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# Lower operational limits to volatile fatty acid degradation with dilute wastewaters in an anaerobic fluidized bed reactor

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ABSTRACT

A general concern that anaerobic treatment of dilute wastewaters is limited by the inability of methanogenic and related syntrophic organisms to reduce substrate concentrations adequately was evaluated using a 35 °C granular activated carbon-containing laboratory-scale fluidized bed reactor fed an acetate-propionate equal chemical oxygen demand (COD) mixture synthetic wastewater. Contrary to general expectations, effluent acetate and propionate concentrations remained near or below their detection limits of 0.4 mg COD/L with influent COD of 200 mg/L, 17 min hydraulic retention time, and organic loading as high as 17 kg COD/$m^3$ d, or with influent COD values ranging from 45 to 2010 mg COD/L and organic loadings of 4.2–4.5 kg COD/$m^3$ d. The effluent acetate concentrations in these well-fed systems were at or much below reported threshold limits for starving non-fed cultures, suggesting that a better understanding of threshold values and factors affecting treatment efficiency with anaerobic treatment of dilute wastewaters is needed.



## 1. Introduction

Climate change concerns resulting from fossil fuel usage and increasing energy costs have brought a growing interest in reducing energy usage at wastewater treatment plants (Stenstrom and Rosso, 2007). One approach for achieving this is through greater reliance on anaerobic wastewater treatment, which produces renewable energy in the form of biogas, rather than consuming energy as necessary in conventional aerobic treatment (Foresti et al., 2006; van Lier et al., 2001). Another significant advantage of anaerobic treatment is a low resulting biomass production, allowing reduction in costs for sludge handling and disposal. Because of these potential advantages, anaerobic treatment of low strength wastewaters is receiving increased attention (Aiyuk et al., 2006; van Lier et al., 2001). However, anaerobic treatment systems are often considered unable to reduce biodegradable organic substances to sufficiently low concentrations to meet more stringent effluent requirements (Aiyuk et al., 2006; Oliveira and Von Sperling, 2008). This raises a question about what factors prevent reaching low concentrations. Among the various factor sited is an inability of the methanogens themselves to achieve low effluent concentrations (Jewell, 1987). If so, then this is critically important for treatment of dilute wastewaters of any type since methanogens are necessary components of all methanogenic anaerobic treatment systems. The purpose of this study was to examine this potential limitation using a fluidized bed reactor, a reactor that allows treating a dilute wastewater at short hydraulic detention time (HRT) with reasonably high organic loading rates (OLR) (Rittmann and McCarty, 2001).

There have been several reports about a "threshold" for substrate utilization by methanogens, which is considered to be the concentration below which substrate consumption stops. Such a threshold would provide a lower bound on substrate utilization, a factor that would impact on potential efficiency of anaerobic treatment. Pavlostathis and Giraldo-Gomez (1991) provided a summary of reported threshold values for both hydrogenotrophic and acetotrophic methanogens. Indicated was that such thresholds are related to the bacterial species present and their physiological conditions. Thresholds for hydrogenotrophic methanogens, based upon gas-phase hydrogen concentrations, varied from $30(10^{-5})$ atm to $1000(10^{-5})$ atm for temperatures in the 28–39 °C range. For acetotrophic methanogens at 37 °C, reported thresholds for acetate covered the wide range of 0.25–71 mg/L. The lowest values of 0.25, 0.42 and 4.1 mg/L were reported for granular sludge, *Methanothrix soehngenii*, and another *Methanothrix* sp., respectively. The *Methanothrix* genera is now classified under the generic name of *Methanosaeta*. Threshold values at more intermediate levels of 14–92 mg/L were reported for a range of other acetoclastic species of the genera *Methanosarcina*, *Methanobacterium*, *Methanospirillum*, and *Methanobrevibacter*. It thus appears that significant presence of *Methanosaeta* would be required if anaerobic treatment is to result

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in very low acetate concentrations. Lower limits for utilization of other volatile fatty acids not directly used by methanogens are not well studied, but would be of importance as well. Threshold values represent the lowest concentrations reached through starvation after feeding of a culture is stopped. There is little information on how close to such threshold values might result in an operating anaerobic treatment system. This is of critical importance.

Threshold limits would be expected to be lower than operational limits, the values that result under quasi-steady-state conditions during wastewater treatment where organisms are actively growing. In order to evaluate lower operational limits for volatile fatty acids, dilute wastewater (COD concentrations less than 2000 mg/L) containing only two important volatile fatty acids, acetate and propionate, was treated in an anaerobic fluidized bed reactor (AFBR). In the case of propionate conversion, three organisms are involved, a syntroph that converts propionate to 3 mol $H_2$ and 1 mol acetate, a hydrogenotrophic methanogen that converts 4 mol $H_2$ to one of methane, and an acetoclastic methanogen to convert acetate into methane and carbon dioxide. Examined in this study was the possible relationship between minimum operational concentrations achieved during steady–state reactor operation and reported threshold limits.

## 2. Methods

### 2.1. Experimental procedures

The AFBR used consisted of a reactor column and two settlers as described in detail previously (Shin et al., 2011). The 3.93 L reactor column consisted of a 2000 mm long by 50 mm dia. acrylic tube containing 450 g of 10 × 30 mesh granular activated carbon (MRX-M, Calgon Carbon Corp., Pittsburgh, USA) as support medium for bacterial growth. This fresh GAC filled about 25% of the reactor volume when not fluidized. A magnetic pump (Pan World, NH-100PX-Z, Korea) was used to circulate reactor fluid through a porous plate installed in the reactor bottom in order to maintain GAC fluidization. The first of two identical settlers connected to the reactor was used to prevent the loss of GAC from the reactor column and the second to prevent possible GAC migration into the recirculation pump. Each was made from 300 mm long by 100 mm dia. tube and had a total volume of 2.35 L. Eight sampling ports were installed on the reactor column at 250 mm intervals. The effluent flowed out through a U-shaped trap. The AFBR was operated in a 35 °C constant-temperature chamber, the temperature generally used for studies of threshold values by others.

A stock feed solution, kept in a 4 °C refrigerator, was supplied to the recirculation line by a peristaltic pump (Masterflex, Model No. 7520–57, USA). Tap water was added separately to provide the desired influent flow rate and substrate concentration. The AFBR was acclimated for 97 days after inoculating initially with 500 mL anaerobic sludge from a lab-scale CSTR treating primary sewage sludge. For the first 21 days, the reactor was operated in batch mode, after which continuous feeding and Period 1 began (Table 1). During Period 1, which lasted 7 days, a variable mixture consisting as COD of methanol (20–50%), sodium acetate (40–50%), and sodium propionate (0–40%) was fed to the AFBR. Here, methanol was added to stimulate more rapid growth of methanogens on the GAC. By the end of Period 2, which lasted 69 days, the AFBR appeared to reach steady-state operation. Then a feed consisting of an equal COD mixture of acetate and propionate without methanol was used for the remainder of the study during which the influence of both influent COD and organic loading rate on effluent volatile fatty acid (VFA) concentrations and overall reactor performance were evaluated.

In order to supply necessary nutrients for biological growth about 25 mL of filtered supernatant liquid per g COD of volatile acid mixture was added to the feed. This amounted to about 3–6 mg COD, 12–13 mg total Kjeldahl N, and 3–14 mg total P added per g VFA COD. Ammonia–N and bicarbonate concentrations were also adjusted to correspond with the changes in the influent COD. The GAC bed-expansion was maintained between 120% and 300% by adjusting the recirculation flow rate, which varied over the study period depending upon the extent of biological growth on the GAC. Such growth reduces particle density and the upflow velocity needed for fluidization.

For this study, 15 operational periods were involved as listed in Table 1. The HRT is defined as the ratio of reactor volume (3.93 L) to influent flow rate. Periods 1 and 2 represent the near 100 days required for the reactor to reach quasi-steady-state operation. Periods 3–5 were conducted to evaluate performance with decreasing influent COD concentration from 2010 to 130 mg/L while holding the organic loading rate (OLR) just above 4 kg COD/m$^3$ d. During Period 6 when the influent COD was reduced further to 52 mg/L, a significant adverse effect of influent dissolved oxygen (DO) concentration on performance occurred that resulted in increase in effluent volatile solids and reduced activity by the methanogens as reported previously (Shin et al., 2011). Because of this problem, the influent was then treated to remove DO for all remaining periods of operation. To accomplish this the tap water feed was heated to 90 °C, purged with nitrogen gas in a closed water tank, and then cooled down to 35 °C. With this pretreatment, influent DO was controlled to <1 mg/L.

**Table 1**
AFBR operational characteristics during different operational Periods.

| Period | Days | Inf COD (mg/L) | Inf flow L/d | Recycle flow L/d | HRT h | ORL kg/m$^3$ d | Alkalinity added (mg/L) | $NH_3$–N added (mg/L) | $PO_4$–P added (mg/L) | Supernatant % feed |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 21–28 | 1560 | 8.2 | 1730 | 11.5 | 3.2 | 1000 | 78 | 6.0 | 5.0 |
| 2 | 28–97 | 3110 | 8.2 | 2590 | 11.5 | 5.9 | 1000 | 78 | 6.0 | 5.0 |
| 3 | 97–187 | 2010 ± 260 | 8.2 | 3170 | 11.5 | 4.2 | 500 | 78 | 6.0 | 5.0 |
| 4 | 187–207 | 523 ± 20 | 33 | 3170 | 2.8 | 4.4 | 125 | 19 | 1.5 | 1.2 |
| 5 | 207–236 | 130 ± 11 | 131 | 1150 | 0.72 | 4.3 | 31 | 4.6 | 1.8 | 0.31 |
| 6 | 236–289 | 52 ± 6 | 393 | 3460 | 0.24 | 5.2 | 10 | 1.5 | 0.6 | 0.10 |
| 7 | 289–315 | 266 ± 27 | 66 | 3460 | 1.43 | 4.4 | 62 | 9.2 | 3.6 | 0.63 |
| 8 | 315–343 | 212 ± 16 | 164 | 3460 | 0.58 | 8.8 | 30 | 3.7 | 1.4 | 0.25 |
| 9 | 343–370 | 217 ± 18 | 328 | 3170 | 0.28 | 18 | 0 | 1.8 | 0.7 | 0.13 |
| 10 | 370–378 | 236 ± 26 | 656 | 3170 | 0.14 | 39 | 0 | 1.2 | 0.7 | 0.13 |
| 11 | 378–398 | 252 ± 17 | 492 | 3170 | 0.19 | 32 | 0 | 1.1 | 0.4 | 0.06 |
| 12 | 398–417 | 200 ± 12 | 656 | 2880 | 0.14 | 33 | 0 | 1.0 | 0.5 | 0.08 |
| 13 | 417–431 | 203 ± 7 | 325 | 2880 | 0.29 | 17 | 0 | 1.6 | 0.4 | 0.06 |
| 14 | 431–526 | 45 ± 4 | 394 | 0 | 0.24 | 4.5 | 0 | 1.5 | 0.7 | 0.12 |
| 15 | 526–567 | 2010 ± 10 | 8.2 | 1300 | 11.5 | 4.2 | 1000 | 73 | 28 | 5.0 |