), which are subsequently converted to methane and carbon dioxide by the acetogenic and methanogenic bacteria in the second phase.

Propionate, a key intermediate of acidogenesis, is rich in the effluent of the first reactor serving as the major substrate for the acetogenic bacteria in the second reactor (Hanaki *et al.*, 1987). However, it is also known to have the lowest tolerance level, among the VFA, for the anaerobic bacteria (Bajpai and Iannoii, 1988). When an anaerobic treatment system is overloaded, propionate tends to accumulate in the digester, and is difficult to be removed during recovery (McCarty and Mosey, 1991). This is due to the fact that degradation of propionate to acetate is thermodynamically infeasible unless the by-product hydrogen can be readily removed by the hydrogen-consuming bacteria (Boone and Xun 1987).

Among the high-rate anaerobic technologies, the Upflow Anaerobic Sludge Blanket (UASB) process (Lettinga *et al.*, 1980) has gained worldwide popularity in recent years. In a UASB reactor, bacteria

aggregate forming granules with high settleability and bioactivity. In addition, each granule forms an ecosystem which facilitates the syntrophic association between the hydrogen-producing acetogens and hydrogen-consuming methanogens (Fang *et al.*, 1994). This study was conducted to examine the efficacy of the UASB process treating wastewater containing high levels of propionate and the microstructure of the propionate-degrading granules.

MATERIALS AND METHODS

The UASB reactor (Fang *et al.*, 1994) used in this study was 2.8 l in volume with an internal diameter of 84 mm and a height of 500 mm. Five evenly distributed sampling ports were installed over the height of the reactor. Total biomass in the reactor was estimated periodically based on the profile of the volatile suspended solids (VSS) of the samples taken from these ports. On top of each reactor was a gas–liquid–solid separator with an internal diameter of 114 mm and a height of 250 mm.

Prior to this study, flocculent sludge from a local anaerobic sludge digester was partially granulated in a 65 l UASB reactor for two months, using sucrose as the organic substrate. About 1.5 l of this partially granulated sludge was used to seed the reactor, which was continuously fed with synthetic wastewater by a peristaltic pump. The wastewater was composed of propionate as the sole organic substrate, plus trace metals and balanced nutrients using a formulation of a previous report (Fang and Chui, 1993a). Throughout this study, the reactor was operated at 37°C with a constant hydraulic retention time (HRT) of 12 h. The sampling strategies and the analytical procedures, such as the methane content in biogas, the VFA levels in effluent etc., followed those reported previously (Fang and Chui, 1993a).

The COD loading rate, which was proportional to the propionate concentration in the wastewater, started at

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4 g/l·d, corresponding to 2000 mg/l of COD in wastewater. The reactor was operated at each loading rate for at least 10 days to ensure reaching a steady state, as evidenced by the steady COD removal efficiency and the constant pH in the effluent. In order to examine the microstructure of the fully developed granules, the reactor was operated at 10 g-COD/l·day for over 5 months before granules were sampled for microstructure analysis using scanning and transmission electron microscopies (SEM and TEM). The instruments and the sample preparation procedures were as reported previously (Fang and Chui, 1993b).

RESULTS AND DISCUSSION

COD removal efficiency

The pH in the reactor was kept at a constant level of 7.0–7.5 throughout the study. At a constant HRT of 12 h, the COD loading rate was proportional to the COD level in the wastewater. Figure 1 illustrates (a) the efficiency of COD removal, (b) the total biogas production rate, and (c) the COD loading rate as well as the COD concentration in the wastewater throughout this study. The COD removal was calculated from the soluble COD in the effluent and the total COD in the wastewater. As illustrated in Fig. 1(a), the COD removal efficiency was consistently 97–99% before day 275. Thereafter, the COD removal efficiency was drastically reduced to about 78% when the COD loading rate was increased to 30 g/l·day. The experiment was terminated on day 290.

Figure 2 illustrates the average COD removal efficiency and the average methane production rate at each COD loading condition. Figure 2(a) illustrates that the COD removal efficiency was 97–99% for loading rate up to 23 g-COD/l·day, which corresponds to 11500 mg/l of COD in the wastewater and a food-to-microorganism (F/M) ratio of 0.64 g-COD/g-VSS·day. The maximum COD loading rate was comparable to the maximum propionate-converting activity of 25–26 g-COD/l·day in a UASB reactor at 55°C (Wiegant *et al.*, 1986).
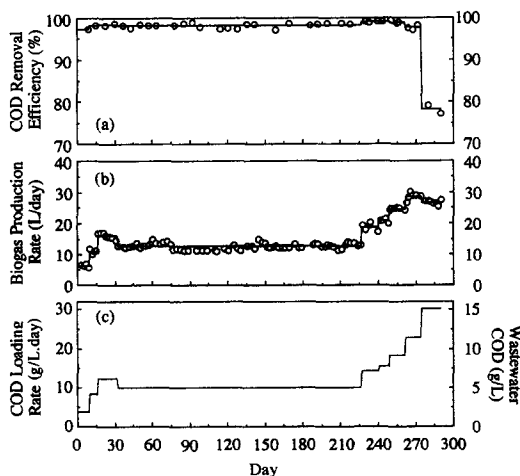

Fig. 1. Performance of UASB reactor: (a) COD removal efficiency; (b) biogas production rate; (c) COD loading rate and concentration in wastewater.
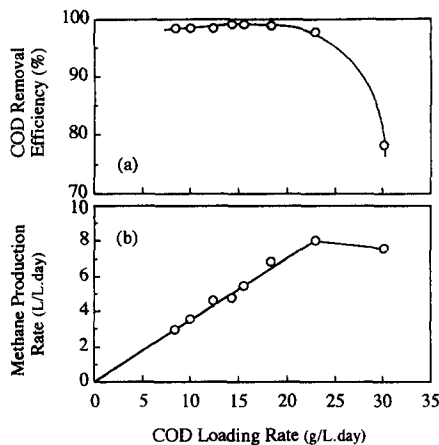

Fig. 2. (a) COD removal efficiency; (b) methane production rate, at various COD loading rates.

At the loading rate of 23 g-COD/l·day or lower, the effluent had less than 50 mg/l of acetate, 100 mg/l of propionate, and negligible quantities of *n*- and *i*-butyrates and *n*- and *i*-valerates. At 30 g-COD/l·day, although the acetate was still less than 100 mg/l and other VFA remained negligible, the propionate concentration in the effluent increased to the level of 1600 mg/l. This indicated that converting propionate to acetate was the rate-limiting step, which was also observed by Wiegant *et al.* (1986) under thermophilic condition.

Methane production

The methane content of the biogas was found to be 70–80% throughout the study. Figure 2(b) illustrates that the volumetric methane production rate increased linearly with the COD loading rate, until reaching a maximum of 8.0 l/l·day at 23 g-COD/l·day. Since each gram of methane was equivalent to 4 g of COD, the specific methane production rate (SMPR) for the biomass could be estimated from the methane production rate and the total biomass in the reactor. Figure 3 illustrates that the SMPR increased linearly with the specific substrate utilization rate (SSUR) with a slope of 0.95, until reaching a maximum of 0.60 g-COD/g-VSS·day at the SSUR of 0.63 g-COD/g-VSS·day. The slope indicates that of all the COD removed, 95% was converted to methane and the rest was presumably
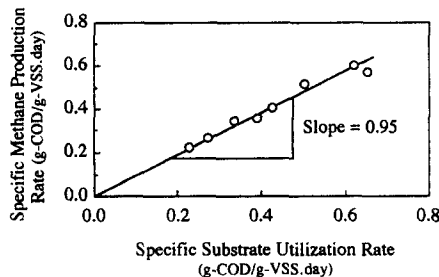

Fig. 3. Specific methane production rate at various SSUR.

Fig. 4. *Methanothrix* under TEM (bar = 2 μm).

Fig. 6. Syntrophic microcolonies of *Syntrophobacter*-like bacteria in juxtaposition with *Methanospirillum hungatei* and the electron dense *Methanobrevibacter*-like bacteria under TEM (bar = 4 μm).

converted to biomass. The biomass in the reactor had a COD/VSS ratio of 1.24. Accordingly, the sludge yield was estimated to be 0.040 g-VSS/g-COD, which is within the reported range of 0.025–0.051 (Pavlostathis and Giraldo-Gomez, 1991). The biomass was periodically removed from the reactor for the VSS profile and microscopic analyses, and to avoid excess biomass accumulation.

Microstructure of granules

Propionate-degrading granules were 1–2 mm in size and had satisfactory settleability. Although layered microstructure was reported for granules treating wastewater of sucrose (MacLeod *et al.*, 1990) and brewery (Fang *et al.*, 1993), propionate-degrading granules were densely packed but did not exhibit any patterned structure. SEM and TEM photos illustrate that granules were composed of microcolonies of *Methanothrix* (0.6 μm), as illustrated in Fig. 4, and several other microcolonies with juxtapositioned syntrophic associations between the hydrogen-producing acetogens and hydrogen-consuming methanogens. Juxtapositioned syntrophic associations between these bacterial allowed the rapid removal of hydrogen, which would otherwise hinder the propionate
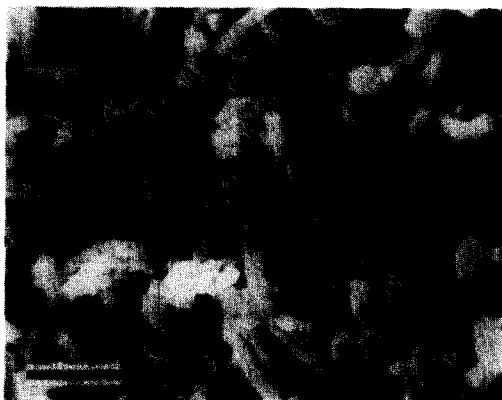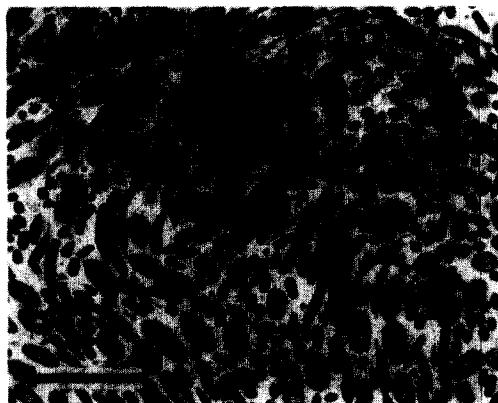
degradation, as elucidated from thermodynamic analysis. Among the syntrophic microcolonies, the most prevalent type was composed of *Syntrophobacter*-like bacteria (0.6–1.0 × 1.0–4.5 μm) in juxtaposition with *Methanospirillum hungatei* (0.3 μm) and the electron dense *Methanobrevibacter*-like bacteria (0.3 × 0.9 μm), as illustrated in Fig. 5 (SEM) and 6 (TEM). *M. hungatei* converts either formate or H_2/CO_2 to methane, and can be identified by TEM from its well-documented features, such as spacer between adjacent cells, structural elements in the cell spacer, flagella through the end plug, and the cell division mechanism (Zeikus and Bowen, 1975; Beveridge *et al.*, 1987; Southam *et al.*, 1990).

SUMMARY AND CONCLUSION

The following conclusions could be drawn regarding the UASB treatment of wastewater containing propionate at 37°C in 12 h of retention:

1. The UASB process consistently removed 97–99% of propionate up to the COD loading rate of 23 g/l·day. Of all the COD removed, 95% was converted to methane, the rest was converted to biomass with an average sludge yield of 0.040 g-VSS/g-COD.

2. This was no accumulation of acetate in the effluent, even when the reactor only removed 78% of COD at 30 g-COD/l·day, suggesting that propionate conversion to acetate was the rate-limiting step.

3. Each gram of propionate-degrading granules in the reactor had a daily maximum capacity of converting 0.60 g of COD into methane. The granules were densely packed but did not exhibit any patterned microstructure. A typical propionate-degrading granule was composed of microcolonies of *Methanothrix* and several syntrophic microcolonies with hydrogen-producing

Fig. 5. Syntrophic microcolonies of *Syntrophobacter*-like bacteria in juxtaposition with *Methanospirillum hungatei* and the electron dense *Methanobrevibacter*-like bacteria under SEM (bar = 3 μm).

acetogens in juxtaposition with hydrogencon-
suming *M. hungatei* and *Methanobrevibacter*-
like bacteria.

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