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Energy Generation by Methanation of Persistent Wastes

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ABSTRACT

A 15-L anaerobic fixed-film reactor (AFFR) was evaluated for treating a trade effluent containing inhibitory concentrations of persistent branched-chain fatty acids, namely 2-ethylhexanoic acid (2-EHA) and neopentanoic acid (NPA), at a total of 17,000 mg COD/L. The AFFR was packed with fire-expanded clay spheres, and start-up was accomplished in 60 d. The organic load was increased in steps from 1.1 to 8.5 g COD/L/d. Total COD, 2-EHA, and NPA removal efficiencies were maintained above 70, 98, and 75%, respectively. The reactor could recover from a shock load of 150% increase in organic load. Combined mechanisms of organic adsorption and biodegradation rendered the AFFR more stable with shock loads. Methane gas produced from the process could be used for preheating the effluent.

Index Entries: Anaerobic fixed-film reactor; branched-chain fatty acid; persistent organics; methanation.

INTRODUCTION

Branched-chain fatty acids (BCFA) of lipid origins have been identified in bacterial cytoplasmic materials, and have also been isolated from degras, animal fats, and preen gland waxes (*1*). More recently, BCFAs of xenobiotic origins have been discharged in certain trade effluents or produced

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through degradation of other trade wastes. For instance, neopentanoic acid (NPA) and 2-ethylhexanoic acid (2-EHA) are discharged by the pharmaceutical industry (2). 2-Methybutanoic acid and 3-methylbutanoic acid are produced through degradation of amino acids, namely leucine, isoleucine, and valine (3). These BCFAs are rarely found in municipal sewage and are not readily acclimatized by microorganisms in communal sewage treatment works. A number of these compounds have been found to be persistent in aerobic treatment facilities and have an adverse impact on the environment (4).

In the classification of BCFAs by their biodegradability, Chua et al. (5) suggested that BCFAs with a methyl or ethyl substituent at the α- or β-carbon from the carboxylic end of the carbon chain could form a class of persistent BCFAs. These BCFAs are different from the natural lipid-origin anteiso fatty acids described by Smith (1), which are substituted at the antepenultimate position (third carbon from the alkyl end). The substituents at the α- or β-positions are assumed to interfere with the cleaving mechanism of β-oxidation in the degradation of these compounds. BCFAs with multiple branching could form another class of recalcitrant BCFAs. These compounds are different from those isolated from preen gland waxes, which have single-methyl substitutions at up to four separate positions in the carbon chain (1). The recalcitrant BCFAs are substituted with two methyl groups at one carbon, either at the α- or β-positions, resulting in a quaternary carbon. The recalcitrance of these BCFAs is attributed to the presence of quarternary carbons, which renders cleavage by β-oxidation very difficult. These persistent and recalcitrant BCFAs become inhibitory when their concentrations reach around 2000 mg/L.

The anaerobic process has gained popularity as an energy-efficient method for waste-water treatment. Sachs et al. (6) and Chua et al. (7) described methanation of persistent organics in anaerobic reactors. Anaerobic reactors, such as the upflow anaerobic sludge blanket reactor (UASB) and the anaerobic fixed-film reactor (AFFR), treat waste waters by adsorption and biodegradation mechanisms. The biological pellets or support media in the reactor adsorb the organic constituents of the waste water and provide a long retention for the persistent compounds. This renders the reactors more stable for the treatment of trade effluents with persistent organic compounds. In addition, the packing materials in the AFFR serve as an excellent attachment medium for microorganisms. The high specific surface area of the medium enables the growth of a dense biofilm. This results in a high biomass concentration in the reactor and prevents biomass washout after a temporary inhibition owing to shock loads.

However, only few have investigated and reported on anaerobic treatment of high-strength trade effluents containing inhibitory concentrations of BCFAs. This study evaluated an AFFR for treating a high-strength trade effluent containing 2-EHA, NPA, and ethanoic acid (EA).

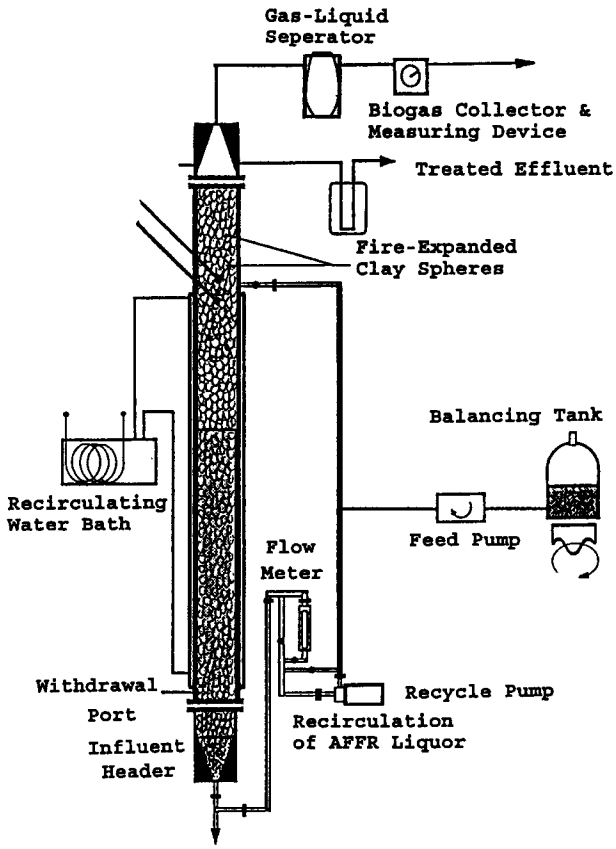

Fig. 1. Schematic of AFFR system.

METHODS

Anaerobic Fixed-Film Reactor

The 15-L AFFR was comprised of a column with a length-to-diameter ratio of 15 (Fig. 1). Fire-expanded clay spheres with an average diameter of 1.5 cm were used as the packing medium (Fig. 2). Voidage of the randomly packed reactor was 0.52. The reactor was operated in an upflow manner. Mixing in the packed bed was achieved by recirculating the AFFR liquor.

System Start-Up and Operation

The AFFR was filled and continuously fed with screened anaerobic digester sludge for a period of 30 d. The AFFR was then fed with the trade effluent at a low loading rate of 0.90 g COD/L/d for a period of 30 d. The effluent contained 4000 mg/L of 2-EHA, 2000 mg/L of NPA, and 3800 mg/L of EA, giving a total COD of 17,000 mg/L. The effluent was supplemented

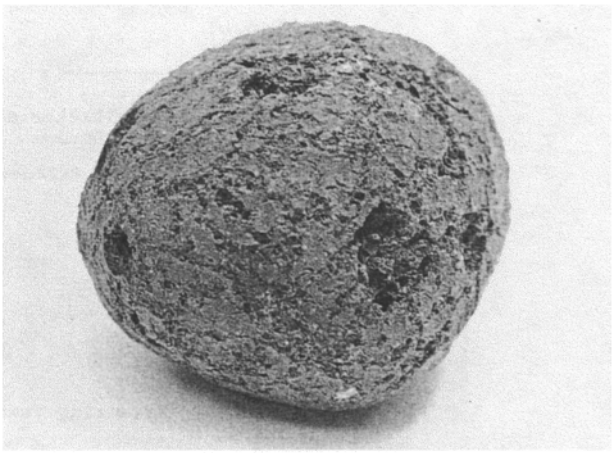

Fig. 2. Packing medium—fire-expanded clay sphere.

with nitrogen and phosphorous to a C:N:P ratio of 150:5:1. In addition, trace minerals and a growth factor, which were described elsewhere (*7*), were also added, and the effluent was adjusted to a pH of 7.2 by adding 10*M* sodium hydroxide. The AFFR liquor was recirculated at a slow rate. Acclimatization of the microorganisms to the effluent was indicated by a stable production of biogas with about 75% of methane, and system start-up was accomplished. The AFFR was then operated with an organic load of 1.13 g COD/L/d. The AFFR liquor was recirculated at a rate equivalent to replacing the entire liquid content three times per hour. The organic load was increased in steps, allowing the AFFR to attain stable operation in each step, up to 17.00 g COD/L/d at which reactor failure occurred.

Analytical Methods

COD and MLVSS were determined in accordance with APHA Standard Methods (*8*). 2-EHA, NPA, and volatile fatty acids (VFAs) were measured with a gas chromatograph (Perkin-Elmer Model 8700) using a Chromasorb WAW 100/120 mesh and FFAP (15%) column. Biogas was collected, and the production rate was measured by water displacement. Biogas quality was analyzed with a gas chromatograph (Shimadzu Model GC-14A) with a 2-m Porapak Q 80/100 mesh column.

RESULTS AND DISCUSSION

The porous surfaces of the fire-expanded clay spheres served as an excellent medium for cell immobilization. Biofilms were established on the packing medium toward the end of the seeding and acclimatization period. The high specific surface area of the medium and the turbulence within the packed bed enabled the growth of a dense and firmly attached

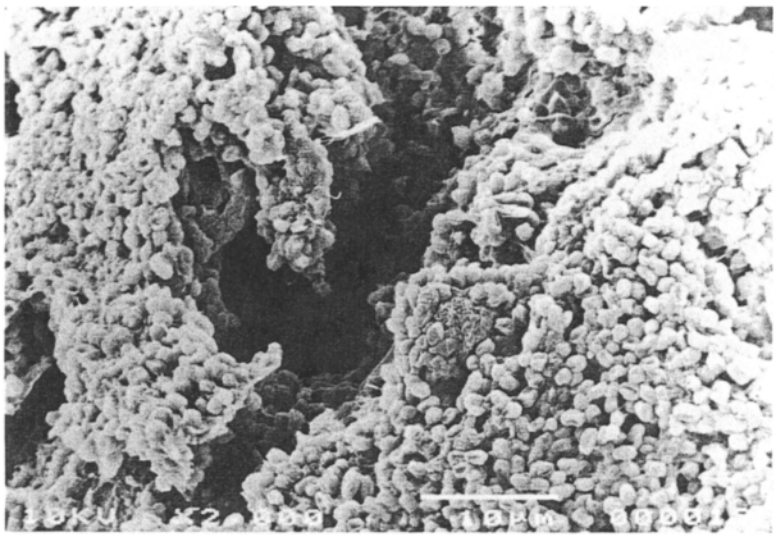

Fig. 3. Electron micrograph of the biofilm on the surface of a fire-expanded clay sphere.

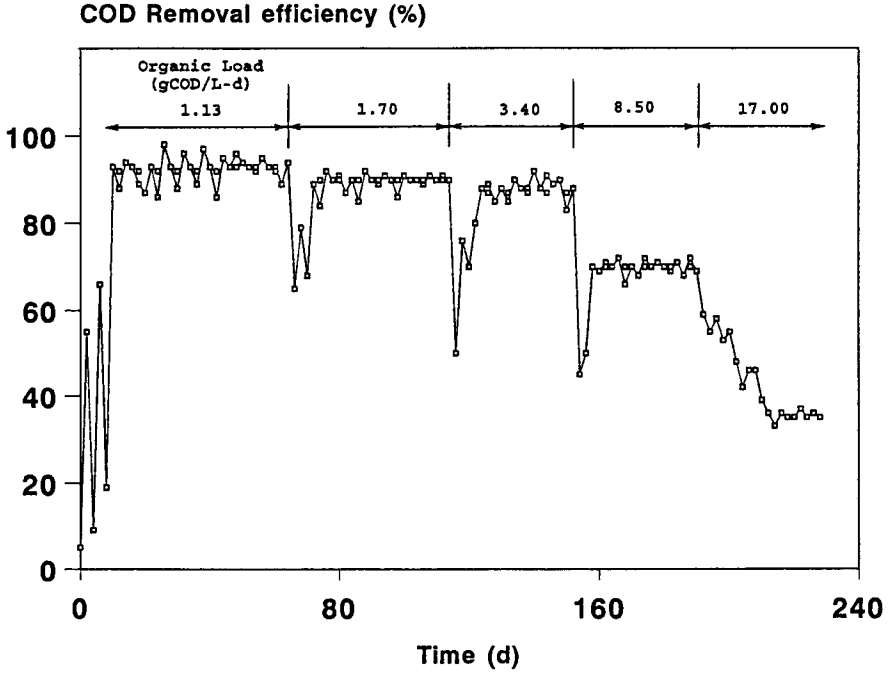

Fig. 4. Response of the AFFR system to shock loads.

biofilm. A high biomass concentration was maintained in the reactor (Fig. 3).

The effectiveness of the AFFR in treating the effluent and the response of the system to shock loads are shown in Fig. 4. At organic loads of 1.13, 1.70, 3.40, and 8.50 g COD/L/d, total COD removal efficiency was main-

tained above 70%. These results indicated that the high-strength trade effluent containing persistent BCFAs could be effectively treated by the acclimatized anaerobic biofilms. The performance of the AFFR as a pretreatment for the effluent surpassed that reported by other workers (*6*). Changes of organic load from 1.13 to 1.70, from 1.70 to 3.40, and from 3.40 to 8.50 g COD/L/d represented 55, 100, and 150% increments, respectively. Response to these shock loads was in the form of a temporary drop in COD removal efficiency. The reactor was able to resume stable operation a few days after each shock load was introduced. The anaerobic microbial ecosystem comprises several groups of interactive microorganisms, which convert the organic matters into methane and carbon dioxide (*5,9*). Operation of an anaerobic reactor relies on a balanced population in the ecosystem. When a shock load was introduced, inhibition of one or more groups of the microorganisms caused a drop in COD removal efficiency. However, immobilization of microorganisms as biofilms in the AFFR prevented a washout of the temporarily inhibited microorganisms. This allowed a new balance of microbial population to be established and gradual resumption of operation. The AFFR design also had the advantages of the combined effects of adsorption and biodegradation in treating waste waters. The adsorption properties of the fire-expanded clay spheres, which were used as the packing medium in the AFFR, were described by Chua (*10*). The fire-expanded clay spheres adsorbed the organic constituents of the waste water and provided a long retention time for the persistent compounds. It renders the AFFR more stable for the treatment of the high-strength trade effluent with variable organic load and reducing the effects of shock loads to the system.

The AFFR performance at different organic loads is summarized in Table 1. As the organic load was increased in steps from 1.13 to 8.50 g COD/L/d, the COD removal rate increased from 1.05 to 5.95 g COD/L/d, whereas the COD removal efficiency decreased from 93 to 70%. The highest organic load of 8.50 g COD/L/d achieved was equivalent to a hydraulic retention time of 2 d. While maintaining the treated effluent with a COD level acceptable for discharge into public sewers, the AFFR could operate at a maximum organic load of 8.50 g COD/L/d. The biogas, with an average of 84% methane, generated at different organic loads was equivalent to specific methane production rates that ranged between 0.28 and 0.32 L/g COD. These specific methane production rates were very close to the stoichiometric value of 0.35 L/g COD, giving rise to very low VSS concentrations in the treated effluent. The methane production from each cubic meter of the trade effluent was equivalent to 2.2×10^5 kJ of energy generation. This heating value was in excess of the amount required for preheating the effluent through 30°C.

The removal efficiency of 2-EHA was maintained at 98% and above throughout the operation, whereas that of NPA decreased from 90 to 75%. These observations were consistent with that of Chua et al. (*5*), which showed that higher degree of branching in the NPA molecule affected its

Table 1
Performance of AFFR at Different Loadings

Organic load (g COD/L/d)	1.13	1.70	3.40	8.50	17.00
Hydraulic retention time (d)	15	10	5	2	1
COD removal rate (g COD/L/d)	1.02	1.53	2.99	5.95	5.61
COD removal efficiency (%)	93	90	88	70	33
Biogas production rate (L/d)	7	9	19	30	28
Methane conc. (%)	82	84	86	85	80
Specific methane production (L/g COD)	0.32	0.28	0.31	0.28	0.27
2-EHA removal efficiency (%)	100	100	100	98	75
NPA removal efficiency (%)	90	85	85	75	50
EA removal efficiency (%)	88	80	75	66	25
pH	7.2	7.2	7.2	7.2	4.0

degradability. NPA was a more persistent BCFA than 2-EHA under anaerobic conditions. The acidogenic population probably had a higher affinity toward 2-EHA than NPA, and degraded 2-EHA to a very low residual concentration before utilizing NPA. Removal efficiency of EA at each organic load was the lowest among the three components of the effluent. This was because as EA was being degraded, it was also being produced as an intermediate product in the degradation of 2-EHA and NPA.

When the organic load was increased to 17.00 g COD/L/d, equivalent to a hydraulic retention time of 1 d, a drastic decrease in COD removal efficiency was observed. After a few days of operation at the high loading rate, COD removal efficiency decreased to 33% and the pH of the AFFR liquor dropped from 7.2 to 4.0. Ethanoic acid and other VFA concentrations built up rapidly in the treated effluent. Removal efficiencies of NPA and 2-EHA decreased to 50 and 75%, respectively. The reactor could not resume stable operation and was considered to have failed. Biofilms were gradually washed out from the AFFR.

CONCLUSIONS

Start-up of the AFFR was achieved in 60 d, with a continuous-seeding protocol. Stepwise increase in the organic load, or decrease in the hydraulic retention time, resulted in an increase of COD removal rate to an optimum

of 5.95 g COD/L/d. The corresponding hydraulic retention time was 2 d, and the COD removal efficiency was 70%. The AFFR could recover from a shock load of 150% increase in organic load. The system was effective in treating the trade effluent that contained persistent BCFAs. Methane gas generated from the process could be recovered and used for preheating the effluent.

ACKNOWLEDGMENTS

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