

## ANAEROBIC TREATMENT OF A PETROCHEMICAL WASTEWATER FROM A TEREPHTHALIC ACID PLANT

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### ABSTRACT

Anaerobic treatment of terephthalic acid plant wastewater was tested using two UASB reactors (T and U) and a downflow tubular fixed film reactor. UASB T was inoculated with sludge sampled from an anaerobic stabilization pond receiving waste activated sludge from a petrochemical industry treatment plant. UASB U and the fixed film reactor were inoculated with anaerobically adapted activated sludge from a municipal plant. Raw effluent had to be settled and neutralized before reactor feeding. Sedimentation resulted in 70% TSS and 37% COD removal. UASB digesters presented comparable treatment efficiencies with rather low COD removals: the best results were 46.4% for UASB T at 2.6 kg COD/m<sup>3</sup>-d and a hydraulic retention time ( $\theta$ ) of 2.7 days and 43.9% for UASB U at 2.2 kg COD/m<sup>3</sup>-d and  $\theta$  of 3.2 days. The performance of the tubular reactor was much higher, 74.5% COD removal at 1.89 kg/m<sup>3</sup>-d and  $\theta$  of 3.4 days. The better efficiencies of this last digester are explained mainly by a higher VSS content and a better resistance to toxicity caused by the aromatics present in the wastewater. A primary settling-anaerobic-aerobic process is proposed as an alternative to the conventional aerobic process for treating terephthalic wastewater, but disposal of solids from primary sedimentation and cost of neutralization have to be considered before application.

### KEYWORDS

Aromatic compounds; Terephthalic acid; p-Toluic acid; UASB; Fixed film reactor; Anaerobic inoculum.

### INTRODUCTION

Polymer-grade terephthalic acid (1,4-benzenedicarboxylic acid) is among the top 50 chemicals manufactured in the United States (C&EN, 1988; Webber, 1984). In 1990, its production in the world was estimated at 6.52 10<sup>6</sup> ton/year and should increase in the future to about 9 10<sup>6</sup> ton/year. Apart from the USA, the principal producers are Japan, Taiwan, South Korea and the EEC (Savostianoff, 1990). In Latin America, purified terephthalic acid (PTA) is made in Mexico and Brazil, and represents around 6% of world production. This proportion will increase due to the augmentation of plant capacities and the construction of a new factory in Colombia. Polyester textile fibers are the principal outlet for PTA. Other important end products are polyester resins used to make bottles for carbonated drinks (PET bottles), and polyester films which have many applications in the audio-visual, photographic, computer, packaging and decorative fields. Smaller amounts are used to make technical plastics (Savostianoff, 1990).

The American Amoco process is the established technology for polymer-grade terephthalic acid manufacture (75% of world production). It consists of a liquid-phase air oxidation of p-xylene at 173-230 °C and 1.5-3.0



10<sup>6</sup> Pa, using acetic acid as solvent, Co acetate and Mn acetate as catalysts and bromine as a renewable source of free radical. The acid obtained is then purified by dissolution in water at 250 °C under pressure, followed by an hydrogenation in the presence of a noble metal (Pd) on a carbon support (Bemis *et al.*, 1982; Weissermel and Arpe, 1981). During the process, two principal byproducts are formed, 4-formylbenzoic acid and p-toluic acid (4-methylbenzoic acid). These petrochemicals together with terephthalic, benzoic and acetic acids are found as the main organic pollutants in the wastewaters generated by the oxidation and the purification steps. Approximately 3-4 m<sup>3</sup> of wastewater with around 10 kg COD/m<sup>3</sup> are produced for 1 PTA ton manufactured.

The PTA wastewaters are generally treated by a three stage activated sludge process, an arrangement which allows more than 90% total COD (Chemical Oxygen Demand) removal and has proved to be resistant to shocks of twice the normal organic load when applied to a synthetic PTA plant effluent (Lau, 1978). Moreover, it has been reported that terephthalate and p-toluic acid are highly degraded by activated sludge (Lund and Rodriguez, 1984). In addition, the three stage process can treat this acidic effluent (pH 4.5) without previous neutralization. However, the aerobic treatment of this kind of wastewater presents some disadvantages: long hydraulic retention time (3-5 days), high O<sub>2</sub> (energy) requirement (Lau, 1978), possibility of sludge bulking (Brugnaro and Polo, 1985), and high consumption of anhydrous ammonia and phosphoric acid which have to be added to the effluent limited in nitrogen and phosphorus.

In the future, PTA production expansion will occur mostly in developing countries. Indeed, a more economical wastewater treatment technology would be desirable. For the countries of the intertropical zone with a hot climate, the use of anaerobic digestion, alone or in combination with other processes, seems to be a good economic alternative to conventional aerobic processes.

In the case of terephthalic acid wastewaters, no information is available about methanization of 4-formylbenzoic acid and PTA, but this last compound is anoxically degradable by denitrification (Afring *et al.*, 1981; Nozawa and Maruyama, 1988) and its orthoisomer, phthalic acid, can be methanized (Chou *et al.*, 1978; Shelton and Tiedje, 1984; Battersby and Wilson, 1989). Horowitz *et al.* (1982) reported the mineralization to CH<sub>4</sub> and CO<sub>2</sub> of p-toluic acid by freshwater lake sediment, and the methane fermentation of benzoic acid is a well established phenomena (Berry *et al.*, 1987; Evans and Fuchs, 1988; Holliger *et al.*, 1988). In addition, a survey on the reactivity and fate of a dimethyl terephthalate (DMT) plant wastewater (somehow similar to PTA effluent) after deep-well injection showed that this effluent was degraded by methanogenic activity when highly diluted with the native ground water (Leenheer *et al.*, 1976). In 1980, moreover, in the Netherlands the feasibility of anaerobic treatment of DMT wastewater using a UASB (Upflow Anaerobic Sludge Blanket) reactor was demonstrated at laboratory and pilot scale, but the effluent had to be pretreated with NaOH to eliminate formaldehyde which was inhibitory for the bacteria (Grontmij, 1980). Leenheer *et al.* (1976) considered that only the readily biodegradable compounds (acetic, formic acids and methanol) were degraded to methane and that aromatics (terephthalic, p-toluic, benzoic, phthalic acids) were removed by physical interactions with the injection zone mineral constituents. In contrast, Grontmij (1980) did not consider the aromatic components of the effluent which represent nevertheless around 16-19% of the COD according to Leenheer *et al.* (1976) and Reule (1990). Recently, two papers confirmed the possibility of DMT effluent anaerobic treatment employing a two stage fluidized bed reactor (Reule, 1990) and an upflow expanded granular sludge bed reactor (Frankin and Koevoets, 1991). All these data suggest that PTA factory wastewater might be anaerobically treated even if its aromatic COD proportion is 59%. According to a patent (Ely and Olsen, 1989), it seems that Amoco Corporation studied the anaerobic alternative for PTA effluent using a downflow filter. Unfortunately, no operation data were given in order to evaluate the performance of the described system.

In this work, we present results on a comparative basis of laboratory scale anaerobic treatment of terephthalic acid plant wastewater using the UASB process and the tubular fixed film process.

## MATERIAL AND METHODS

### Reactor Design.

2 identical laboratory UASB reactors (U and T) and a laboratory tubular fixed film reactor with respective working volume of 3 l and 4.75 l were used (Fig. 1). The UASB reactors were built with a glass column of 45 cm height and an internal diameter of 9.6 cm. The fixed film reactor made of a 100 cm high plexiglas column

with an internal diameter of 9.6 cm was packed using 67 cm high, 1.27 cm diameter PVC tubes. The tubes provided a specific area of  $221 \text{ m}^2/\text{m}^3$ . The digesters were placed in a controlled temperature room at  $33 \pm 2^\circ\text{C}$  and were continuously fed with peristaltic pumps, in an upflow mode for the UASB and a downflow mode for the fixed film reactor. Biogas was evacuated at the top of the columns and directed to a gas meter device filled with an acidified brine ( $\text{pH} < 4$ ) to avoid  $\text{CO}_2$  dissolution.

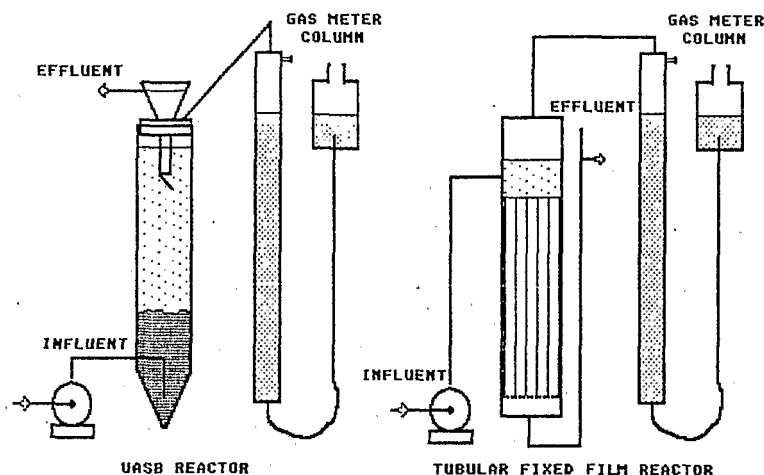


Fig. 1. Schematic diagram of the laboratory reactors.

#### Inoculum.

2 sludges from different sources were used as seed in the case of the UASB digesters in order to assess any limitations owing to the kind of inoculum. The seed for UASB T was obtained from an anaerobic stabilization pond receiving waste sludge from the aerobic wastewater treatment system of a PTA plant. The seed for reactor U was an anaerobically adapted activated sludge from the conventional wastewater treatment plant of the National University campus at Mexico City. The fixed film reactor had been used during a previous experiment (Monroy *et al.*, 1988) and had already developed a biofilm on its tubular packing from the same kind of inoculum used for UASB U.

#### Wastewater Characteristics.

The effluent employed in this study was sampled on a weekly basis at the entrance of the first aeration basin of a PTA production wastewater treatment plant. The effluent had already passed through an equalization basin with several days hydraulic retention time and had been supplemented with nitrogen and phosphorus. During the experiment, the wastewater was kept at  $6^\circ\text{C}$ . Raw effluent analysis is given in Table 1 together with the main aromatic compounds found in the mother liquor of the purification unit, which is one of the major wastewater constituents. The raw wastewater had a high content of fast settling suspended solids, so it was decided to feed the reactors with primary settled wastewater. Sedimentation was performed directly in the containers used for effluent transport at the temperature of storage. The pH of decanted wastewater was then adjusted to 6.15 (standard deviation ( $s$ )=0.22); an average of 3.15 g ( $s$ =1) industrial  $\text{NaHCO}_3$  was necessary for one liter of effluent. A characterization of the settled, neutralized influent is presented in Table 2. The values correspond to an average calculated over the 7 and half months of the experiment.

TABLE 1 Characteristics of Raw Wastewater.

Parameter	Concentration
Raw wastewater	
pH	4.5
COD	9500 mg/l
BOD <sub>5</sub>	5500 mg/l
TSS	2200 mg/l
Acetic acid	500-1000 mg/l
Mother liquor (*)	
Terephthalic acid	2670 mg/l
p-toluic acid	480 mg/l
Benzoic acid	354 mg/l
4-formylbenzoic acid	20 mg/l

(\*) Supernatant after 10 min sedimentation.

TABLE 2 Characteristics of Neutralized, Settled Influent.

Parameter	Concentration		
	mean (mg/l)	n	s
Total COD	6477	75	941
Soluble COD	5958	50	836
TS	6644	31	1674
TVS	3459	31	1551
TSS	704	32	413
VSS	406	30	287
N-NH <sub>4</sub> <sup>+</sup>	93.2	27	39.3
Alkalinity (as CaCO <sub>3</sub> )	1777	62	619

(\*) n = number of samples; s = standard deviation.

#### Start-Up and Operation.

Each UASB received 1 litre of wastewater, 1 litre of tap water and 1 litre of sludge. Feeding with raw wastewater resulted in pump clogging problems, so continuous operation could only begin one month later, when primary settled wastewater was used. Then, 3 hydraulic retention times ( $\theta$ ) were tested for UASB digesters: 7 days (day 0-108), 3 days (day 109-134), and 2 days (day 135-194). The fixed film reactor was drained of its previous contents and filled with settled wastewater and tap water in equal proportions. Continuous feeding started immediately, with a  $\theta$  of 10 days in order to initiate sludge acclimatization. Two other  $\theta$  were applied, 5.8 days from day 21 to 87 and 3.4 days from day 88 to day 164. An additional  $\theta$  of 2.9 days was maintained for the two last weeks.

#### Analytical Procedures.

Total and soluble COD; Biochemical Oxygen Demand (BOD<sub>5</sub>); Total, Fixed and Volatile Solids (TS, TFS, TVS); Total, Fixed and Volatile Suspended Solids (TSS, FSS, VSS); pH; alkalinity to pH 4.3 and ammonium nitrogen were determined as indicated in *Standard Methods* (APHA, 1980). Total COD, pH and alkalinity were measured twice a week. Soluble COD, TS, TFS, TVS, TSS, FSS, VSS, N-NH<sub>4</sub><sup>+</sup> were measured once a week. BOD<sub>5</sub> was analysed 3 times during steady state periods. The atomic absorption spectrophotometer

(Varian spect AA-20) was used to determine heavy metals and Na, K, Mg and Ca. The samples for atomic absorption spectrophotometry were prepared according to *Standard Methods* (APHA, 1980). The Sludge Volume Index (SVI) was adapted from the usual technique (APHA, 1980): in a 100 ml test tube, 25 ml of reactor sludge were diluted with 75 ml of settled effluent; after mixing, the 30 min settled sludge volume was determined and the SVI was obtained dividing this value by the TSS content of the 25 ml sludge. A maximum settling velocity was calculated with the steepest slope of the settling curve obtained during SVI determination. With the experimental conditions employed this velocity corresponds to a hindered settling velocity (V<sub>iii</sub>). The size of granules was estimated with the method described by Mahoney *et al.* (1987). Counts of anaerobic bacteria were performed using the Most Probable Number (MPN) technique with 5 tubes per dilution (Guyot *et al.*, 1990 a). Cultivation media and the inoculation techniques were that of Hungate (1969) and Balch *et al.* (1979). Gas production was obtained by water displacement and methane content was measured by gas chromatography using a thermal conductivity detector (Noyola *et al.*, 1988).

## RESULTS AND DISCUSSION

### Effect of Decantation on Effluent Characteristics.

Under the primary settling conditions (pH 4.5, 6°C, batch mode), TSS and COD removal efficiencies were 70% and 37% respectively (Tables 1 and 2). The solubility of terephthalic acid in water (19 mg/l, 25°C) and its specific gravity (1.5) indicate that this compound should be almost eliminated as a settled solid during the operation. Xu *et al.* (1988) showed that terephthalic acid (pK<sub>1</sub> = 3.51; pK<sub>2</sub> = 4.46) can be separated from a PTA alkaline wastewater by acidification-flocculation-sedimentation. Actually, precipitation of PTA starts at pH 5.1, is almost complete at pH 4.5 and is entirely finished at pH 3.8. When applied to a PTA wastewater containing an amount of terephthalic acid similar to our case, the acidification (pH < 4, 23-26°C) -flocculation-sedimentation process produced an effluent with 41 mg/l of PTA. Nevertheless, acidification without flocculation produces PTA particles with a diameter of about 5 µm, negatively charged and difficult to separate by sedimentation (Xu *et al.*, 1988). Thus, in our study, a significant fraction of initial PTA should remain in a near colloidal form, measured as part of the influent VSS (Table 2). The other aromatic compounds found in PTA plant effluent are soluble in water at the concentration reported in Table 1 and they should not be affected.

### Reactor Performance.

The principal results of steady state operation for the three reactors at each  $\theta$  tested are summarized in Table 3. At around 7 days hydraulic retention time, only one month of continuous feeding was necessary for UASB start-up, but the COD removal efficiencies of both reactors were low (Table 3).

TABLE 3 Characterization of the Steady State Periods for Each Reactor.

Parameters	UASB T	UASB U	TFF	UASB T	UASB U	TFF	UASB T	UASB U	TFF
Days of operation	30-108	30-108	21-87	109-134	109-134	88-164	135-194	135-194	165-178
Hydraulic retention time (d)	6.8	6.9	5.8	2.7	3.2	3.4	2.0	2.2	2.9
Organic load (kg COD/m <sup>3</sup> d)	0.9	1.0	1.08	2.6	2.2	1.89	3.2	2.8	2.1
Organic specific load (*)	0.1	0.16	0.05	0.29	0.38	0.09	0.36	0.49	0.1
Surface load (g COD/m <sup>2</sup> d)	-	-	4.78	-	-	8.4	-	-	9.98
E% Total COD	33.8	23.3	77.4	46.4	43.9	74.5	37	38.3	73.24
E% Soluble COD	32.2	23.1	77.5	47.7	44	73	33.8	34.6	74.8
E% TSS	24.7	23.1	27.3	25	n.d.	33	13.1	18.9	n.d.
E% VSS	20.7	23.5	24	17.1	14.7	n.d.	n.d.	n.d.	n.d.
Gas production (Nm <sup>3</sup> /m <sup>3</sup> d)	0.17	0.13	0.47	0.47	0.35	0.63	0.45	0.4	0.67
CH <sub>4</sub> %	59.6	57.7	62	60.6	63.1	n.d.	50.2	52.9	n.d.
CH <sub>4</sub> yield (Nm <sup>3</sup> /kgCODrem)	0.32	0.35	0.34	0.23	0.23	n.d.	0.19	0.19	n.d.
Specific activity (*)	0.036	0.039	0.039	0.136	0.165	0.066	0.134	0.186	0.073
Effluent pH	7.6	7.6	8.5	7.5	7.5	8.1	7.4	7.4	7.86
Sludge pH	7.15	7.2	-	7.2	7.2	-	7.05	7.08	-

Note: TFF = Tubular Fixed Film Reactor; n.d. = not determined.

(\*) Organic specific load in kg COD/kg VSS-d and Specific activity in kg COD rem/kg VSS-d

In order to allow for sludge adaptation, the same  $\theta$  was maintained till day 108, but no improvement could be obtained (Table 3). Another explanation for the low COD removal efficiencies could be a deficiency in some trace metals necessary for methanogenic bacteria as it is often the case with industrial effluents (Speece, 1983). To test this hypothesis, from day 82 to day 122, a mixture of metals (Table 4) was added to the digester influent, but no amelioration was observed. The period of test, corresponding to 8  $\theta$  values, was considered long enough. As a consequence, the metal addition was stopped. Analysis of trace nutrients was performed on a sample of settled wastewater. The results presented in Table 5 confirmed that there was no limitation due to these compounds. The particularly high content of cobalt and manganese is explained by the use of Co and Mn acetate as catalysts in the process of terephthalic acid production.

TABLE 4 Composition of Trace Metal Solution Added to the Wastewater During Days 82 to 122 (\*).

compound	concentration in the cocktail g/l	concentration in the wastewater mg/l
ZnCl <sub>2</sub> . 4H <sub>2</sub> O	1	0.48 (as Zn)
MnCl <sub>2</sub> . 4H <sub>2</sub> O	1	0.28 (as Mn)
CoCl <sub>2</sub> . 6H <sub>2</sub> O	1	0.25 (as Co)
MgCl <sub>2</sub> . 6H <sub>2</sub> O	100	11.96 (as Mg)
NiCl <sub>2</sub> . 6H <sub>2</sub> O	0.2	0.05 (as Ni)
CuCl <sub>2</sub> . 2H <sub>2</sub> O	0.05	0.019 (as Cu)
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> . 4H <sub>2</sub> O	10	5.4 (as Mo)

(\*) Each compound was dissolved in a separate solution and 1 ml of each solution was added to 1 litre of influent.

TABLE 5 Inorganic Composition of Settled Terephthalic Acid Plant Wastewater.

Compound	Na	Mn	K	Co	Fe (*)	Ca	Pb	Zn	Mo	Cu	Cd	Mg	Ni
Concentration mg/l	430	75.6	60	56.6	13.3	12.4	11.3	4.76	4.66	3.33	1	0.86	0.26

(\*) Includes all oxidation states.

Over this first period of operation (day 30 to 108), UASB T presented a better behaviour than UASB U: higher COD removal, biogas production and stability. The superiority of reactor T during the first months of operation may be explained by the origin of the inoculum, a higher quantity of seed sludge and better microbial and sedimentation characteristics (Table 6). At lower  $\theta$  (3 and 2 days), UASB reactors achieved better COD removal efficiencies than at 7 days. However the improvement was limited only to 46% in the best case for UASB T at a  $\theta$  of 2.7 days. It seems that higher upflow velocities and gas production rates led to better sludge bed mixing and improved mass transfer, so better COD removal efficiencies were obtained at lower  $\theta$  or higher organic loads. The difference in UASB performance, observed during the first period, tended to disappear as similar removal efficiencies were achieved for the rest of the study. This behaviour was the result of sludge evolution, as may be noticed in Table 6. At the end of the experimental work, sludges U and T presented good similar settling characteristics (SVI, VIII), but their MPN counts were different: sludge U maintained its hydrogenophilic methanogen counts while they decreased in sludge T; acetoclastic methanogenic bacteria remained at the same level, and propionate and butyrate users decreased. In addition, granule size was very small for both reactors indicating that PTA wastewater does not favour granule formation. Results in Table 6 show that at the end of the study, sludge U had better microbial characteristics than sludge T, which was supposed adapted to some extent to the wastewater. As a consequence, aerobic sludge from municipal treatment plants, once it has been adapted anaerobically, may be considered as a good inoculum alternative

when granular sludge or anaerobic digested sludge are not available. A similar observation was made by Wu *et al.* (1987) with different industrial wastewaters.

TABLE 6. Characteristics of UASB Sludges at the Beginning and at the End of the Study (\*).

	UASB T	UASB T	UASB U	UASB U
Day of operation	0	194	0	194
TSS g/l	42.3 (100%)	57.4 (100%)	26 (100%)	56.3 (100%)
FSS g/l	16.1 (38%)	26.9 (46.9%)	8.6 (33%)	29.9 (53%)
VSS g/l	26.2 (62%)	30.5 (53.1%)	17.4 (67%)	26.4 (47%)
g VSS/reactor	26.2	26.2	17.4	11.4
SVI ml/g	33.3	29.9	86.8	26.2
Viii m/h	1.8	3.2	0.84	3.47
Granule size mm	n.d.	0.31 (s = 0.39)	n.d.	0.22 (s = 0.23)
Bacterial Counts (bacteria/g VSS)				
Hydrogenophilic methanogens	7.7 E10	4.9 E7	3.7 E10	9.4 E10
Acetoclastic methanogens	3.1 E8	4.9 E8	5.0 E8	4.7 E8
Propionate users	2.8 E9	< 3.9 E6	5.8 E8	8.4 E7
Butyrate users	1.5 E9	< 3.9 E6	n.d.	7.5 E7

(\*): s: standard deviation; Ex = 10<sup>x</sup>; n.d: not determined.

Start up of the fixed film reactor was longer than that of the UASB digesters. Biogas production began on day 38 but a stable production and a stable COD removal required 73 days to establish. This long adaptation period is not surprising since the tubular reactor had already formed a biofilm during a previous study (Monroy *et al.*, 1988) with acetate and propionate as substrate. These feeding conditions selected a particular microflora, which had to adapt again to the new wastewater containing recalcitrant compounds. Nevertheless, the COD removal efficiency (77.4%) and the biogas production (0.46 m<sup>3</sup>/m<sup>3</sup>·d) obtained during the first steady state (day 73 to 87) were much higher than those reached by the two UASB reactors (Table 3). In the second steady state ( $\theta = 3.4$  days) COD removal efficiency (74.5%) stayed close to the previous value. When  $\theta$  was again reduced on day 165 to 2.9 days, the COD removal efficiency decreased slightly (Fig. 2). Unfortunately, wastewater supply stopped and the steady state was not fully characterized. Nevertheless,  $\theta$  may well be shorter than three days without a sharp drop in COD removal efficiency. The UASB and the fixed film reactor response to shock loads and to periods without feeding are reported elsewhere (Guyot *et al.*, 1990 b; Noyola *et al.*, 1990). All these results show that the fixed film reactor was much more efficient to treat PTA effluent than UASB reactors, as indicated in Fig 2.

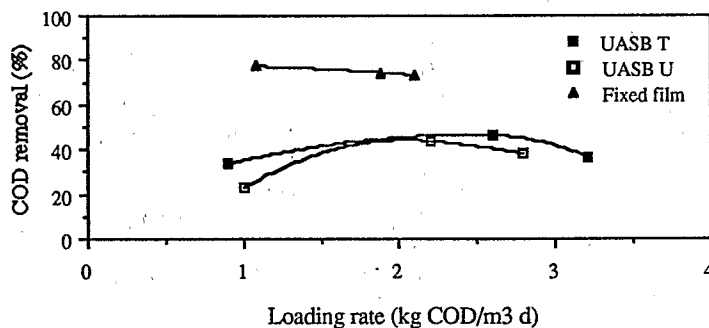


Fig. 2. COD removal efficiencies for each reactor versus applied organic load.

### Reasons for Superiority of Fixed Film Reactor over UASB Reactors When Treating PTA Plant Effluent.

Several facts can explain this result.

**VSS content and mass transfer.** At the end of experimentation, the VSS content of the fixed film reactor (100.2 g) was much higher than that of the UASB (Table 6). Fixed film reactor VSS content was estimated by subtracting its drained volume (2.5 l) from its void volume (4.75 l) and applying a film density of 0.116 kg VSS/m<sup>2</sup> for a 2.6 mm biofilm thickness (Van den Berg and Lentz, 1980). Thus, when similar loading rates (kg COD/m<sup>3</sup>·d) were applied to each digester, the organic specific loads (kg COD/kg VSS·d) were lower in the case of the fixed film reactor (Table 3). However, even when the same organic specific load was applied, the tubular reactor had a better behaviour. For instance, at 0.09 kg COD/kg VSS·d, its COD removal efficiency was 74.5% (day 145-164) while at 0.1 kg COD/kg VSS·d (day 30-108), the COD removal efficiency of UASB T was only 33.8% (Table 3). This indicates that mass transfer phenomena might have been of importance. In the downflow fixed film digester, the tubular packing favors an homogeneous distribution of wastewater and practically all the biofilm surface is in contact with the substrate. Moreover, the biogas bubbles on their way up along the tubes create perturbations which may increase the liquid-solid transfer. On the contrary, the biogas production of UASB reactors was not sufficient to create by itself an adequate biomass-substrate contact in the sludge and so, only a fraction of the bed was really active and could contribute to COD removal.

**Biomass distribution and resistance to toxic compounds.** As discussed previously, residual terephthalic acid is still present after primary settling in the form of near colloidal VSS. In order to assess its biodegradability, an anaerobic test was run in serum bottles during 70 days. The inoculum used for the test was sludge T, diluted to 20% (v/v) with a mineral medium (Balch *et al.*, 1979). The experiment showed that settled wastewater (0.56 g COD/g VSS) as well as terephthalic acid (0.183 g/g VSS), inhibited biogas production with respect to a control containing the same amount of sludge but without substrate (Fig. 3).

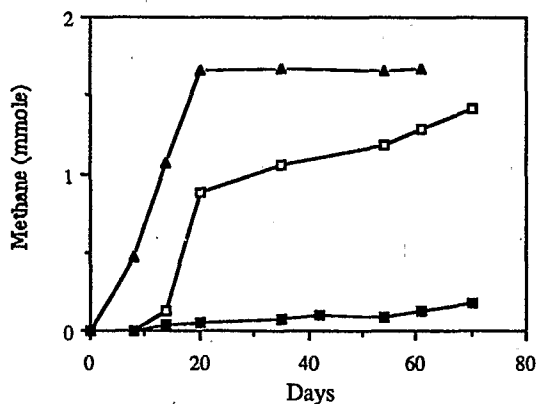


Fig. 3. Cumulative methane production of batch cultures in serum bottles containing sludge (0.6 g VSS) (control; ▲), sludge and settled wastewater (0.56 g COD/g VSS) (□), sludge and terephthalic acid (0.183 g/g VSS) (■).

In the fixed film reactor design, the biomass is distributed all along the column, whereas for the UASB, the biomass is located at the bottom. The presence of toxic compounds in the wastewater under the form of suspended solids would affect more the UASB reactors because the TSS could accumulate into the sludge bed and inhibit it, while the upper part of the tubular reactor biofilm would be untouched and active. In addition, the downflow operation of the fixed film digester would allow a continuous wash out of the settled TSS. On this subject, it has been shown in batch conditions that dimethyl terephthalate plant wastewater is toxic for methanogenic bacteria even at a moderate concentration. Only 10% waste or less could be tolerated for growth



and methane production (DiTommaso and Elkan, 1973). In the Grontmij report (1980), this inhibition was explained by the presence of formaldehyde in the effluent.

Scanning electron microscopic observations of sludge sampled on day 169 from UASB T and U showed precipitates entrapped in the granules (Fig. 4) which supports the hypothesis of a possible UASB inhibition by settled VSS. From the TSS and VSS removal efficiencies of UASB reactors (Table 3), it can be estimated that 30 g TSS and 7 g VSS were eliminated by UASB U and that 20 g TSS and 7 g VSS were eliminated by UASB T during the entire operation period. Part of these TSS and VSS could have been removed by simple physical means, the upflow velocities in the UASB reactors being very small (0.25-0.9 cm/h). The methane yields of the 2 last steady states were well under the theoretical value (0.35 m<sup>3</sup> CH<sub>4</sub>/kg COD) (Table 3), indicating that not all the COD removed was actually biodegraded.

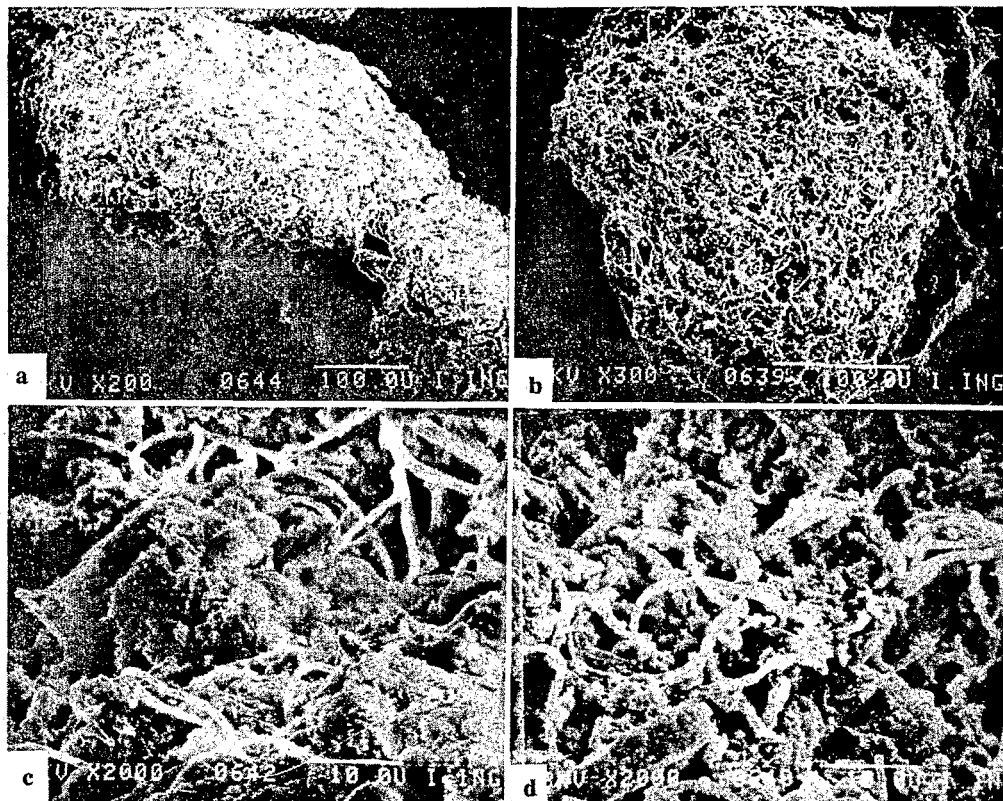


Fig. 4. Scanning electron micrographs of UASB reactor granular sludge. (a) Entire granule from UASB T. (b) Same for UASB U. (c) Detail showing precipitates entrapped in a granule from UASB T. (d) Same for UASB U.

Moreover, it must be considered that resistance to aromatic toxicity may be greater when bacteria are fixed on a support. Dwyer *et al.* (1986) showed that a consortium composed of a phenol oxidizing bacteria, a *Methanotrix*-like bacteria and an H<sub>2</sub>-utilizing methanogen could tolerate higher concentrations of phenol when immobilized in agar than in the form of suspended cells.

#### Process Integration for PTA Wastewater Treatment.

Anaerobic treatment of industrial wastewater is a very effective pretreatment process but, in order to comply with discharge standards, a secondary wastewater treatment is usually needed.

In previous work (Noyola *et al.*, 1990) a system consisting of primary settling, anaerobic fixed film reactor and aerobic treatment was proposed for PTA wastewater treatment. This approach was also taken by a research team in China, from laboratory work to a real scale plant, which is now under start-up (Yang, 1991); the plant will treat 8400 m<sup>3</sup>/d discharged by a PTA factory. The treatment system, primary settling, hybrid anaerobic reactor and fixed media activated sludge achieves 95% COD removal with a  $\theta$  of 40 hours. The anaerobic reactor reaches 70% COD removal, 0.4-0.6 m<sup>3</sup> biogas/kg COD removed with an organic load of 8 kg COD/m<sup>3</sup>-d and 37°C (Yang, 1991).

The higher performance obtained in that work supports our observation that a higher organic load could have been treated by the downflow fixed film reactor (Fig. 2). Nevertheless, our results clearly showed that the UASB reactor was inhibited, which was not the case in the Chinese work. In fact, that study compared UASB, anaerobic filter and hybrid reactors, and the conclusion was that all performed in a similar manner (Yang, 1991). At the moment, we do not know the details of that research work, and an explanation of the differences encountered cannot be proposed. However, the sludge blanket of the hybrid reactor may eventually be inhibited by the toxic VSS that are not retained in the primary settler. The process proposed by the Chinese group has been recently protected by a patent (Yang, 1990).

Apparently, Ely and Olsen (1989) investigated a different approach for Amoco Corporation. Like in our study, they used an anaerobic downflow filter followed by an optional aerobic treatment, but instead of a primary decantation to avoid the precipitation of fast settling, poorly soluble aromatic acids in the filter, they increased the solubility of these aromatics by the addition of NaOH to the reactor influent. Caustic soda raises the wastewater pH, moving the acid-base equilibrium of the aromatics towards the more soluble deprotonated forms. The solubility of terephthalic acid in water is 19 mg/l at 25 °C against 140 g/l at 25 °C for its disodium salt.

In the integrated process suggested in the present paper, some points should also be considered:

Disposal of primary settled solids. The solids are mainly organic (92% W/W) and an analysis performed by a private laboratory showed that at least 40% was terephthalic acid. It is not the purpose of this work to discuss the disposal of that solid waste, but their characteristics may suggest that either PTA should be recovered or disposed of directly in an industrial landfill, due to the expected low biodegradability. Nevertheless, PTA precipitation under acidic pH seems to be used in Asia for its recovery from PTA production wastewater or polyester fiber wastewaters (Motojima *et al.*, 1986; Tan *et al.*, 1986; Yang *et al.*, 1989).

Consumption of chemicals for settled wastewater neutralization. The study was realized in controlled conditions of wastewater pH and alkalinity, but the quantity of NaHCO<sub>3</sub> needed was high, 3.15 g/l, which is not economically feasible at real scale. The capacity of anaerobic sludges to generate their own alkalinity and to adapt to treat unneutralized or partially neutralized acidic effluents is a well known phenomena (Brune *et al.*, 1982; Nel and Britz, 1986; Moreno *et al.* 1990). In our case, at the beginning of the study, an attempt to start-up the UASB reactors with unneutralized settled wastewater failed due to sludge acidification. Moreover, as indicated by Figure 5, when fed with neutralized influent, the fixed film reactor which presented the best behaviour, produced little alkalinity, 1174 mg CaCO<sub>3</sub>/l during the first steady state (day 73-87), and 1136 mg CaCO<sub>3</sub>/l during the second (day 145-164).

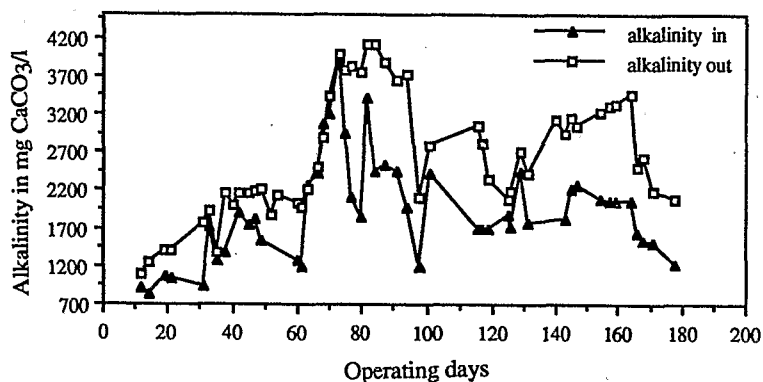


Fig.5 Evolution of influent and effluent alkalinity during the operation of the fixed film reactor.

The use of other neutralization agents, CaO, NaOH, Na<sub>2</sub>CO<sub>3</sub>, may lower the cost of neutralization. Other technical alternatives to reduce the requirement for neutralization chemicals consist of applying high effluent recycle to the reactor in order to take advantage of the effluent buffer capacity (Witt *et al.*, 1980; Ferguson *et al.*, 1984). Moreover, gas stripping to reduce CO<sub>2</sub> in the recycle stream can also decrease base addition and recycle ratios (Ferguson *et al.*, 1984). All these alternatives would have to be studied at laboratory scale to determine if neutralization of PTA wastewater for anaerobic treatment can be realized at an economical level. Effluent recycle and CO<sub>2</sub> stripping were also retained in Amoco patent (Ely and Olsen, 1989) to decrease caustic soda requirements for aromatic acids dissolution. In contrast, primary settling, which eliminates insoluble aromatics, reduces chemicals consumption for reactor influent neutralization and should be more economical on this point.

### CONCLUSION

A lab scale arrangement consisting of a static primary sedimentation of PTA raw wastewater, followed by an anaerobic treatment of the settled wastewater with a downflow fixed film reactor gave an overall reduction of 84% in COD and 80% in TSS for an hydraulic retention time of 3.4 days.

The use of UASB reactors for the biological step was not successful. This failure is mostly explained by sludge inhibition caused by toxic characteristics of the wastewater. The tubular reactor was not affected because of its different biomass distribution and its higher VSS content. Each reactor presented good resistance to shock loads and periods without feeding.

Anaerobically adapted aerobic activated sludge was a good inoculum for seeding the anaerobic reactors and may be recommended when granular or anaerobic digester sludges are not available.

These results indicate that the arrangement proposed is a good alternative to the conventional aerobic process used to treat PTA effluent. Nevertheless, two major problems have to be studied before applying this system: disposal of primary settled solids and reduction in chemical consumption for effluent neutralization.

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