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Evaluation of anaerobic treatment of selected petrochemical wastes

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Abstract

Anaerobic toxicity assays and biochemical methane potential studies were performed on three waste streams (acrylic acid, ethylene oxide and total wastes) from a petrochemical facility. The acrylic waste contained high concentrations (> 350 mg l^{-1}) of acetic acid, acrylic acid, formaldehyde and benzaldehyde and low concentrations (< 100 mg l^{-1}) of allyl alcohol and acrolein. The oxide waste contained high concentrations (> 950 mg l^{-1}) of ethylene glycol, formaldehyde and acetaldehyde and low concentrations (< 50 mg l^{-1}) of other compounds. The total waste was the combination of all waste streams generated at the plant. Unacclimated anaerobic glucose–acetate enrichment culture and a culture acclimated to the acrylic waste were used. The oxide waste with total organic carbon (TOC) concentrations of about 1400 mg l^{-1} was found to be readily degradable even without an acclimation period. The total waste showed no inhibition to the unacclimated glucose–acetate culture at a TOC concentration of about 250 mg l^{-1}; however, the culture was inhibited at a TOC concentration of about 450 mg l^{-1}. The acrylic waste caused inhibition at a TOC concentration of 269 mg l^{-1} in the unacclimated culture. An acclimated culture degraded a TOC concentration of 223 mg l^{-1} of the acrylic acid stream but was inhibited by a concentration of 643 mg l^{-1}. A reduced acrylic waste load with a significant portion of the acetic acid removed was degradable at a TOC concentration of 138 mg l^{-1}. © 1997 Elsevier Science B.V.

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1. Introduction

The anaerobic treatment of petrochemical wastes has recently become the focus of a great deal of study. This was primarily due to the increased emphasis of regulations on industrial facilities and the potential benefits resulting from anaerobic digestion. The benefit of lower sludge production and handling costs of anaerobic treatment along with the production of methane gas as an end product are economically attractive attributes. In addition, air stripping of volatile organic compounds (VOCs) by aerobic treatment systems can be substantially reduced by converting to or pretreating with covered anaerobic basins. Information is available concerning the aerobic biodegradation of compounds which are commonly found in petrochemical wastes; however, there is little information on anaerobic biodegradation of whole petrochemical waste streams.

Three wastewater streams were selected for study from a petrochemical manufacturing facility which currently uses primary treatment and secondary aerobic biological treatment processes for wastewater purification. The waste streams which were of particular interest were those from the ethylene oxide units (oxide waste) and the acrolein and acrylics units (acrylics waste). These two waste streams comprised a majority of the organic loading to the wastewater treatment system. The total plant wastewater (influent waste), which was composed of combined wastewater from all units at the plant was also studied.

Table 1 shows the typical composition of the acrylic and oxide waste streams during normal operation. High concentrations of acetic acid, formaldehyde, acrylic acid and benzaldehyde along with lower concentrations of allyl alcohol and acrolein are characteristic of the acrylic waste. Oxide waste consists of significant amounts of ethylene glycol, formaldehyde and acetaldehyde along with traces of other compounds. The compounds found in these two streams are the primary constituents of total waste; the remaining organic fraction is composed of the wastes from the other units at the plant.

Table 1
Characterization of waste streams for serum bottle studies

Stream	Component	Concentration (mg l^{-1})
Acrylic waste	Acetic Acid	14851
	Formaldehyde	5302
	Acrylic Acid	1795
	Benzaldehyde	377
	Allyl Alcohol	72
	Acrolein	48
Oxide waste	Ethylene Glycol	24347
	Formaldehyde	10797
	Ethlyene Glycol	40000
	Formaldehyde	5400
	Acetaldehyde	950
	Ethylene Glycol	11000
	Formaldehyde	125
	Acetaldehyde	25

Little information is available from the literature on the anaerobic treatment of these compounds at the concentrations found in these waste streams, particularly when they exist to make up a complex waste stream.

Acrolein is an industrial herbicide/pesticide. It has been reported as readily utilizable by most aerobic microorganisms. Richards and Shieh reported that in static flask tests the compound was degraded to below detectable limits to β-hydroxypropionaldehyde with a toxicity level of 46 mg l^{-1} [1]. Tabak et al. reported that concentrations of 5 and 10 mg l^{-1} of acrolein were degraded completely in seven days in aerobic static flask tests [2]. Wierzbicki and Wojcik reported 97–100% removal of acrolein at a concentration of 200 mg l^{-1} in an activated sludge system [3]. Less information is available on the anaerobic degradation of acrolein. Hovious et al. reported activity ratios of 0.94 to 1.8 (ratio of gas produced in test bottle to gas produced by an acetate fed control) for concentrations of 10 and 20 mg l^{-1} of acrolein at volatile solids concentrations of 14,400–15,300 mg l^{-1}; however, the removal of acrolein was not reported [4].

Acrylic acid is an intermediate product in the production of resins, adhesives and synthetic fibers. Wastewater from acrylate processes usually contain acrylic acid and light esters of acrylic acid [5]. Hayashi et al. reported that the *Arthrobacter* sp. Strain NO-18 was capable of growth with acrylic acid as the sole substrate [6]. Using a sewage dilution technique, Ludzack and Ettinger reported 35% of the theoretical oxidation of acrylic acid at a feed concentration of 12 mg l^{-1} after a 20 d acclimation period [7]. Dohanyos et al. investigated the anaerobic breakdown of acrylic acid by means of an upflow biofilm reactor [5]. Removal of acrylic acid was greater than 98% at concentrations ranging from 10–15 g COD l^{-1} (g chemical oxygen demand l^{-1}) with a loading rate of 2–2.5 kg m^{-3} d^{-1} and a retention time of 5.5–6 d in an acclimated biomass. When the retention time was decreased to 1.6 d (7.8 kg m^{-3} d^{-1}), the process destabilized and methane formation stopped. Propionic acid was observed in the latter third of the reactor while acrylic acid was detected only in the first third of the reactor.

Acetaldehyde is found in various chemical manufacturing operations and is a byproduct of most hydrocarbon oxidations [8]. Gerhold and Malaney investigated degradation of acetaldehyde by Warburg respirometry [9]. A concentration of 500 mg l^{-1} in activated sludge exerted 11% of the theoretical oxygen demand after 6 h, 21.5% after 12 h, and 27.6% after 24 h, which was considerably higher than other aldehydes used in the study. Suzuki and Fujji reported that aerobic biodegradation rates of benzaldehyde were similar to those of phenol [10]. Pitter reported that 200 mg l^{-1} of benzaldehyde as COD was 99% degradable in 120 h using activated sludge as the seed [11]. Ludzack and Ettinger reported that concentrations of 200–400, 600 and 800 mg l^{-1} were degraded 50, 19 and 7% in 10 d in biochemical oxygen demand (BOD) tests [7].

Biodegradation of formaldehyde has been studied extensively. Adroer et al. reported that *Pseudomonas putida* strain A2 degraded 400 mg l^{-1} of formaldehyde in 1.25 h to methanol and formic acid [12]. Behrens and Hannes used an activated sludge system to degrade 460 mg l^{-1} of the compound by more than 99% with a retention time of 9 hr [13]. Using Warburg respirometry, Ludzack and Ettinger reported that 500 mg l^{-1} was degraded 47% over a time of 0.125–5 d [7]. They also reported that a 94% reduction was achieved over 0.33–5 d using a concentration of 333 mg l^{-1} of formaldehyde. Influent concentrations of 110, 184, 266 and 360 mg l^{-1} of formaldehyde were

degraded 23%, 16%, 15%, 23% and 28% using a trickling filter [8]. Bhattacharya and Parkin [14] performed anaerobic degradation studies using anaerobic acetate and propionate enrichment cultures. Anaerobic acetate culture removed up to 80% with an initial formaldehyde concentration of 100 mg l^{-1} and a 40 d retention time. Anaerobic propionate culture removed up to 80% at an initial concentration of 800 mg l^{-1} and a 15 d retention time.

Allyl alcohol is used as a contact pesticide for weed and seed control and is a byproduct of incomplete combustion in the chemical industry [8]. Van der Waarde et al. reported the growth of a *Pseudomonas* sp. on allyl alcohol in an acrolein and propionaldehyde acclimated culture [15]. They also reported that the culture degraded acrylic acid but not acrolein. Wierzbicki and Wojcik reported that allyl alcohol was removed up to 100% in an activated sludge system at an initial concentration of 150 mg l^{-1} [3]. BOD studies performed by Ludzack and Ettinger showed that concentrations ranging from 200–1000 mg l^{-1} were degraded 57% in 10 d [7]. Hovious et al. studied the activity ratio of allyl alcohol in an anaerobic culture [4]. At a solids concentration of 17000 mg l^{-1}, the activity ratios at 100, 300, 500 and 1000 mg l^{-1} of allyl alcohol were 0.94, 0.74, 0.70 and 0.80, respectively, indicating that allyl alcohol may be a slight inhibitor to anaerobic digestion.

Ethylene glycol is primarily used in the production of antifreeze, heat transfer agents, polyester fibers and films, asphalt, emulsifiers, paint, brake fluids, glycol diacetate, and an active ingredient in deicing fluids for airplanes and runway deicers [16]. Extensive information is available regarding the biodegradation of ethylene glycol. Kilroy and Gray reported that ethylene glycol was degradable in an activated sludge plant [17]. 0.025% ethylene glycol in the influent was treatable at an F:M (food:microorganism) ratio of 0.4–0.6 kg BOD kg^{-1} MLSS d^{-1} (kg BOD/kg mixed liquor suspended solids d). BOD removal was 99.0% and COD removal was 83.1%. Daugherty found that *Pseudomonas aeruginosa* grew on ethylene glycol at a concentration of 200 mg l^{-1} and were inhibited at a concentration of 1000 mg l^{-1} [18]. Pitter reported that 200 mg l^{-1} of COD as ethylene glycol aerobically degraded by 96.8% using a culture obtained from an activated sludge plant [11]. Evans and David reported that 2 mg l^{-1} of ethylene glycol degraded within 3 d [19]. At 10 mg l^{-1} the effluent concentration varied between 1.8 and 9.1 mg l^{-1} after a day of treatment and was totally degraded in 14 d. Gerhold and Malaney performed aerobic tests using activated sludge and a Warburg respirometer [9]. A concentration of 500 mg l^{-1} utilized 40.2% of the theoretical oxygen demand in 24 h. Battersby and Wilson reported that 50 mg of carbon l^{-1} as ethylene glycol was completely degradable anaerobically after 1–2 weeks of incubation with 2–3 g (dry weight) of municipal digester sludge with less than 1 day acclimation [20]. The ratio of actual gas production to theoretical gas production was $106 \pm 8.8\%$. Dwyer and Tiedje reported that a methanogenic consortium composed primarily of *Methanobacterium* sp. and *Desulfovibrio* sp. degraded 40 mM ethylene glycol completely in approximately 55 hr with acetate and ethanol being the primary intermediates [16]. Hovious et al. indicated that ethylene glycol was readily anaerobically biodegraded up to 900 mg l^{-1} [4]. An activity ratio of 1.3 was found for ethylene glycol concentrations of 300 and 900 mg l^{-1} at a volatile solids concentration of 9000 mg l^{-1}.

Several researchers have investigated the anaerobic degradability of other compounds

commonly associated with petrochemical wastes [21–23]. Anaerobic treatment of petrochemical wastes has been reported by Khandaker and Young [24]. They studied the treatability of petroleum condensate wastewater containing methanol, aldehydes and organic acids. When the waste stream was diluted to a loading rate of 0.6 g COD l^{-1} d^{-1}, there was a 90% COD reduction with an influent COD of 38 000 mg l^{-1}. Chemical manufacturing wastewater containing organic acids and alcohols were studied and it was found that 85% of the waste was biodegradable. When the waste stream was diluted to 35% of a loading rate of 1 g COD l^{-1} d^{-1}, it indicated inhibitory effects, demonstrating that not all of the waste streams were biodegradable and that only certain waste streams would be good candidates for anaerobic treatment. It must be reemphasized, however, that little information is available on anaerobic treatability of petrochemical waste streams. The objectives of this research were to determine the toxicity and anaerobic degradability of selected petrochemical waste streams.

2. Materials and methods

2.1. Cultures

One anaerobic culture used in this study was an acetate-fed enrichment culture developed from an anaerobic digester. It was enriched by running semi-continuously at a 50 d solids retention time (SRT) with a COD loading rate of 1000 mg l^{-1} d^{-1} as acetic acid and kept in a constant temperature room (35 ± 1°C). The basal nutrient medium contained (in mg l^{-1}): NH_4Cl, 1200; $MgCl_2$, 500; KCl, 400; $Na_2S \cdot 9H_2O$, 300; $CaCl_2 \cdot 2H_2O$, 25; $(NH_4)_2HPO_4$, 80; $FeCl_2 \cdot 4H_2O$, 40; $CoCl_2 \cdot 6H_2O$, 2.5; KI, 2.5; $MnCl_2 \cdot 4H_2O$, 0.5; NH_4VO_3, 0.5; $ZnCl_2$, 0.5; $Na_2MoO_4, \cdot 2H_2O$, 0.5; H_3BO_3, 0.5; $NiCl_2 \cdot 6H_2O$, 0.5, Cysteine, 10; $NaHCO_3$, 6000 as $CaCO_3$ [25]. The total alkalinity of the system was 4600 mg l^{-1} as calcium carbonate (pH 7.5), the total suspended solids (TSS) were 2250 mg l^{-1} and the volatile suspended solids (VSS) were 1850 mg l^{-1}. The volatile acids (VA) were below detectable limits.

The second culture used in this experiment (denoted UCC-13) was an anaerobic consortium acclimated to the acrylics waste. It was developed using the contents of an anaerobic reactor started in 1992 at the facility. It was primarily fed the acrylics waste as its sole carbon source. It was run semi-continuously at a 50 d SRT with a volumetric loading rate of acrylic waste of 6.5 ml l^{-1} d^{-1} and organic loading rate of 175.5 mg l^{-1} d^{-1}. The same basal nutrient medium was used.

2.2. Anaerobic toxicity assays and biochemical methane potential

Anaerobic Toxicity Assays (ATA) were performed at 35 ± 1°C using serum bottles with a capacity of 150 or 500 ml as described by Owen et al. [26] using the acrylics waste, oxide waste and influent waste. ATAs were also performed for formaldehyde and benzaldehyde. Serum bottles were cleaned with 1:1 HCl, filled with water which was displaced with nitrogen gas, and sealed with a rubber septum. The bottles were filled anaerobically with 45 ml of acetate culture, 3 ml of nutrient medium and 2 ml of 50 g

l^{-1} yeast extract in the 150 ml bottles or 300 ml of acclimated culture in the 500 ml bottles. They were then fed 1120 mg COD l^{-1} as acetic acid per day until daily gas production was constant (less than 10% variation for seven days). Gas production was measured daily using a gas displacement device which was filled with a salt saturated 5% sulfuric acid and water solution colored with methyl orange [27]. The bottles were spiked with either one of the waste streams or individual compounds. Acetic acid was maintained at 1000 mg COD l^{-1} in the bottles based on daily gas production. Serum bottles for the Biochemical Methane Potential (BMP) studies (35 ± 1°C) were prepared in the same manner as those used in the ATA. The test bottles were spiked with selected concentrations in triplicate, and the acetate feed was stopped in all bottles including controls on the day prior to spiking. Triplicate unspiked controls were run for each experiment.

Table 2 shows the experimental design for the experiments performed. Six bottles containing acetate culture were spiked with acrylic waste in Study 1 at TOC concentrations of 269 mg l^{-1} (Bottles 1B, 2B and 3B) and 776 mg l^{-1} (Bottles 1C, 2C and 3C) and an ATA performed. Study 2 involved an ATA and BMP study using UCC-13 culture and a reduced waste load acrylic waste. The total organics in this new acrylic waste stream were significantly reduced. In the ATA, six 500 ml bottles containing 300 ml of UCC-13 culture were spiked with TOC concentrations of 69 mg l^{-1} (Bottles G4, G5 and G6) and 138 mg l^{-1} (Bottles G7, G8 and G9). In the BMP study, six bottles were prepared and spiked with the same TOC concentrations as in the ATA. Samples were obtained for GC–MS analysis from the ATA bottles. Study 3 involved a BMP study using the present acrylic waste and UCC-13 culture. Two bottles were prepared using 500 ml bottles and 300 ml of culture. Bottles F8 (spiked TOC = 223 mg l^{-1}) and F9 (spiked TOC = 643 mg l^{-1}) were used in the BMP study and were sampled for GC, GC–MS, TOC and COD analysis. Study 4 involved an ATA using benzaldehyde and formaldehyde in the acetate enrichment culture. Benzaldehyde was spiked at concentrations of 50, 100 and 150 mg l^{-1}. Formaldehyde was spiked at concentrations of 18.5, 37 and 55.5 mg l^{-1}. Study 5 involved an ATA using oxide waste as the toxicant in acetate enrichment culture. Spike TOC concentrations of 54.5 mg l^{-1} (Bottle 23), 157.5 mg l^{-1} (Bottle 24), 253 mg l^{-1} (Bottle 25), 464 mg l^{-1} (Bottle 26), 795.5 mg l^{-1} (Bottle 27), 1044 mg l^{-1} (Bottles 28, 38 and 39) and 1392 mg l^{-1} (Bottle 40) were used. Study 6 involved an ATA using influent waste as the toxicant. Spike TOC concentrations of 53.5 mg l^{-1} (Bottle 32), 154 mg l^{-1} (Bottle 33), 248 mg l^{-1} (Bottles 29, 30 and 34), 454.5 mg l^{-1} (Bottle 35) and 779 mg l^{-1} (Bottle 36) were used. Biodegradation of the wastes or compounds was measured with respect to the amount of gas obtained relative to the control.

2.3. Analytical methods

pH was measured by Method 400-H^+ [27] using a Fisher Scientific Model 910 pH meter. Total suspended solids and volatile suspended solids were measured at the beginning and end of the assays according to Method 2540D and 2540E [27]. Total alkalinity, bicarbonate alkalinity and volatile acids in the cultures were measured at the beginning of the assays by titration [28]. Chemical oxygen demand was measured by a

Table 2
Experimental design

Study	Bottles	Experiment type [a]	Waste	Culture	TOC Conc. (mg l^{-1})
1	1A	ATA			0
	1B, 2B, 3B	ATA	Acrylic	Acetate	269
	1C, 2C, 3C	ATA			776
2	G1, G2, G3	ATA			0
	G4, G5, G6	ATA			69
	G7, G8, G9	ATA	Acrylic [b]	UCC-13	138
	G10, G11, G12	BMP			69
	G13, G14, G15	BMP			138
3	Control	BMP			0
	F8	BMP	Acrylic	UCC-13	223
	F9	BMP			643
4	Control	ATA			0
	–	ATA	Benzaldehyde	Acetate	50, 100, 150 [c]
	–	ATA	Formaldehyde		18.5, 37.5, 55.5 [c]
5	21	ATA			0
	23	ATA			54.5
	24	ATA			157.5
	25	ATA	Oxide	Acetate	253
	26	ATA			464
	27	ATA			795.5
	28, 38, 39	ATA			1044
	40	ATA			1392
6	21	ATA			0
	32	ATA			53.5
	33	ATA	Influent	Acetate	154
	29, 30, 34	ATA			248
	35	ATA			454.5
	36	ATA			779

[a] ATA: anaerobic toxicity assay, BMP: biochemical methane potential.
[b] Reduced waste load acrylic waste.
[c] Concentrations in mg l^{-1} of compound.

modified closed reflux method described by the Hach Company (Ames, IA) using 0–1500 mg l^{-1} COD reagent vials. Total organic carbon was measured on a high range Total Carbon Analyzer Model 1524 (Ionics) according to Method 5310B [27].

Intermediate compounds identification was done using a Hewlett–Packard 5890 Series GC with a 5970 Series Mass Selective Detector. A Hewlett–Packard crosslinked HP-5 Capillary column 25 meters in length with a 0.25 mm I.D. and a 0.5 μm film was used. The injection flow was split at 36:1, and column flow was approximately 1 ml/minute. The oven temperature was held at 40°C for 8 min, raised to 88°C at 4°C min^{-1}, and held for 8 min. The mass spectrometer temperature increased from an initial temperature of 40°C at a rate of 20°C min^{-1} to 250°C and maintained for 20 min. The injector temperature was 250°C. The detection limit was 5 mg l^{-1}.

Acrylic acid, acetic acid and propionic acid were quantified using a Shimadzu GC-14A. A 80/120 Carbopack B-DA/4% Carbowax 20M (Supelco Corp., Bellefonte, PA) column was used. The column and FID temperatures were 175 and 200°C, respectively. The carrier gas was helium at a flowrate of 24 ml min^{-1}. The detection limit was 1 mg l^{-1}. Ethylene glycol was quantified using a Hewlett–Packard 58900 Series II GC with TCD detector. The column was a 10 m DB-Wax megabore column with a 0.53 mm ID and 1 μm film thickness. The injector temperature was 170°C and detector temperature 230°C. The oven temperature was held at 40°C for 3 min and raised to 190°C at 8°C min^{-1}. The carrier gas was helium at a flowrate of 3.8 ml/min^{-1}. The flow through the septum purge was 1.7 ml min^{-1}.

3. Results and discussion

The acrylics waste and the oxide waste stream accounted for the majority of the organic loading from the plant site. The effect on the cumulative gas production from the acetate with various concentrations of acrylics waste are shown in Fig. 1 and Table 3 (Study 1). In this study, gas production was measured to evaluate the toxicity of the acrylic waste stream to an unacclimated methanogenic culture. Acrylic waste concentrations of 269 mg l^{-1} TOC (1 ml of sample in 50 ml of culture) showed immediate inhibition of gas production. Bottle 2B showed signs of recovery (i.e., resumption of gas production) after 63 days and the other two bottles (1B and 3B) showed signs of recovery after 100 and 150 days, respectively. Once the bacteria that were exposed to 269 mg l^{-1} TOC concentration recovered, the gas production rates returned to near normal. This was indicated by the almost parallel lines for these three bottles (1B, 2B

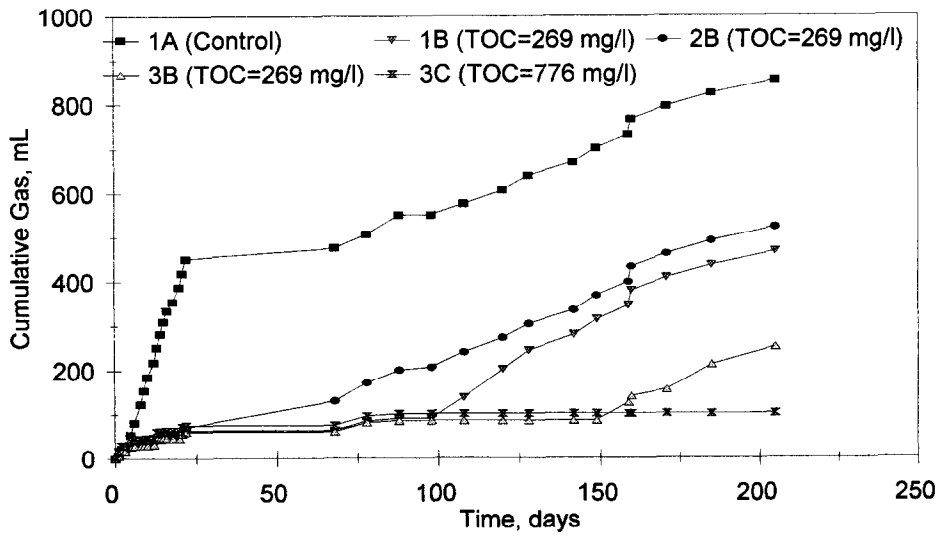

Fig. 1. Study 1: Effect of acrylic waste on cumulative gas formation in acetate enrichment culture.

Table 3
Gas production from selected waste streams

Sample	TOC ($mg\ l^{-1}$)	COD ($mg\ l^{-1}$)	TOC Conc. after spiking ($mg\ l^{-1}$)	Bottles	Theoretical methane (ml at STP)	Theoretical methane (ml at 35°C)	Theoretical CO_2 (ml at 35°C)	Theoretical total gas (ml)	Measured total gas (ml)
Acrylic Waste	11358	30326	223	F8	63.7	71.9	71.7	143.6	123
	11358	30326	643	F9	191.1	215.6	214.9	430.5	121
	13716	36622	269	1B, 2B, 3B	12.8	14.5	14.4	28.9	0
	13716	36622	776	3C	38.5	43.4	43.3	86.7	0
	7284	18754	69	G10, G11, G12	19.7	22.2	22.2	44.4	73
	7284	18754	138	G13, G14, G15	39.4	44.6	44.3	88.9	100
Oxide Waste	2728	7284	1044	28, 38, 39	76.5	86.3	86.0	172.3	142
	2728	7284	1392	40	127.5	143.9	143.4	287.3	187
Total Waste	2727	7281	248	29, 30	12.8	14.4	14.3	28.7	111
	2727	7281	454.5	35	25.5	28.8	28.7	57.5	0

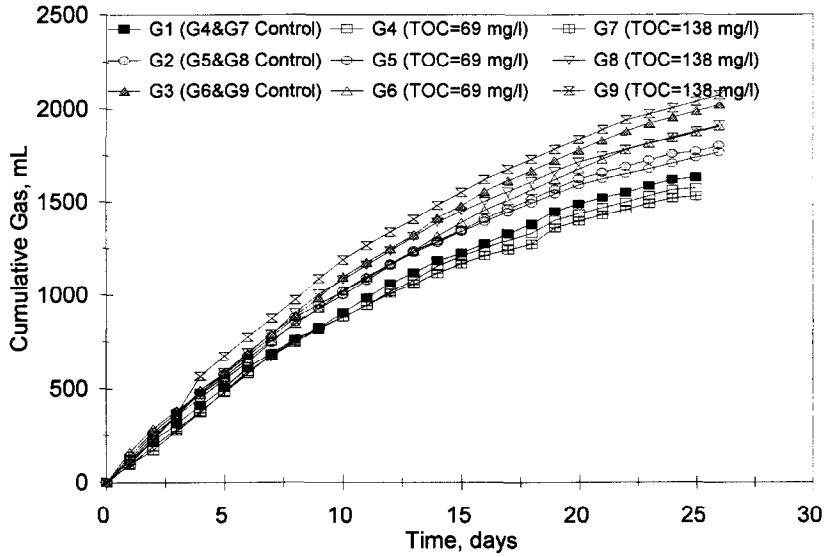

Fig. 2. Study 2: Effect of acrylic waste on cumulative gas formation in acclimated UCC-13 culture (Reduced waste load).

and 3B) and for the control (Fig. 1). Therefore, at a concentration of 269 mg l^{-1} TOC in the acrylic waste stream, the acclimation may vary from 63 to 160 days for a system without prior acclimation. With the 776 mg l^{-1} TOC concentration (Bottle 3C, 3 ml of waste and 50 ml of culture), irreversible inhibition was observed. The acetate enrichment culture did not produce any gas for a period of 210 days which indicates the microorganisms were not able to tolerate 776 mg l^{-1} TOC without prior acclimation.

Study 2 investigated the effect of the reduced waste load acrylic waste stream. An ATA and BMP were performed and gas production monitored to evaluate the toxicity and potential biodegradability of the reduced waste load stream based on gas production. A culture (UCC-13) acclimated to the original acrylic waste stream was used in this study. Fig. 2 shows that at concentrations of 69 and 138 mg l^{-1} TOC, the acrylics waste stream showed no inhibition and were tolerated by the acclimated microorganisms in the ATA. The TOC for the 0.5 ml concentration in G4, G5 and G6 samples represented 69 mg l^{-1} TOC and the TOC for the 1 ml of waste to 50 ml of culture in G7, G8 and G9 samples represented 138 mg l^{-1} TOC. The BMP experiment on acrylics waste demonstrated that the majority of gas was generated in the first 3 days after spiking. The amount of methane gas calculated for the 138 mg l^{-1} TOC was 39.5 ml and was calculated as follows [24]: First, the TOC was measured as 7024 mg l^{-1}. The COD of the waste was then calculated by multiplying 2.67 mol of oxygen/mole of carbon times 7024 mg l^{-1} of TOC to yield 18 754 mg l^{-1} COD. 6 ml of waste was used and it was multiplied by 1 l/1000 ml to yield 113 mg COD. 1 g of COD yields 395 ml of methane at 35°C [29]. Therefore, 395 ml g^{-1} times 0.113 g/1000 ml yields 44.6 ml of methane. Fig. 3 shows that there was no inhibition due to this waste stream. GC–MS analysis showed levels less than 5 mg l^{-1} for acetic acid, acrylic acid and formaldehyde. This

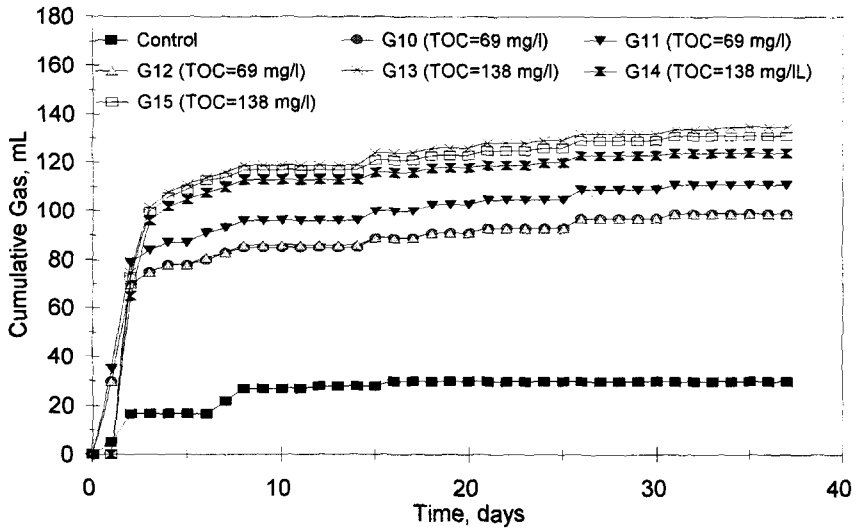

Fig. 3. Study 2: BMP of acrylic waste on acclimated UCC-13 culture (Reduced waste load).

correlates to the BMP data which shows that most of the gas generation occurred within the first two days.

Further studies using the acrylic waste stream (prior to waste load reduction) with the acclimated culture (UCC-13) were conducted (Study 3). This study differed from Study 1 since COD and some key individual constituents in the waste were monitored. The composite sample contained 11,358 mg l^{-1} of TOC. Fig. 4 shows that the 1 ml of waste

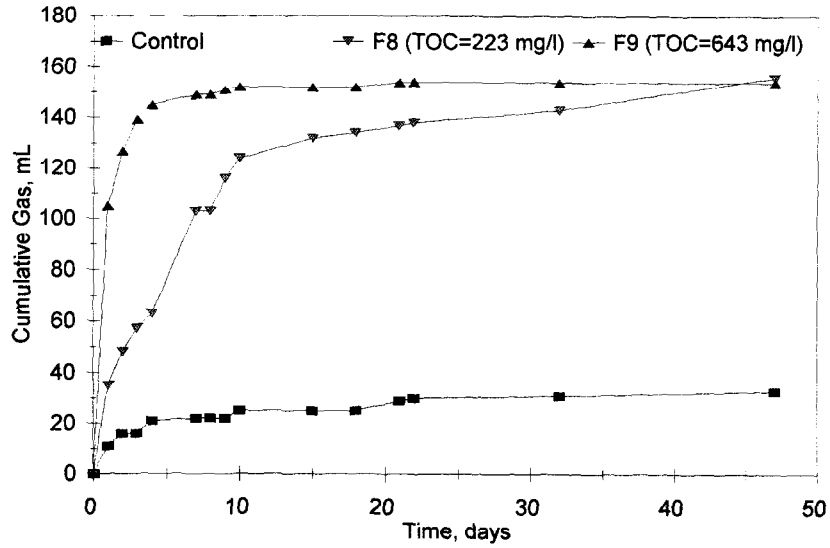

Fig. 4. Study 3: BMP of acrylic waste on acclimated UCC-13 culture.

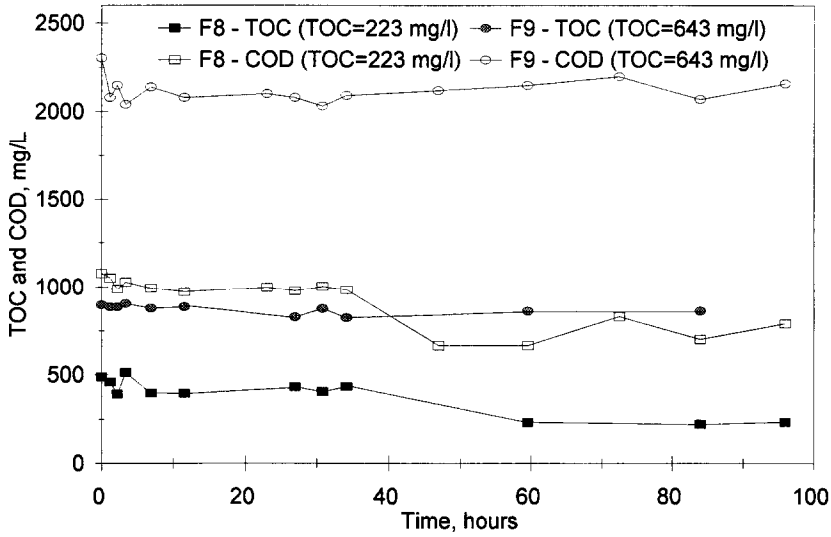

Fig. 5. Study 3: Removal of TOC and COD in acrylic waste by acclimated UCC-13 culture.

per 50 ml of culture (223 mg l^{-1} TOC) produced the majority of gas between 4 and 10 days. The theoretical gas production from this waste was calculated to be 72 ml of methane (Table 3). The total amount of gas produced was 123 ml over the 40 day period. Approximately 60 ml of gas was produced in the first two days, which was probably due to carbon dioxide generation from the acidic acrylics waste (see Table 3). In order to verify this, gas production immediately after spiking was measured in separate bottles and found to nearly equal this gas production. The higher concentration of 643 mg l^{-1} TOC produced the greater majority of gas in the first two days which was due to carbon dioxide generation. The concentration showed inhibition and produced no gas for the remainder of the test. Fig. 5 further verifies that the concentration of 3 ml/50 ml of 643 mg l^{-1} TOC caused inhibition as evidenced by the consistent COD levels for the first 100 hours of the experiment. It can be seen from Fig. 5 that the 1 ml/50 ml or the 223 mg l^{-1} TOC concentration showed a definite reduction in COD levels during the period from 35 to 60 h which indicated degradation of this waste occurred during this period. Fig. 6 showed a significant drop in acetic and acrylic acid concentrations at 34 h. It also showed a slight increase in propionic acid, indicating a biodegradation pathway of acrylic acid through propionic acid. Fig. 6 further shows that there was inhibition at this level of 643 mg l^{-1} of TOC. It can be seen, however, that concentrations of acetic acid dropped to 670 mg l^{-1} in the first 10 h and increased from 720 to 800 mg l^{-1} at 12 h and decreased to 680 mg l^{-1} after 95 h. This indicated that, even at this level, the waste may be biodegraded and form volatile acids.

Study 4 investigated the toxicity of benzaldehyde and formaldehyde to unacclimated acetate enrichment culture. The ATA for benzaldehyde showed no inhibitory effects for concentrations of 50, 100 and 150 mg l^{-1} of benzaldehyde or concentrations of 18.5, 37 and 55.5 mg l^{-1} of formaldehyde (Fig. 7). The results of ATAs on the specific

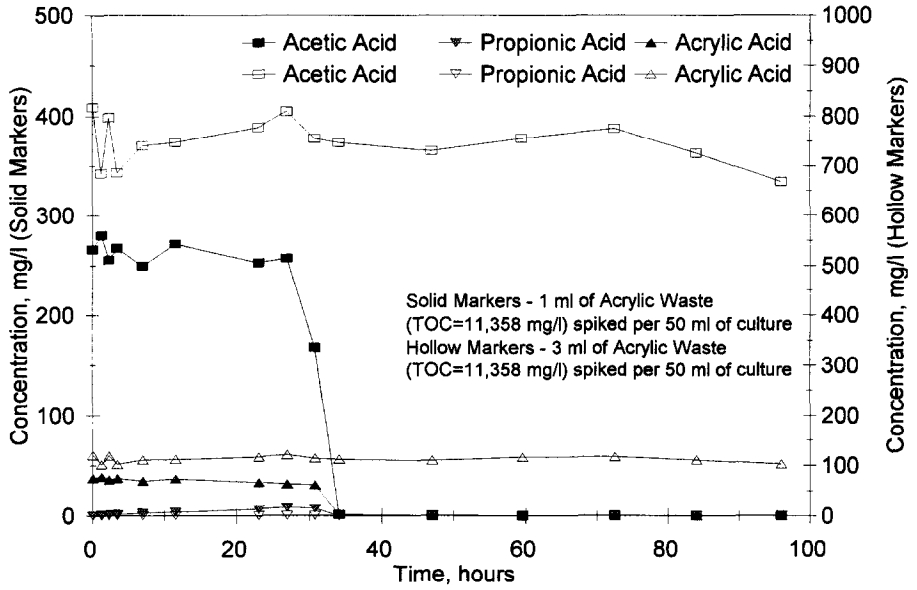

Fig. 6. Study 3: Intermediate volatile acids during acrylic waste degradation by acclimated UCC-13 culture.

compounds in the acrylics waste showed inhibition at acrylic acid levels of 500 to 1500 mg l^{-1} [30]. It also showed that the higher the concentration of acrylic acid, the longer the inhibition period to the unacclimated culture. This supports the belief that the acrylic

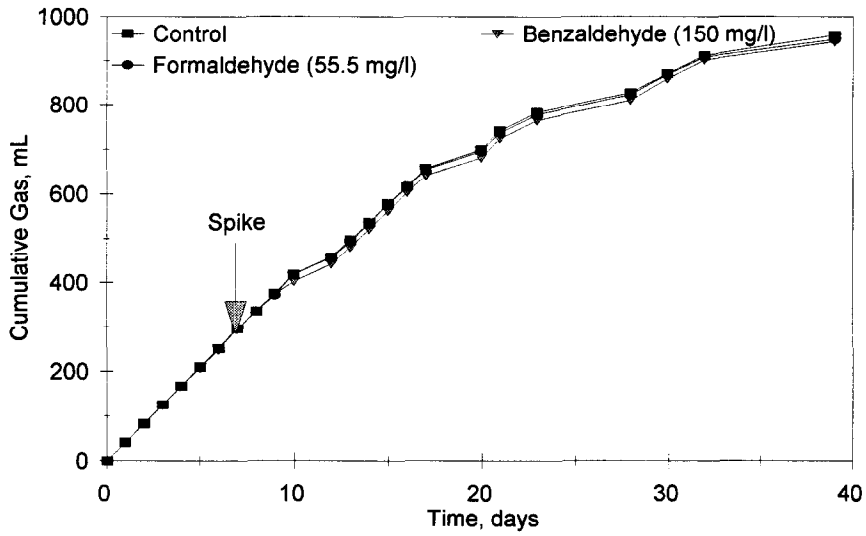

Fig. 7. Study 4: Effect of benzaldehyde and formaldehyde on cumulative gas formation in acetate enrichment culture.

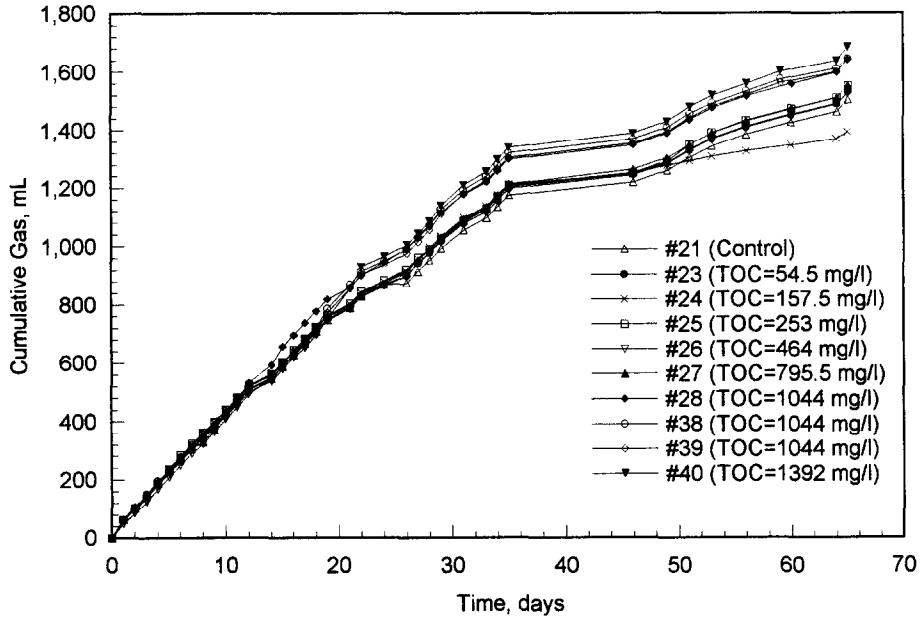

Fig. 8. Study 5: Effect of oxide waste on cumulative gas formation in acetate enrichment culture.

acid is converted to volatile acids which continue to degrade after the acrylic acid is degraded. ATA with allyl alcohol showed a slight inhibitory effect at concentrations from 4000–25 000 mg l^{-1}, and acrolein showed inhibitory effects as low as 10 mg l^{-1}. Acrolein concentrations of 150 mg l^{-1} showed complete inhibition for the 40 day test period [30].

The toxicity and potential biodegradability of the oxide waste stream were evaluated in Study 5 by means of an ATA. Over the course of the study, all bottles spiked with the oxide waste stream produced more gas than the unspiked control. No gas inhibition was observed with 30 ml of the oxide waste in 50 ml of culture (1044 mg l^{-1} TOC) in any sample (Fig. 8). After Day 2 of the oxide waste spiking, the gas production actually increased 50 ml above the control sample. The 50 ml sample (1392 mg l^{-1} average TOC) produced even more gas than the 30 ml samples. It was noted that six days after the spiking, the 50 ml sample continued to produced more gas than the 30 ml sample for the duration of the test. The oxide waste showed no inhibition in gas production and did not require any acclimation period. Also, at the higher TOC (1392 mg l^{-1}) more gas was produced, indicating that prior acclimation for biodegradation of the compounds in the oxide waste stream was not necessary. The key constituents of the oxide waste stream are ethylene glycol (2300 mg l^{-1}), formaldehyde (473 mg l^{-1}) and acetaldehyde (27 mg l^{-1}). Hence it appears that these compounds are anaerobically degradable at the concentrations. The available information from the literature on formaldehyde and acetaldehyde degradation showed that acetaldehyde at concentrations ranging from 30–80 mg l^{-1} and formaldehyde at concentrations ranging from 30–800 mg l^{-1} are

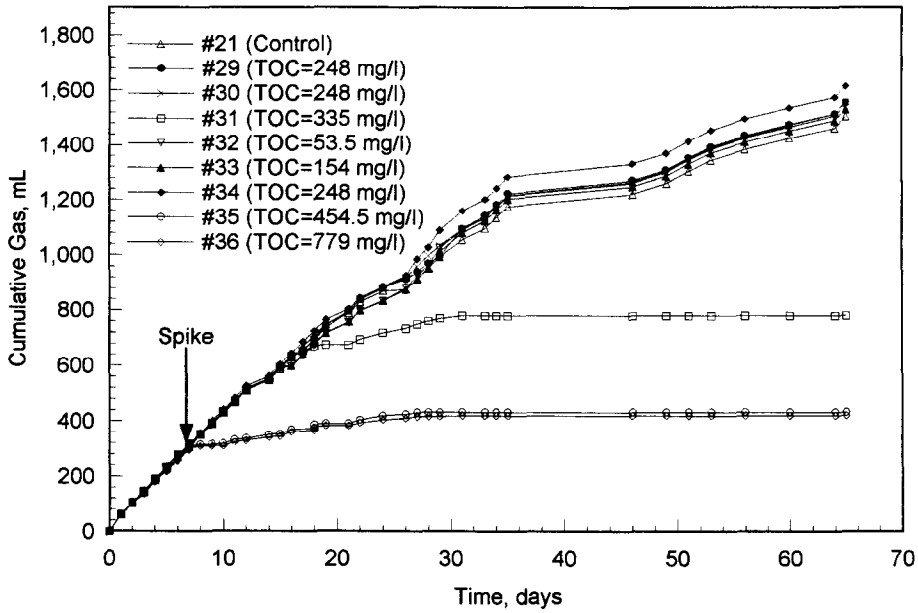

Fig. 9. Study 6: Effect of influent waste on cumulative gas formation in acetate enrichment culture.

anaerobically biodegradable [8,14]. Ethylene glycol ATA and BMP studies showed that at concentrations ranging from 5000–20 000 mg l^{-1}, ethylene glycol was readily biodegradable [30]. Based on these findings, it was concluded that the oxide waste was more amenable to anaerobic treatment than the acrylics waste stream.

The plant facility's wastewater influent stream included all waste streams from the facility and was used in Study 6. An ATA was performed to evaluate toxicity of the waste stream at different TOC concentrations. At concentrations of 455 and 779 mg l^{-1} TOC, the influent waste stream showed immediate inhibition of gas production (Fig. 9) and did not demonstrate recovery until Day 65 of the experiment. The 5 ml sample of the influent waste stream diluted with 50 ml of culture (approximately 248 mg l^{-1} TOC) did not show signs of inhibition. It showed signs of additional gas production after 19 days which indicated degradation of some organics in the waste stream. This only occurred once during the 67 day test period. Inhibition by higher volume spikes can be explained by the presence of the acrylic waste stream, which accounts for approximately 50% of the organic loading in the total influent waste stream and shows inhibition at concentrations as low as 248 mg l^{-1} TOC.

Table 4 compares the reported treatable concentrations of the key compounds in the waste streams with those used in this study and the concentrations found in the whole waste streams. ATA and BMP studies for acrolein, acrylic acid, allyl alcohol and ethylene glycol have been reported elsewhere [30]. The concentration of several key compounds in the whole waste stream is well above concentrations previously investigated. As shown by Stewart et al. [30] and the ATA with the oxide waste, the high concentration of ethylene glycol in the oxide waste is not toxic to the anaerobic process.

Table 4
Comparison of waste stream concentrations to performed studies

Compound	Anaerobically treatable concentrations from available literature (mg l^{-1})			Concentrations used in this study (mg l^{-1})		Average concentration in waste (mg l^{-1})
	Initial	Percent removal	Ref.	Initial	Percent removal	
Acrylics waste						
Acrolein	10–20	NR	[4]	10–150	50–97	14
Acrylic Acid	1000 as COD	> 98	[5]	100500–1500	> 99	1097
Allyl alcohol	1000	NR	[4]	4000–25000	0.4–7	27
Benzaldehyde	NA			150	NM	233
Formaldehyde	800	35–80	[14]	55.5	> 99	3292
Oxide waste						
Ethylene glycol	900	NR	[4]	10000	> 98	2282
Formaldehyde	800	35–80	[14]	90	> 99	473

NR, not reported; NA, not available.

The only concern in this waste stream is the high requirement for alkalinity due to volatile acids production from ethylene glycol. Toxicity to the anaerobic process is evident due to the acrylic waste, which contains amounts of acrylic acid and formaldehyde equal to or above those previously investigated concentrations. However, the presence of acrolein must also be noted since it has been shown to be inhibitory at concentrations as low as 10 mg l^{-1} [30]. It is unclear if toxicity to the anaerobic process caused by this waste stream is due to the presence of a single or more toxic compounds or if synergistic effects play a role in toxicity.

4. Conclusions

Studies with the present acrylics waste using an unacclimated culture showed that inhibition of methanogens occurred at a TOC concentration of 269 mg l^{-1}. Acclimated culture degraded a TOC concentration of 223 mg l^{-1} but was inhibited by a TOC concentration of 643 mg l^{-1}. Thus, the potential for both acclimation of an anaerobic culture and degradation of the acrylic waste by the culture exists. Acclimated culture tolerated a TOC concentration up to 138 mg l^{-1} when fed the reduced acrylic waste. It must be noted that this apparent lower tolerance to the waste stream could be misleading due to the fact that lowering the waste load by removing acetic acid concentrates the potential toxic components of the acrylic waste stream (acrylic acid, acrolein, formaldehyde). This could make the waste stream potentially more toxic than the present waste. No inhibition of gas production was observed when benzaldehyde was spiked to the unacclimated acetate enrichment culture up to a concentration of 150 mg l^{-1}, indicating tolerance of the culture to the compound. The oxide waste showed no inhibition to levels of about 1400 mg l^{-1} TOC with the unacclimated acetate enrichment culture. This shows that the oxide waste was readily biodegradable and would not require prior acclimation. Based on the literature and the performed studies, it is evident that ethylene glycol, formaldehyde and acetaldehyde at the waste concentrations would

not present a problem in an anaerobic treatment process, even when combined. Studies with the influent waste stream showed that inhibition to the anaerobic process occurred at a TOC concentration of about 450 mg l^{-1} in unacclimated culture. No inhibition was observed at a TOC concentration of about 250 mg l^{-1}. The dilution of the highly toxic acrylic waste stream by other waste streams in the plant increased the TOC required to inhibit the unacclimated culture. In spite of the toxicity observed in the acrylic and influent waste streams, all were found to be anaerobically treatable, in particular the oxide waste stream.

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