Biogas Production from Steam-Treated Municipal Solid Waste Wastewater

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ABSTRACT

Biogas production from steam process wastewater carrying the organic fraction of municipal solid waste (MSW) was investigated in a bench-scale system comprised of an anaerobic completely stirred tank reactor (AnCSTR), an anaerobic filter (AnF), and an aerobic trickling filter (ATF). The AnCSTR received rinse water that contains pulp fibers that are derived from MSW. The AnF received the same rinse water from MSW process wastewater; however, the pulp fibers were not present. The ATF received effluent from the AnCSTR and AnF in fed-batch mode. Biogas production was observed at 0.02–0.29 and 0.04–0.47 kg $CH_4 \cdot m^{-3}$ day^{-1} in the AnCSTR and AnF systems, respectively. Chemical Oxygen Demand (COD) removal efficiency was observed at 20% in the AnCSTR and up to 86% in the AnF operating at 10- to 12-day hydraulic retention time (HRT). Introduction of digester sludge in the feed at day 173 (2 days HRT) increased gas production rate in the AnCSTR from 0.13 to 0.29 kg $CH_4 \cdot m^{-3}$ day^{-1} but did not significantly affect gas production rate in the AnF. The ATF stage removed 96% of dissolved COD. System stability was demonstrated in the AnF by full recovery of biogas production after operating the reactor under starvation conditions for 7 days. The average specific removal rate observed in the AnCSTR ($k_{ms} = 0.098$ day^{-1}) was one order of magnitude lower than previously observed values using organic kitchen waste ($k_{ms} = 0.27$ day^{-1}). On the other hand, organics removal rate kinetics in the AnF ($k_{ms} = 0.25$ day^{-1}), were similar to the previously observed value from the organic kitchen waste. The system treated the organic portion of steam process MSW wastewater with concomitant biogas production with as low as 0.01 mg $COD \cdot L^{-1}$ in the final effluent from the ATF.

Key words: anaerobic digestion; steam processing; MSW; biogas; methane; anaerobic filter; aerobic trickling filter

INTRODUCTION

BIOLOGICAL SYSTEMS have the potential to remove up to 90% of the organic component of Municipal Solid Waste (MSW) (Schober *et al.*, 1999). During biological removal of MSW organic matter, up to 60% methane (CH_4) may be produced together with carbon dioxide (CO_2), hydrogen (H_2), and other gases (El-Fadel *et al.*,

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1996; Hamoda *et al*., 1998). The methane produced during anaerobic MSW digestion in bioreactors or landfills may be used as a source of refuse derived fuel (RDF) in homes and industries (Zehnder, 1982; Schlag *et al*., 1993; Lunde, 1995). In this study, unsorted MSW was treated with steam to reduce lignin bonds in paper and other cellulose-rich products and to produce a more easily biodegradable, homogeneous, moist, and friable pulp. Other advantages of the steam pretreatment (not related to biological treatment efficiency), include the moistening and liquefying of the biodegradable contents of MSW resulting in easy extraction of metals, plastic, glass, and other recyclable components of MSW (Cecchi *et al*., 1990; Fruteau de Laclos *et al*., 1997; Mata-Alvarez and Llabres, 1997; Griffin *et al*., 1998).

Steam pretreatment and reactor-based biological MSW treatment methods have been successfully implemented in European and West Asian countries (Fruteau de Laclos *et al*., 1997; Hamoda *et al*., 1998). In spite of their success abroad, steam processing and reactor based biological treatment processes have not been used in the United States due to inherent differences between the U.S. and European MSW and the unavailability of detailed comparative data (Hamzawi *et al*., 1998). A survey of MSW composition in the United Arab Emirates, The Netherlands, and the United States has shown that biodegradable organics such as food waste occupy 50% of the total solid waste generated in the foreign countries as opposed to approximately 30% in the USA (Tchobaglous *et al*., 1993; Abu Qdais *et al*., 1997). Similar trends were observed in MSW in Sweden where biological treatment and refuse derived fuel has been successfully used (Lunde, 1995). Approximately 84 million tons of paper per year (40% of MSW) is disposed in the United States, which is a much higher paper content than is produced in European countries (Abu Qdais *et al*., 1997; U.S. EPA, 1998). During recycling of paper, only relatively clean waste paper is removed for recycling. Paper contaminated with food waste is not recycled, and thus becomes part of the extractable organic portion of unprocessed MSW (Oleskiewicz and Poggi-Varaldo, 1997; Banks and Humphreys, 1998; Kortekas *et al*., 1998).

This study demonstrates the increased biogas production during biodegradation of the organic component of MSW extracted by MSW steam processing. The reactor system was designed to determine the bioavailability of Chemical Oxygen Demand (COD) in MSW for biological degradation in two anaerobic digesters and an aerobic trickling filter system. The two digesters reduced the organic loading and strength of the waste stream before entering the final aerobic stage, the aerobic trickling filter (ATF). The anaerobic continuous stirred tank reactor (AnCSTR) and anaerobic filter (AnF) systems were designed to remove up to 80% of biodegradable organic matter while producing reusable CH_4 from the anaerobic digestion processes (Neumann, 1993). The two substrates studied are representative of rinse water from the pulp cleaning process, treated by the AnF, and the fine non-marketable pulp fibers settled and thickened from the rinse water, and treated by the AnCSTR. The aerobic trickling filter process, installed to receive effluent from the AnCSTR and AnF, was designed to aerobically remove 45% of the organic load accompanied by biomass production (Schober *et al*., 1999). In full-scale systems, clarifiers could be installed between the anaerobic digesters and the aerobic tricking filters to ensure operation of the ATF under minimum settleable and suspended solids. The ATF in this study was used as a polishing step to lower the levels of soluble COD concentration to regulation compliance levels.

Although the pertinent biological processes could be achieved naturally in landfills and composting processes, the reactor system offers more control on the organic loading rates and physical-chemical parameters such as pH, temperature, organic acid accumulation, and the oxidation reduction potential (ORP) of the system. In addition, a higher rate of recovery of methane should result in the reactor system than in a landfill reducing the potential release of greenhouse gases. In addition to energy production, reactor systems have the potential to decrease space requirements for landfills by optimizing the removal of the larger fraction of MSW in compact reactor systems before depositing the nontreatable fraction to the landfills.

MATERIALS AND METHODS

Reactor feed and inoculum

The AnCSTR and AnF were seeded with anaerobic digester sludge from the local wastewater treatment plant in Reno, NV. The digester sludge was sustained by the feed solution comprised of steam treated MSW wastewater from Comprehensive Resources, Recovery and Reuse, Inc. (CR^3, Reno, NV). CR^3 has developed a patented process that steam autoclaves MSW, and then separates recyclable materials, including paper fiber. This MSW is not segregated from the MSW found on the curbside other than the removal of large durable goods. All of the constituents present in MSW are present in the feed substrate that enters the CR^3 process in this study. No separation of the soluble organic fraction from plastics, cellulolytic material, or other recalcitrant material was made prior to treatment by the CR^3 process.

During the CR^3 treatment process MSW with additional water is heated to over 260°F (127°C) and 25

lbs/in^2 pressure (1.7 atmospheres) for at least 30 min. The wet steam environment, combined with the rolling action of the autoclave vessel, reduces the MSW to a moist friable pulp. Metal cans and plastic bottles remain as easily separable fractions for recycle recovery. In the wet steam environment many bonds are modified or transformed. This includes inorganic and organic water extractables of MSW with additional solubilized organic solids. The moist pulp retains virtually all these water phase materials with fine inorganic, plastic, and inks as cocontaminants.

Unsorted MSW of the composition shown in Table 1 was steam treated and passed through 1/2 inch steel screens. Most of the nonbiodegradable components of the raw MSW, i.e., glass, metals, and plastic were retained on the 1/2 inch steel screens, whereas 20% of the fraction passing the screen was the reusable pulp for production of recycled paper. Materials retained on the screens were conveyed to a hand sorting facility. The remaining solution consisted of suspension of fine pulp particles in an organic rich solution was later used as feed to the laboratory-scale bioreactors. The MSW process wastewater contained paper fiber, carbohydrates, proteins, lipids, and about 3.5% miscellaneous compounds (Table 2). Data in Table 2 show that the majority of com-

pounds in the heat processed MSW wastewater were readily biodegradable based on the high volatile fraction (85%) and the low residual ash content of ignited samples. The high value of the pollution factor (F_o) estimated from dry weight and volatile fraction (Table 2) indicates that the steam treated MSW contributed high levels of BOD and was characteristically highly biodegradable. The feed to the AnF was the rinse water, while the feed to the AnCSTR consisted of settleable solids, predominantly paper fibers, suspended in the rinse water.

System setup and operation

The anaerobic reactors (Fig. 1) were constructed from double-walled clear acrylic. Each reactor consisted of two tubes, one (30.5-cm internal diameter by 91.4 cm high) placed inside the other (9.5-cm internal diameter by 68.6 cm high), creating an annular space of 2.54 cm (1 inch) for heated water to pass through. The anaerobic reactors were hot water jacketed at 35 ± 1°C. The two anaerobic reactors had total working volumes of 60 L (AnCSTR) and 30 L (AnF). The two reactors decanted to standpipes that regulated the hydraulic profile of their interiors. The AnCSTR and AnF reactors were designed to utilize soluble organics and the majority of the suspended solids as

Table 1. Material balance for 1,000 tons dry[a] raw MSW from Reno, Nevada.

Component	Tons	1/2″ Size splitting pass (tons)	Retain (tons)	Remarks
Paper	500	250		
Cellulose long	260	260		Steam treatable
Cellulose short	185	185		Extractable portion
Minerals—Ink	30	30		
Starch furnish	25	25		
Food	75	75		Biodegradable
Glass and others	210			
Glass	60	20	40	Nonbiodegradable
Leather—Carpets	20		20	
Building debris	20		20	
Wood—yard waste	70	25	45	
Rags—fabrics	40		40	
Metals	100			
Aluminum	15		15	Nonbiodegradable
Steel, etc	85		85	
Plastics	115			
Film—LDPE[b]	60	40	20	Nonbiodegradable
PET[c]—HDPE[d]	25		25	
PVC—HD plastics	30		30	
Total	1000	660	340	

[a]The raw MSW had a moisture content of 20%; [b]LDPE, low density polyethelene plastics; [c]PET, polyethylene terephthalate; [d]HDPE, high-density polyethelene plastics.

Table 2. Characteristics of the settleable solids substrate in the steam treated MSW process waste stream.

Component	Gravimetric content g/kg	Ignition analysis g/kg	Remarks
Cellulose	460		This study
Lignin	99		This study
Lignocellulose	76		This study
Soluble carbohydrates	190		This study
Total fiber	580		This study
Soluble protein	65		This study
Total lipids	70		This study
Volatile component		835	This study
Ash		164	This study
Miscellaneous		35	This study
Total composition	1,000	1,000	This study
Stoichiometry			
Carbon, C	369		This study
Hydrogen, H	49.9		This study
Oxygen, O	329		This study
Nitrogen, N	11.7		This study
Oxygen demand (based on C)	1280		This study
Polluting potential, F_o[a]	770		

[a]$F_o = \text{OD} \times \text{VSF} \times f_d \times (1 - m) \times W \times \rho_{ws}$, where F_o is the polluting potential (M); OD is the stoichiometric oxygen demand to oxidize the waste completely ($M_{o2}M_s^{-1}$); VSF is the volatile solids fraction; f_d is the biodegradable fraction (≈ 0.80); m is the moisture content; W is the refuse component wet base; and ρ_{ws} is the wet refuse density ($M_s L^{-3}$).

substrate. Effluent was recycled at the recycle/influent flow ratios (Q_R/Q) of 24 for the AnCSTR and approximately 10 for the AnF with solids return. The recycle ratio for the AnCSTR was high because the recirculation pump provided mixing for the system. The AnF was fed from the bottom of the reactor with no mixing; thus, a lower recirculation rate was used.

The effluents from the two anaerobic reactors were fed in batches directly to an ATF as a polishing step. The ATF and the AnF were filled with pall rings (Jaeger 1″ Tri-Packs, Houston, TX) for the attachment of bacteria. The ATF consisted of a 50-gallon Nalgene tank filled with pall rings topped with inverted weighing dishes to facilitate uniform dispersal of the influent. The effluent from the ATF was discharged to a clarifier where solids were removed and a fraction of the liquid was returned to the ATF at $Q_R/Q = 10$, after passing through a clarifier sump. To keep the ATF aerobic, air was injected at 10 psi into the recycle stream just before reentering the ATF. Feed solution was delivered to the reactors by double-headed peristaltic pumps (Master Flex Model 7554–70, Cole-Palmer Instrument Co., Vernon Hills, IL) connected by Tygon tubing to the feed tank and the recycle lines for the AnF and AnCSTR.

Feeding, mixing, and recycle rates for the system were controlled by a single automatic timer (Chrontrol XT,

Model E-94400, Cole-Palmer). Carbon, nitrogen, and phosphorus were kept in balance at the ratio of 100:5:1.5 in both the AnF and the AnCSTR. With each batch of feed received the total nitrogen and total phosphorus were determined. The nutrient balance was maintained by adding ammonia in the form of ammonium chloride and phosphorus in the form of potassium phosphate in a ratio determined by influent needs. On average, 920 mg of NH_4Cl and 26 mg of KH_2PO_4 were added to the feed tanks for each of the reactors until waste activated sludge was utilized to provide the 100:5:1.5 ratio of C:N:P. In the last phase of operation the feed from CR3 was amended with waste activated sludge at 30%. The pH was maintained at 7.0 ± 0.2. pH adjustment was made through the addition of Na_2CO_3 to the feed tank when necessary due to a pH drop below 6.8.

Reactor startup

The AnCSTR and AnF were seeded with 60 and 30 L of anaerobic digester sludge beginning at days 1 and 14, respectively. Later, at day 58, the ATF was seeded with 60 L of return activated sludge from the local wastewater treatment plant. Performance data was collected for a period of 173 days beginning at AnCSTR seeding. Organic loading rate (OLR) was varied by changing the hydraulic
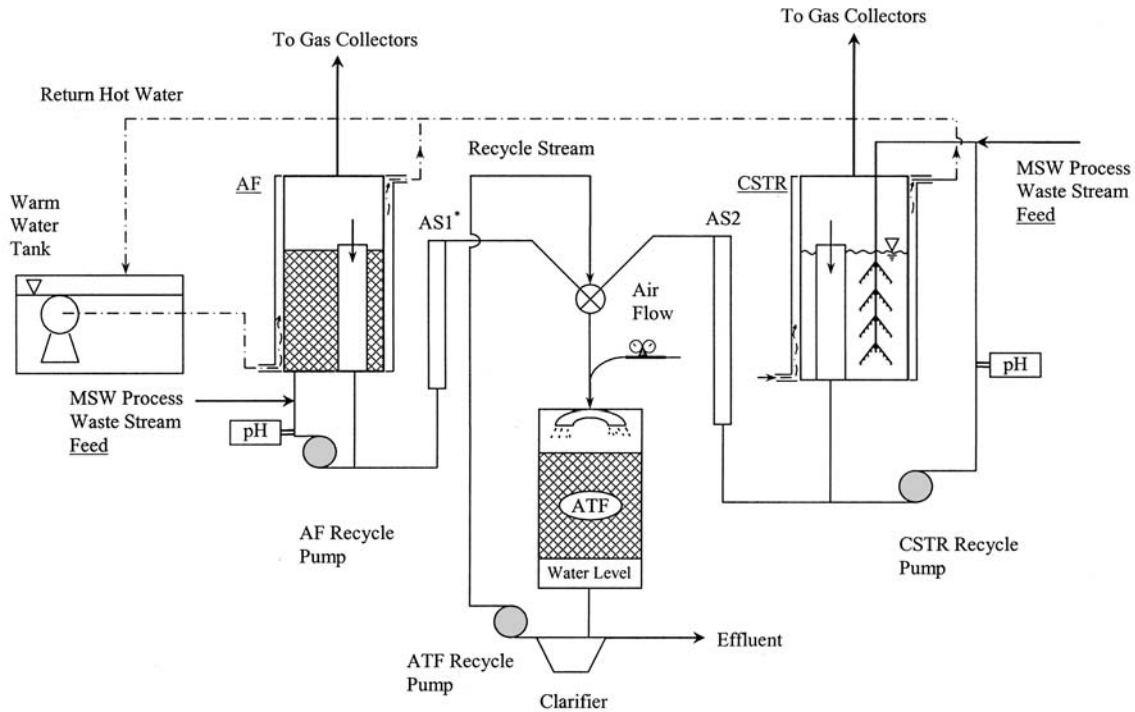
* AS1 & 2 Adjustable Standpipes for AF and CSTR, respectively.

Figure 1. Schematic of the MSW wastewater treatment system comprised of the anaerobic filter (AnF), anaerobic completely stirred tank reactor (AnCSTR), and the aerobic trickling filter (ATF).

retention time (HRT) from 120 to 6 days, which resulted in OLRs ranged from 0.30–1.84 and 0.52–2.41 kg · m^{-3} day^{-1} in the AnCSTR and AnF, respectively. The complete influent loading schedule is shown in Table 3.

Analytical methods

pH was measured on-line with direct data acquisition facilitated by a data logger (Fluke Data Logger Series II

Model 2625A, Blairsville, PA) that stored the information on an IBM compatible PC. The pH probes (Signet pH/ORP model 2720 pre-amp, ALSCO Industrial Products, Inc., Lithia Springs, GA) were installed on the recirculation lines and connected directly to transmitters with displays. COD, total nitrogen, total phosphorus, and calcium were measured by HACH analytical kits following procedures described in the Standard Methods for the Examination of Water and Wastewater (American

Table 3. Loading and operation schedule for the bioreactor system.

	AnCSTR operation				AnF operation				ATF operation	
Phase	Time days	HRT days	Avg. OLR (kg · m^{-3}day^{-1})	Phase	Time days	HRT days	Avg. OLR (kg · m^{-3}day^{-1})	Phase	Time days	Type of influent
I	1–55	120	0.30	I	43–98	—	Batch feed			
II	55–100	60	0.58	II[a]	98–140	15	0.52			
III	100–130	30	0.72	III	140–152	10	1.06	I	58–100	Batch feed
IV	130–150	15	1.45	IV	152–173	6	2.41	II	100–155	Batch feed
V	150–173	12	1.84	V[b]	173–220	6	2.41	III	155–173	Batch feed
VI[b]	173–220	12	1.85					IV	173–220	Batch feed

[a]A 2-week starvation period took place in the AnF during this phase of operation; [b]MSW feed was adjusted to maintain OLR from previous phase while adding waste activated sludge for nutrient addition.

Public Health Association [APHA], 1992). COD was measured 5 days a week. Mixed liquor suspended solids (MLSS), volatile solids, and volatile suspended solids were determined using the filtration methods also described in Standard Methods (APHA, 1992) and were measured from all systems twice per week.

Gas composition

Effluent gas was collected using two polyvinyl chloride (PVC) inverted tubes suspended in acidified salt solution (10% NaCl, 2% H_2SO_4, pH 0.5) (Eastman and Ferguson, 1981). The acidified salt solution prevented the adsorption of biogas into the water. Daily volumetric gas flow was computed from total tube displacement and pressure was measured in a single leg manometer for each reactor (Fig. 1). Effluent gases were characterized using the Fyrite (Flue) Gas Analysis System (Bacharach Inc., Pittsburgh, PA). Fyrite gas analysis yields the percentage of carbon dioxide present in the off gas from the reactors (Bacharach, PA). The methane concentration was assumed to be the majority of the remaining gas produced by the system. Gas from the manometers was released to fume hoods on a weekly basis.

RESULTS AND DISCUSSION

System performance

Reactor performance was correlated to the amount of biogas produced per day in the AnCSTR and AnF systems. Given the low ORP and high pH ranges during operation (ORP = −200 to −120 and pH = 7.0–7.5), high levels of methanogenesis was expected in the AnCSTR and AnF. The non-CO_2 gas fraction produced was thus used as an indicator of the energy (methane) producing potential of the system. However, existence of impurities (H_2, NH_3, and H_2S gases) was not ruled out, since the influent contained both carbon sources and proteinaceous nitrogen and sulfur sources.

The data in Fig. 2A shows that the amount of biogas produced was directly correlated to organic loading in the AnCSTR system ($r^2 = 0.93$) (refer to Table 3 for the OLR for each phase of operation of the AnCSTR). The biogas production rate increased from 0.05 to 0.46 kg · m^{-3} day^{-1} in the AnCSTR with increasing OLR (from 0.72–1.84 kg · m^{-3} day^{-1}). The AnCSTR had a suspended solids concentration of 8708 mg/L $\pm$ 758. This value is skewed due to the suspended solids represented by the pulp in the wastewater added to the AnCSTR.

The correlation between gas production and OLR in the AnF system was not as clear due to a shorter length of time for the phases with different OLR's as shown Fig. 2B. However, the trend observed from the three available loading conditions show the beginning of a near linear correlation between gas production and organic loading as gas production increased from 0.42 to 0.77 kg · m^{-3} day^{-1} with increasing OLR from 0.52 to 2.41 kg · m^{-3} day^{-1} ($r^2 = 0.78$). The system became less stable when operated under lower hydraulic retention times of 12 and 6 days probably due to increased cell and MLSS wash out in the effluent.

Under ideal conditions, the net carbon influx into the system should equal the accumulated carbon in biomass and carbon efflux through the effluent and gases. Gas collected from the AnCSTR system contained an average of 46% CO_2 and 54% CH_4 and impurities. Similar results were obtained in the AF with 52% CO_2 and approximately 48% containing CH_4 and other gaseous impurities. For the purpose of the mass balance analysis in this study, H_2 and NH_3 evolution was assumed insignificant due to the low ORP levels and high pH ranges, conditions that favor methanogenesis.

System stability

Reactor stability was tested by operating the reactors under near starvation conditions and observing biogas production soon after reintroducing high organic loading in the feed. Figure 2B shows a rapid decrease in the production of gas in the AnF between days 118–130 during minimum biomass maintenance. Influent feed concentration during this phase was maintained at a minimum to ensure that the MSW feed supply was completely depleted. Soon after reintroducing organic carbon (0.72 COD kg · m^{-3} day^{-1}) biogas production successfully recovered in the AnF without the need for reinoculating the system. The fact that starvation does not affect subsequent performance has been cited as one of the major advantages of the anaerobic digestion of industrial wastes (Jewell and Nock, 1994). In the AnCSTR, the effects of operating the reactors under starvation conditions were minimized by the presence of less biodegradable settleable solids from earlier phases.

The MSW wastewater feed to the system was supplemented with waste activated sludge from a sewage treatment plant while operating the system under the highest hydraulic and organic loading rate to study the effect of nitrogen and phosphorus addition on microbial activity as biogas production (AnCSTR phase VI, AF phase V). Prior to the introduction of the waste activated sludge, nitrogen and phosphorus were balanced by the addition of micronutrients to the MSW feed. During phase VI for the AnCSTR (phase V for the AnF), nitrogen and phosphorus was no longer balanced in the feed since the added waste activated sludge, which was 30% of the water and
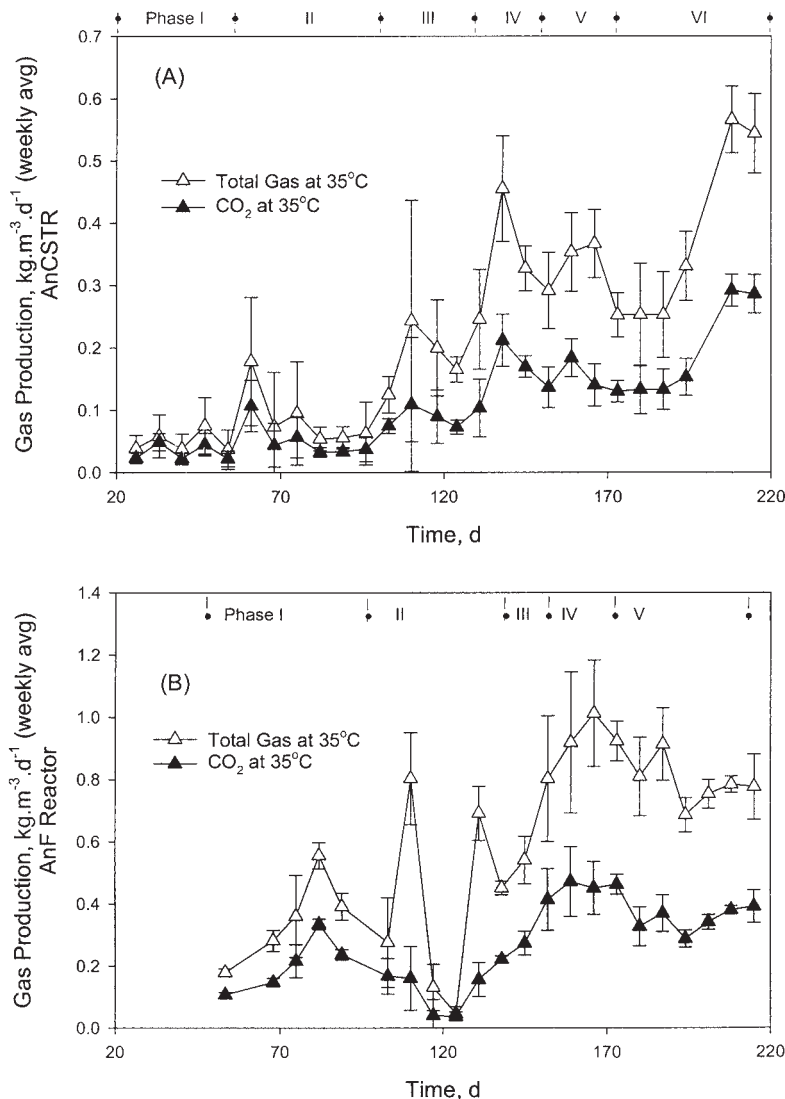
Figure 2. Weekly average gas production for **(A)** AnCSTR, processing the settleable substrate, and **(B)** AnF, processing the soluble substrate.
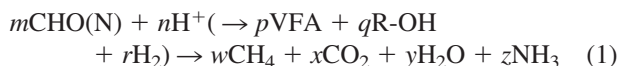
5% of the organic load in the systems, acted as both a wetting agent and a source of nutrients in the steam autoclave process. A significant increase in gas production was observed in the AnCSTR after amendment of the feed with the waste activated sludge. The increase in gas production indicated a positive response to increased microbial activity in the AnCSTR. On the contrary, gas production in the AnF did not increase after adding waste activated sludge, but rather decreased slightly. These results show that the AnF system operated closer to optimum conditions with nitrogen and phosphorus addition via soluble nutrients not waste activated sludge, as can be seen in the drop in gas production in Phase V in Fig. 2B. This difference in response of the two reactors is most

likely due to the amount of hydrolysis the two reactors had been performing prior to this point, with the AnCSTR hydrolyzing pulp particles while the AnF was digesting only soluble organic material.

The advantage of utilizing the waste activated sludge as a micronutrient supplement is recognized through the potential savings in chemical costs for balancing MSW wastewater treatment systems. Such system enhancements may be achieved in actual reactors by coupling the treatment of MSW to municipal wastewater treatment processes. Currently, coupled treatment of domestic wastewater and organics from MSW is still experimental (Cecchi *et al.*, 1994; Hamzawi *et al.*, 1998; Stroot *et al.*, 1998; Llabres *et al.*, 1999).
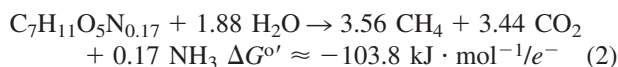
Carbon balance and bioenergetics

Complete anaerobic degradation of a mixture of organic compounds originating from paper and organic kitchen waste is achieved through a variety of pathways represented by the general stoichiometry below (Young and Yang, 1987; Schink, 1988; Metcalf and Eddy, 1991; Chirwa and Wang, 2000):

$$m\text{CHO(N)} + n\text{H}^+ (\rightarrow p\text{VFA} + q\text{R-OH} \\ + r\text{H}_2) \rightarrow w\text{CH}_4 + x\text{CO}_2 + y\text{H}_2\text{O} + z\text{NH}_3 \quad (1)$$

During anaerobic digestion of organic refuse, volatile fatty acids (VFA), alcohols (R-OH), hydrogen gas (H_2), methane, carbon dioxide, and ammonia may be produced (El Fadel *et al.*, 1996; Griffen *et al.*, 1998). The stoichiometric coefficients in Equation (1) depend on the prevailing redox, pH, and culture conditions in the reactor. For example, CO_2, H_2, R-OH, and VFAs accumulation is expected during fermentative metabolism (pH <6). The produced VFAs lower the pH of the medium. Conversely, VFA and CO_2 removal in a methanogenic culture raises the pH and decreases the ORP of the culture. For normal operation, pH buffers are employed to maintain the pH at a desirable operational range (pH = 6.9–7.2) and Na_2CO_3 was only required in these two systems during startup of the first phase in each reactor.

In this study, gas production is represented by the stoichiometric equation determined from the C, H, O, N composition in MSW substrate (Table 2), assuming complete breakdown of cellulose, carbohydrates, and proteinaceous compounds to gases:

$$\text{C}_7\text{H}_{11}\text{O}_5\text{N}_{0.17} + 1.88 \text{ H}_2\text{O} \rightarrow 3.56 \text{ CH}_4 + 3.44 \text{ CO}_2 \\ + 0.17 \text{ NH}_3 \quad \Delta G^{\text{o}\prime} \approx -103.8 \text{ kJ} \cdot \text{mol}^{-1}/e^- \quad (2)$$

where $\Delta G^{\text{o}\prime}$ is calculated from free energies of formation (Garrels and Christ, 1965; Morel and Herring, 1993). The above reaction is guaranteed to be thermodynamically favorable when methane production is greater than 40% (>2.8CH_4). Ideally, up to 70% (4.9 mol CH_4) methane is expected per mol of substrate under methanogenic conditions (Tchobanoglous *et al.*, 1977). Based on experimental data from this study, a theoretical specific yield (s_{theo}) of 0.406 kg (5.68 m³) CH_4 per kg of substrate degraded was expected. The AnCSTR performed closer to the theoretical methane production in phases with sufficiently long HRTs for significant hydrololysis to occur and sufficiently long operation times for reactor stability (phases III–IV). The AnCSTR operating under low OLR (phases I–II) converted carbon source to CH_4 gas at a rate 80% lower than the theoretical cumulative rate ($s_{\text{min}} = 0.101$ kg CH_4/kg carbon source as $C_7H_{12}O_5N_{0.17}$), mainly due to slow startup after seeding. The system operated below its capacity during low OLRs and long HRTs (120

and 60 days) (Fig. 3A). The low relative biogas production efficiency in phases I–II suggests that the culture was not completely established during these phases. Apparently, loading conditions were changed prematurely during phases I and II, as indicated by the phase lengths shorter than the hydraulic retention times. One consequence of shortening the HRTs later in phases V–VI was incomplete hydrolysis of polymeric organic compounds accompanied by acids accumulation and a higher CO_2 fraction released. During intermediate hydraulic loading rates (phases III–IV), gas production rate approached the slope for theoretical cumulative gas production rate with a value of $s = 0.335$ kg CH_4/kg carbon source (about 20% lower than the theoretical slope, $s_{\text{theo}} = 0.406$ kg CH_4/kg carbon source as $C_7H_{11}O_5N_{0.17}$).

In phase VI (AnCSTR), the influent was amended with waste activated sludge. With the sudden change in influent quality, the behavior of the system changed completely. The maximum cumulative biogas production per kg substrate degraded increased beyond the theoretical slope by about 15% ($s = 0.461$ kg CH_4/kg carbon source as $C_7H_{11}O_5N_{0.17}$). These results showed that operation under activated sludge feed resulted in higher specific biogas yield indicating stimulated biological activity under nutrient rich conditions.

Figure 3b shows that the AnF column behaved optimally and almost uniformly during the entire period of operation. A healthy biomass with an average approximate concentration of 2,400 mg/L was observed in the AnF. A lag period of minimum gas production rate was observed during phases I when the culture was not completely established. Residual gas production during the period of no organic feed (deliberate starvation period in phase II) caused the apparent increase in the slope in Fig. 3B. Biogas production in the AnF converged towards an optimum value of 0.243 kg CH_4/kg substrate degraded. This value represents approximately 30% efficiency in the AnF. However, the AnF quantitatively produced more methane gas than the AnCSTR due to the high amounts of substrate degraded. Forty percent (40%) more carbon source was cumulatively degraded in the AnF than in the AnCSTR over the 220 days operation period. Figure 3 shows that up to 5.50 kg organic substrate (as $C_7H_{11}O_5N_{0.17}$) was degraded in the AnF where as only 3.95 kg was degraded in the AnCSTR. Introducing waste activated digester sludge did not affect the performance of the AnF (Fig. 3B).

The stochiometric analysis given above shows that biogas production was directly influenced by the loading characteristics, i.e., OLR and HRT, and substrate composition. The mass balance analysis confirms the results from Fig. 2, that the AnCSTR operated below its full potential where as biogas production in the AnF was near
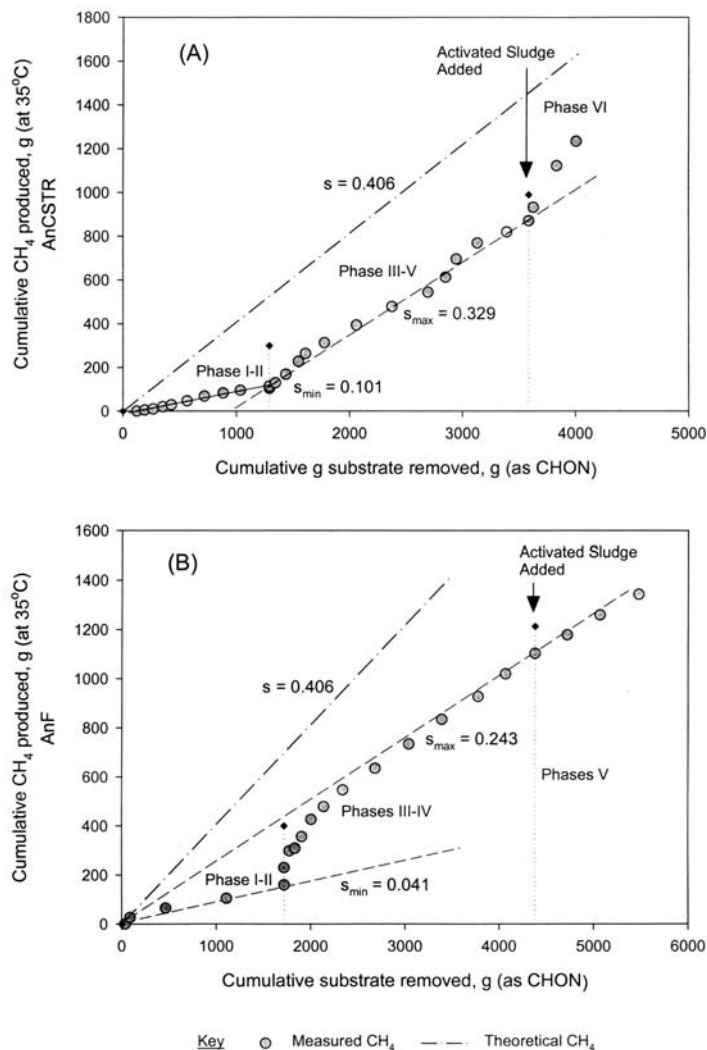
Figure 3. Cumulative mass balance between methane production and substrate removal in **(A)** the AnCSTR, and **(B)** the AnF digester.

optimal. The energy potential from the stoichiometry ($\Delta G^{o\prime} \approx -103.87\,\text{kJ} \cdot \text{mol}^{-1}$) was comparable to energy released during degradation of easily biodegradable substrates such as acetate ($\Delta G^{o\prime} \approx -90\,\text{kJ} \cdot \text{mol}^{-1}$) and benzoate ($\Delta G^{o\prime} \approx -121\,\text{kJ} \cdot \text{mol}^{-1}$) (Schink, 1988; Morel and Hering, 1993). Performance of the systems may be improved by operating the reactors for at least two HRTs before changing loading conditions. Increasing the HRT above an optimum range may result in starvation conditions followed by decreased biological activity and lower biogas production (Phases I–II, AnCSTR). At very short hydraulic retention times, biomass is lost through the effluent, thereby rendering the system unstable. The gas composition in the AnF (52% CO_2 and 48% CH_4)

and the low gas production efficiency conditions (0.041–0.243 kg CH_4/kg substrate (as $C_7H_{11}O_5N_{0.17}$)) indicate that the culture conditions in the AnF were more acidogenic than in the AnCSTR. However, the periods of operation at each HRT in the AnF were mostly sufficient (Table 3). The amount of organic acids produced affected how the final stage, aerobic trickling filter, performed in polishing the effluent.

Reaction rate kinetics

The biodegradation rate kinetic coefficient, k_{ms} (T^{-1}), was determined for each reactor to compare performance of the individual units. The mass balance on substrate S

is based on the Monod and particulate matter hydrolysis kinetics:

$$V \cdot \frac{dS}{dt} = Q \cdot (S_{in} - S) + V \cdot k'_h F'_o$$

$$- V \frac{1}{Y} \frac{\hat{\mu} S X}{K_s + S}, \quad (3)$$

where S_{in} is the influent COD concentration (ML^{-3}), S is the effluent COD concentration (ML^{-3}), F_o' is the polluting potential as COD concentration (ML^{-3}), k_h' is the hydrolysis rate coefficient (T^{-1}), $\hat{\mu}$ is the maximum specific cell growth rate (T^{-1}), K_s is the half velocity substrate concentration (ML^{-3}), Y is the cell yield coefficient ($M_x M_s^{-1}$), Q is the hydraulic flow rate ($L^3 T^{-1}$), V is the reactor liquid volume (L^3), and t is the time (T).

The value of F_o' was estimated from the process water's polluting potential, F_o, presented in Table 2. For shorter hy-draulic retention times, the contributions from hydrolysis of particulate matter are assumed insignificant. Under ideal operating conditions, the specific substrate utilization rate may be defined as a constant, ($k_{ms} = \hat{\mu}/Y(T^{-1})$). Thus, substrate removal kinetic in the reactor may be simplified to:

$$V \cdot \frac{dS}{dt} = Q \cdot (S_{in} - S) - V \frac{k_{ms} S X}{K_s} + S \quad (4)$$

Equation (4) can was solved for substrate concentration S at any time t using a fourth-order Runge-Kutta routine (no steady-state conditions assumed). The values of the coefficients k_{ms} and K_s were determined by a least-squares parameter optimization procedure using the Marquardt-Levenberg Algorithm (Press *et al.*, 1992). Optimum values of k_{ms} and K_s ($k_{ms} = 0.098$ day^{-1} and $K_s = 115$ mg COD $\cdot$ L^{-1}) were determined using data from phases III to V as the reactor approached steady-state
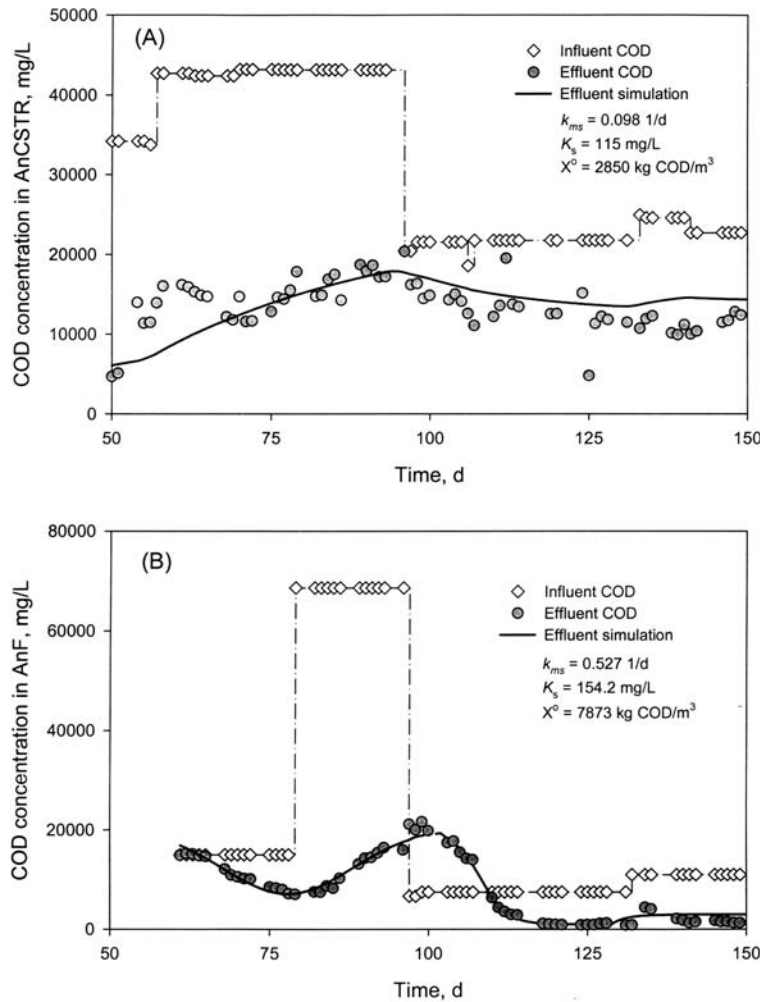

Figure 4. Model simulation of effluent COD concentration in **(A)** AnCSTR, and **(B)** AnF digester.

conditions ($V \cdot dS/dt \Rightarrow 0$). A much higher value, $k_{ms} = 0.196$ day^{-1} (for the AnCSTR reactor), was obtained under amended influent concentration (phase V, days 173–220). An average biomass concentration of 2,850 mg COD $\cdot$ L^{-1} was used during simulation. A similar analysis was used to determine kinetic parameters in the AnF reactor. The AnF equation was formulated to simulate plug-flow conditions under low to no recycle flow rate and completely mixed flow conditions at higher recycle rate. This was achieved by adjusting the influent concentration by dilution with the recycle stream ($S_{in \cdot dl} = Q \cdot S_{in} + Q_R \cdot S/(Q + Q_R)$)):

$$V \cdot \frac{\partial S}{\partial t} = Q \cdot (S_{in \cdot dl} - S) - \int^V \frac{k_{ms}S}{K_s + S} dV \quad (5)$$

where $S_{in \cdot dl}$ is the dilution adjusted influent concentration (ML^{-1}), V is the $f(l)$, is the reactor volume (L^3) as a function of length, and l is the distance from bottom of the reactor (L).

Due to the high rate of recirculation in the AnF, $Q_R/Q \geq 100$, conditions in the AnF approximated completely mixed. However, during computation no assumptions were made regarding the degree of mixing since the effect of the recycle flow stream was built into the equation. Concentration across the reactor was computed numerically by the fourth-order Runge-Kutta method for each time step. Closer to steady-state operation was assumed during the majority of the phases since the AnF phase operation times were much longer than the corresponding HRTs (Table 3). Substrate derived from biodegradable particulate matter is assumed insignificant due to low particulate and suspended matter

in the feed to the AnF.

The effluent COD concentrations simulated by optimized parameters in the kinetic expressions [Equations (3) and (4)] are shown in Figs. 4A and B for the AnCSTR and AnF, respectively. Parameter values listed in Table 4 resulted in 89% confidence in the simulated effluent COD for the AnCSTR and 93% confidence in the AnF. The k_{ms} value obtained in the AnF ($k_{ms} = 0.251 \pm 0.041$ day^{-1}) was within the range of the previous data determined for paper and organic kitchen waste, $k_{ms} = 0.27$ day^{-1} (Schober et al., 1999). The specific substrate utilization rate coefficient did not change significantly after introducing waste activated sludge feed in the AnF system ($k_{ms} = 0.263 \pm 0.010$ day^{-1}).

The reaction rate parameters were also important in determining the affect of OLR and HRT on system performance. Results showing the effects of OLR on the reaction rate are plotted in Fig. 5A and B for the AnCSTR and AnF, respectively. Average values of optimum kinetic parameters are used over the studied range of loadings for the MSW process wastewater. Figure 5a shows unstable performance in the AnCSTR under high OLR (HRT = 12 and 6 days), as demonstrated by the scatter in reaction rate (r_s) data and a lower average reaction rate than in the preceding phases (IV–V). At very short HRTs, poor performance was expected since the substrate did not spend enough time in the reactor for sufficient hydrolysis of recalcitrant materials to occur.

Acidogenic vs. methanogenic activity

The above reactor performance studies and mass balance analyses showed that gas production in the reactor

Table 4. Reactor performance and biological data.

	AnCSTR operation				*AnF operation*		
Phase	r_s ($\times 10^3$) mg/L-day	pH	COD removal %	Phase	r_s ($\times 10^3$) mg/L-day	pH	COD removal %
I	0.23 ± 0.03	—	—				
II	0.41 ± 0.13	—	—	I	1.09 ± 1.82	—	—
III	0.28 ± 0.10	7.0 ± 0.0	39 ± 13	II	0.11 ± 0.50	7.1 ± 0.1	18 ± 95
IV	0.82 ± 0.11	7.2 ± 0.1	52 ± 5	III	1.09 ± 0.02	7.1 ± 0.1	86 ± 2
V	0.55 ± 0.29	7.1 ± 0.2	29 ± 15	IV	2.09 ± 0.21	7.1 ± 0.1	88 ± 2
VI[a]	0.42 ± 0.30	7.2 ± 0.2	23 ± 16	V[a]	2.06 ± 0.12	8.1 ± 0.1	85 ± 5
	Equation 3	*Equation 4*		*Equation 5*			
k_{ms} (1/day)	0.098 ± 0.006	0.133 ± 0.004		0.251 ± 0.041			
K_s (mg/L)	115 ± 2	103 ± 13		154.2 ± 8			
k_h	0.13	—		—			
F_o (mg/L)	770	770		—			

—No steady-state conditions reached; [a]operation under a feed of waste-activated sludge.

was inconsistent with pure methanogenesis, as indicated by the high percentage of carbon dioxide in the effluent biogas. To evaluate the degree of acidogenesis and hydrolysis in the system, pH was monitored through the entire period of operation. During the initial moments after feeding volatile organic acids accumulated in the reactors so that the pH in the AnF and AnCSTR dropped at every batch feeding. The pH drop was typically less than one/tenth of a pH unit (7.1–7.0) during feeding and recovery occurred within 3 h of operation in both the AnF. The production of the acids and other smaller, soluble organic byproducts was important for the proper operation of the ATF receiving effluent from the two anaerobic reactors. During anaerobic digestion, the conversion of lower carbon number organic molecules (4 carbon to 8 carbon compounds) to VFAs is rapid when compared to

the conversion rate of VFAs to methane and carbon dioxide. However, the accumulation of the acids may be limited by the rate of hydrolysis of polymer compounds such as cellulose and ligno-cellulose to smaller compounds. In this study, the suspended nonsettleable solids in the AnF were degraded faster than the settleable solids fed to the AnCSTR resulting in higher VFA formation in the AnF (Fig. 6A and B).

The apparent low efficiency in the AnCSTR was mainly due to the accumulation of nonbiodegradable settleable solids in the reactor. The settleable solids in the wastewater were not susceptible to anaerobic digestion at the hydraulic residence times used in this study. Figure 6 shows the dynamics of the solids in all three reactors with time. Volatile solids in the reactors increased disproportionately with increases in hydraulic loading
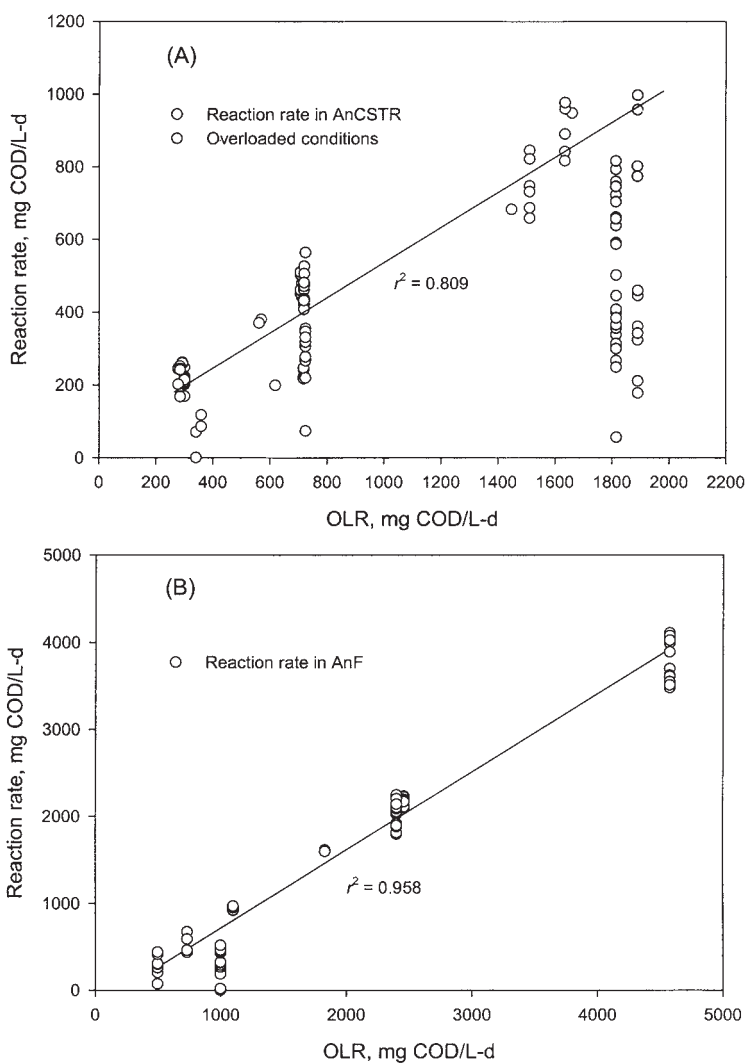

Figure 5. Effect of organic loading on substrate removal rate in **(A)** AnCSTR, and **(B)** AnF digester.

and OLR. These results are consistent with the results from Jewell and Nock (1994) on the anaerobic digestion of high fiber pulp and paper mill sludges. Jewell and Nock reported suspended solids removal efficiencies decreasing from 63 to 18% with increasing OLR from 0.5 to 2 g per week in a batch system.

Aerobic systems and/or stabilization pond systems may be used to polish the effluent biochemical oxygen demand (BOD) to meet EPA effluent standards (<15.0 mg/L). In this study, the ATF reactor removed up to 96% of the COD in the effluent from the two anaerobic reactors. Biofilm growth was abundant in the top layers of the ATF with an estimated mass of 7.5 g/L of biomass in the reactor. However, the performance of the ATF was not processes limiting, thus was not studied in detail.

CONCLUSIONS

In this study, a biogas containing approximately 48% methane was produced through anaerobic digestion of organic matter extracted from MSW by a steam pretreatment process. In addition, both the settleable and nonsettleable substrates were amenable to degradation under anaerobic conditions. However, complete removal of solids may not be achieved within an economic time frame under the current reactor configuration. Kinetic rates were lower in AnCSTR than in the AnF and the kinetic rate obtained for the AnF was within the range of previously observed values for domestic refuse. In the ATF, the effluent quality from the overall process would meet the organic carbon requirements for sewer disposal and reuse in the process.
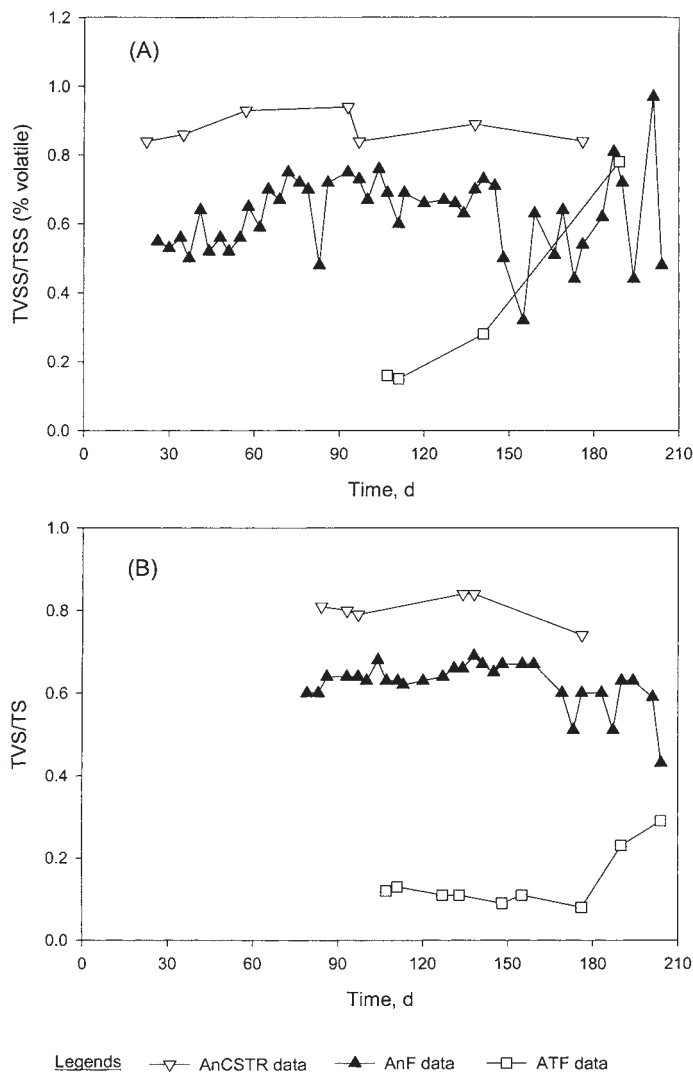

Figure 6. Flux of solids in the reactors. **(A)** Analysis of the suspended solids, and **(B)** analysis of total solids in the AnCSTR, AnF, and ATF components.

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NOMENCLATURE

BOD_5	5-day biochemical oxygen demand (ML^{-3})
COD	chemical oxygen demand (ML^{-3})
F_o	polluting potential of MSW process wastewater (M)
F_o'	polluting potential as COD concentration (ML^{-3})
HRT	hydraulic retention time (T)
k_h'	coefficient of hydrolysis (T^{-1})
k_{ms}	maximum specific substrate removal rate (T^{-1})
K_s	half velocity substrate concentration (ML^{-3})
l	length of reactor (L)
ORP	oxidation reduction potential (V)
Q	feed flow rate (L^3T^{-1})
Q_R	recycle flow rate (L^3T^{-1})
r_s	reaction rate $(ML^{-3}T^{-1})$
s	gas production efficiency per g substrate utilized (MM^{-1})
s_{lterm}	long-term gas production efficiency (slope) per kg substrate utilized (MM^{-1})
s_{min}	minimum gas production efficiency (slope) per kg substrate utilized (MM^{-1})
s_{theo}	theoretical gas production efficiency (slope) per kg substrate utilized (MM^{-1})
S	substrate concentration (ML^{-3})
S_{in}	influent substrate concentration (ML^{-3})
t	time (T)
TS	total solids concentrations (ML^{-3})
TSS	total suspended solids concentration (ML^{-3})
TVS	total volatile solids concentration (ML^{-3})
$TVSS$	total volatile solids concentration (ML^{-3})
V	volume (L^3)
Y	biomass yield from organic substrates $(M_xM_s^{-1})$

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