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ANAEROBIC TREATMENT OF POLYETHYLENE TEREPHTHALATE (PET) WASTEWATER FROM LAB TO FULL SCALE

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ABSTRACT

In the last decade Polyethylene Terephthalate (PET) production is growing. The wastewater of the "Catalana de Polimers" factory in Barcelona (Spain) has two main streams of similar flow rate, esterification (COD=30,000 mg/l) and textile (COD=4000 mg/l). In order to assess the anaerobic treatment viability, discontinuous and continuous experiments were carried out. Discontinuous biodegradability tests indicated that anaerobic biodegradability was 90 and 75% for esterification and textile wastewater. The textile stream revealed some tendency to foam formation and inhibitory effects. Nutrients, micronutrients and alkali limitations and dosage were determined.

A continuous lab-scale UASB reactor was able to treat a mixture of 50% (v) esterification/textile wastewater with stable behaviour at organic loading rate larger than 12 g COD/l.d (0.3 g COD/g VSS.d) with COD removal efficiency greater than 90%. The start-up period was very short and the recuperation after overloading accidents was quite fast, in spite of the wash-out of solids. From the laboratory information an industrial treatment plant was designed and built, during the start-up period COD removal efficiencies larger than 90% and organic loading rate of 0.6 kg COD/kg VSS.d (5 kg COD/m^3.d) have been reached. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved.

KEYWORDS

Anaerobic treatment; industrial UASB; industrial wastewater; PET; Polyethylene terephthalate; viability.

INTRODUCTION

The industrial applications of the anaerobic technology have been limited to the treatment of food and beverage wastewater. Anaerobic microorganisms are commonly perceived as sensitive to the toxicity of many chemical pollutants, nevertheless at least 50 anaerobic digestors distributed world-wide are operating treating chemical and petrochemical wastewater (Macarie, 1996).

Polyethylene terephthalate (PET) has an increasing commercial importance. Besides the more traditional polyester fibre production, PET is taking the place of polyvinyl chloride (PVC) in many applications, mainly in bottles for spring water. The process using direct esterification of terephthalic acid (TPA) with ethylene glycol has gained acceptance because of the greater availability of highly purified TPA (Considine, 1974).

The first step is the preparation of the intermediate diester, bishydroxyethyl terephthalate (bisHET), also called prepolymer, under conditions of an excess of glycol (1.2-1.5 mole/mole), high temperature (200–250°C) and pressure (2–10 atm). The water produced may be distilled off under these conditions with minimum loss of glycol, (B_p = 197°C at atmospheric pressure). In the second step the prepolymer is exposed to conditions which will lead to polycondensation by raising the temperature to about 280°C while simultaneously reducing the pressure to 0.5–1 mm Hg. Ethylene glycol is distilled off under these conditions of temperature and pressure. When the desired molecular weight is reached, PET is discharged into cold water to quench it and then passed to a dicer or granulator, or it is transferred while still molten directly to the spinning unit. In line with this fabrication scheme, esterification wastewater will be mainly composed of non reacted raw materials, mainly ethyleneglycol, and products of secondary or degradation reactions, being terephthalic acid esters, methanol, acetaldehyde and crotonaldehyde being the most significant (Chang *et al*, 1993 and Ullmann, 1997).

In factories producing polyester fibre it is common to find a second stream of wastewater. The basic process for making polyester fibres is called melt spinning. An extruder accepts dried chips of PET and melts them, the molten polymer flows through a spinnerette provided with holes of diameters varying from 0.1 to 1 mm. On emerging from the spinnerette the filaments are cooled and solidify. In order to improve the physical characteristics of the fibre a bath with different chemicals and commercial unknown formulation is used. Remains of this bath are present in the textile wastewater.

Reviewing the literature related with biological treatment of materials and by-products involved in PET synthesis, some interesting information is founded. Fajardo *et al.* (1997) concluded that is possible to treat anaerobically the easily biodegradable compounds (acetic, benzoic and formic acids) as they would not be significantly inhibited by terephthalic acid (TPA). Kleerebezem *et al.* (1997) found that for a lab-scale UASB reactor neutralised terephthalic acid (disodium terephthalate) could be degraded at a loading rates of 4.5 g COD/l.d and hydraulic retention time of 24 h. Ramakrishna and Desai (1997) using "biomass support particles" (BSP), treated wastewater from a dimethyl terephthalate plant with 95% COD removal at organic loading rate as high as 20 g COD/l.d. without feed neutralization. Ejlertsson *et al.* (1996) assured the complete degradation of diethyl phthalate and phthalic acid in diluted and homogenised solid waste treated in a biogas digestor. Brackin *et al.* (1996) using fluidized bed technology with a loading rate of 5 g COD/L.d. removed 98% of the COD of an industrial wastestream that contained maleic, fumaric and phthalic acids and di-n-butylphthalate. Stewart *et al.* (1995) studied the anaerobic treatability of some organic toxicants in petrochemical wastes. Ethylene glycol was found to be degraded to less than 5 mg/l with spikes up to 10,000 mg/l. Higher concentrations led to pH inhibition even with a design initial bicarbonate alkalinity of 6,000 mg/l as $CaCO_3$. Nitschke *et al.* (1996) proved that wastewater containing diethylene glycol, used as de-icing agent at many airports during winter time, may cause severe disturbances in conventional sewage plants. Horng *et al.* (1997) concluded that the addition of 7% of hydrolyzed aerobic sludge to the effluent of a PET industry increases the anaerobic sludge activity and promotes anaerobic sludge granulation.

To study the feasibility of the anaerobic treatment of the wastewater produced by "Catalana de Polimers", PET factory, in Barcelona and in accordance with the background, the objectives of the research were (1) to determine the anaerobic biodegradability of the two main wastestreams of the PET process, (2) to generate information about the operational problems of a continuous reactor, (3) to determine the design parameters for an industrial facility, (4) to establish the needs of alkali, nutrients, micronutrients and other additives.

MATERIALS AND METHODS

The biodegradability tests measuring the CH_4 accumulated production were carried out in shacked flasks of 500 ml provided with a septum in order to take liquid samples (Vallecillo *et al.*, 1998). Granulated anaerobic sludge (SSV/SST=0.7) from an industrial UASB reactor treating beer wastewater was used. Experimental conditions were: reactor volume=500 ml; T=32°C; sludge concentration=4.6 g/l; sludge methanogenic activity >0.7 gCOD/gVSS.d. Initial conditions: COD_{sol}=2915 mg/l; pH=7.45.

The UASB reactor (Figure 1) is a Plexiglas column 6 cm of internal diameter equipped with a gas collector. The reactor was filled with 1 litre of quite mineralized sludge from a beet-sugar factory. The characteristics

of the sludge were: Mean diameter=200-270 μm; TSS=246 g/l; VSS=40 g/l. Temperature was maintained at 32±1°C. Nutrients and micronutrients were supplied to avoid any nutritional limitation. The feed and recirculation peristaltic pumps were controlled following the lecture of the liquid flow meters (FI)

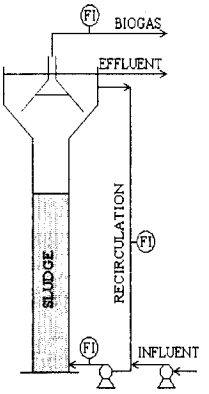

Figure 1. Schematic layout of lab-scale continuous UASB reactor.

Analytical determinations were performed according to *Standard Methods (APHA, 1995).*

RESULTS AND DISCUSSION

Wastewater characteristics

According to the PET fabrication process presented in the Introduction section, two main wastewater streams are identified, esterification and textile wastewater. Both of them have similar flow rate that, for the Catalana de Polimers production, are in the order of 100 $m^3.d^{-1}$. To define the real situation, average, maximum and minimum values of the organic load parameters, for more than 20 significant samples, are shown in Table 1. The suspended solids concentration is negligible. N-NKT, $N\text{-}NH_4$ and $P\text{-}PO_4^{-3}$ concentrations are less than 2 mg/l.

Table 1. Organic load characteristics of esterification and textile wastewater

	Esterification (mg/l)					Textile (mg/l)				
	COD	TOC	BOD	TOC/COD	BOD/COD	COD	TOC	BOD	TOC/COD	BOD/COD
Maximum	33620	11045	25500			3490	850	1380		
Minimum	21520	6210	15000			2500	635	670		
Average	26820	8335	19520	0.31	0.72	2770	705	925	0.25	0.33

The main practical information derived from the experimental results is related to organic load fluctuations and aerobic biodegradability. To minimize influent COD variation providing constant organic loading rate, enough volume of homogenization tanks must be considered. For aerobic conditions the ratio BOD_5/COD clearly indicates that esterification wastewater is easily biodegradable, while the textile stream is few biodegradable. For both streams the macronutrients (N, P) deficiency is obvious.

Neutralization

The esterification wastewater has a very constant and low pH (pH = 3.5). As the stream comes from a distillation process, being practically sterile, the origin of this low pH can be found in its chemical composition and not in the presence of intermediate products of biological degradation (VFA). Figure 2 shows the pH evolution of a 50 ml sample when adding NaOH 0.12 N. To reach a neutral pH, it is necessary to add 0.7 kg $NaOH/m^3$ with a neutralization operation cost of 0.2 US $\$/m^3$.

Desorption of volatile compounds

To verify the presence of volatile degradation compounds generated during the chemical process of esterification, a desorption experiment was performed. At atmospheric pressure a container filled with esterification wastewater was bubbled with nitrogen. The COD evolution indicates the desorption of volatile compounds (Figure 3). Experimental data showed that more than 10% of soluble COD is easily desorbed in less than 1 hour. These results lead to the need to cover the homogeneization tanks in full scale plants.

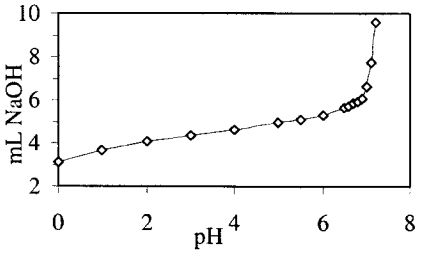

Figure 2. Neutralization of the esterification wastewater (NaOH 0.12 N).

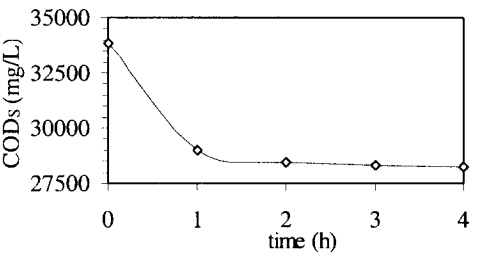

Figure 3. Desorption of volatile compounds.

Nutrients and micronutrients

Taking into account the origin and the very low concentration of N and P in the wastewater the addition of ammonia and phosphate in the industrial plant must be considered. Biodegradability tests performed without addition of N and P showed almost negligible biodegradability, confirming the nutrient limitation. All the subsequent experiments were performed after dosing enough ammonia and phosphate.

To exclude micronutrients limitation a standard solution must be dosed.

Biodegradability tests

Esterification wastewater

Figure 4 shows the evolution of accumulated CH_4 and soluble COD for a typical test with esterification wastewater.

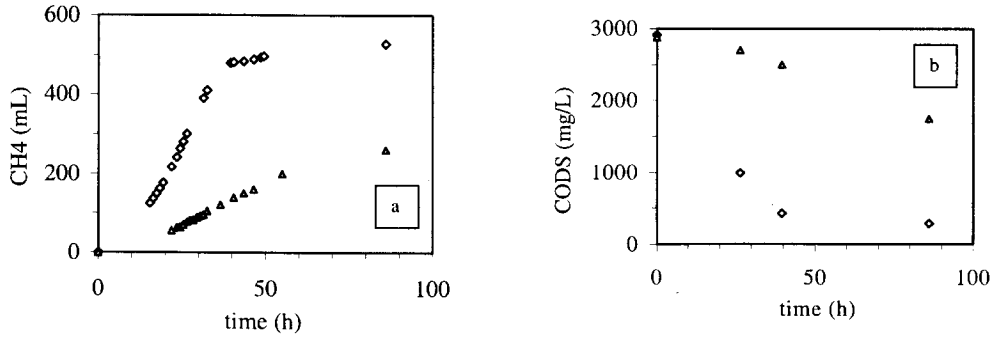

Figure 4. (a) Accumulated methane (b) COD_S time evolution (◊ esterification Δ textile).

The main practical information derived from the test represented in Figure 4 is:

Highly biodegradable wastewater. Anaerobic COD removal >90%.
Maximum specific activity of the sludge 0.45 g COD/g VSS.d.
Specific methane production 0.39 l CH_4 /g COD_{rem}.

A series of activity tests without changing the sludge demonstrated the absence of inhibitory effects. On average, the biodegradability for more than 20 experiments was very high, obtaining soluble COD removal values fluctuating between 80-90%.

Textile wastewater

The experimental behaviour shown by the textile wastewater was clearly different. The main conclusions obtained from the biodegradability tests are:

Biodegradability expressed as soluble COD removal varies between 55-75%.
Maximum specific activity of the sludge < 0.1 g COD/ g VSS.
Specific methane production 0.3 l CH_4/g COD_{rem}.
Sludge disintegration, tendency to inhibition and foam formation.

Continuous UASB lab scale reactor

The lab scale reactor described in the Material and Methods section was used to study the behaviour of (1) esterification stream, (2) 50% (v) mixtures of esterification and textile wastewater.

Period 1

The experimental behaviour appears in Figure 5. During the first time (A in Figure 5) esterification water was diluted 1/10 obtaining an influent with average COD=2325 mg/l. The organic loading rate was increased modifying the dilution rate (B in Figure 5), feed average COD in this period was 6750 mg/l. In the last period (C in Figure 5) a mixture of esterification and textile water with average COD=17,875 mg/l was used.

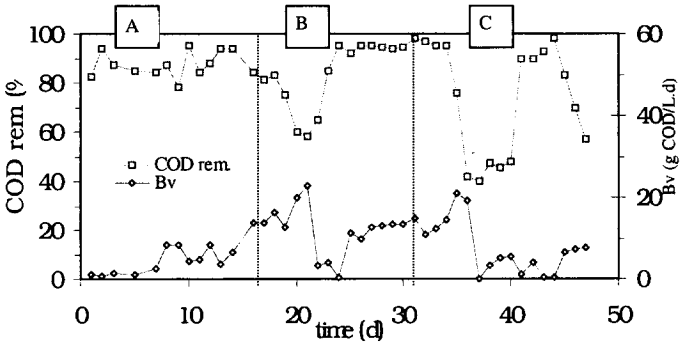

Figure 5. Organic loading rate and COD removal efficiency in a lab-scale UASB reactor.

Remarkable positive aspects are fast start-up, high organic load rate, and fast recuperation after overloading episodes. After only one week of operation it was possible to feed 8 g COD/l.d. (0.2 g COD/g VSS.d.) reaching COD removal efficiencies larger than 85%. In period B, a two days overload of 20 g COD/l.d was followed by a decreasing of the efficiency, but the decrease of the organic loading rate led to the consequent efficiency recuperation. Nevertheless, in period C characterized by the presence of textile wastewater, after four days of stable operation an overloading of 20 g COD/l.d. brought about the complete destabilization of the system, followed by a slow recuperation when the organic loading rate was strongly reduced. In both overloading episodes the VFA concentration increase produced an important pH decrease. The average biogas production was 0.5 l/g COD_{rem} the methane concentration being about 70%. In the final effluent leaving the reactor the concentration of solids was quite high, on average 450 mg TSS/l and 270 mg VSS/l were washed out from the reactor.

Period 2

After inoculation with new sludge a different start-up strategy was tested. Initiating the experiment with diluted esterification wastewater (1/5), the amount of textile wastewater was raised by increasing the ratio textile to esterification volume, until 50% (v/v) of both of them. Figure 6 shows the evolution of the COD

removal efficiency vs. the organic loading rate for the different esterification to textile ratios from 10/0 to 5/5.

If the organic loading rate is controlled avoiding overloading, the stability of the reactor is evident in spite of the influent composition. The increase of the textile wastewater ratio resulted in a decrease of the oxidation-reduction potential (ORP), that moved from –270 mV typical of the esterification stream to –350 mV for the 50% (v/v) influent. The average gas production and concentration was similar in both periods.

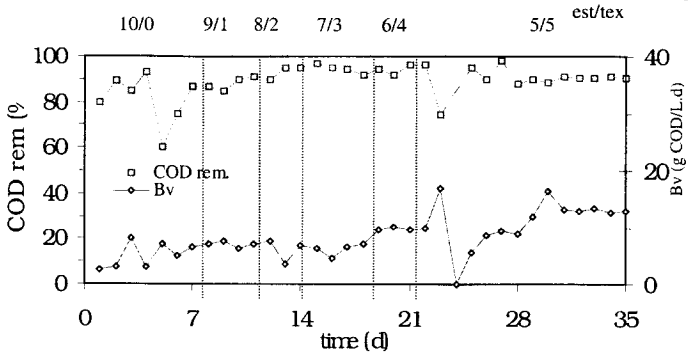

Figure 6. Organic loading rate and COD removal efficiency for different ratios esterification/textile volume.

Laboratory vs. full scale results

One of the problems confronting the designers is that of deducing the most satisfactory arrangement for an industrial unit from experiments with laboratory units. In order to achieve the same kind of flow pattern in two units, geometrical, kinematic and dynamic similarity and identical boundary conditions must be maintained. Geometric similarity prevails between two systems of different sizes if all counterpart length dimensions have a constant ratio. Kinematic similarity exists in two geometrically similar units when the velocities at corresponding points have a constant ratio. Also the paths of the fluid motion must be alike. Dynamic similarity occurs if all corresponding forces at counterpart locations have a constant ratio (Coulson and Richardson, 1990). The kinematic and dynamic characteristics are closely related with the mass transfer process and can affect the physico-chemical and biological behaviour and the global performance of the reactor (Schward *et al.*, 1997).

To quantify some interesting aspects of the scale-up limitations, laboratory and industrial UASB reactors are compared. The main geometric and operation parameters are shown in Table 2. The organic loading rate of both of them is B_v=10 g COD/l.d. and the organic load of the wastewater is COD = 30 g/l.

Table 2. Characteristics of laboratory and full scale reactors.

		Laboratory	Industrial
Length	(L), (m)	0.4	6
Diameter	(D), (m)	0.06	11.3
Area	(A), (m^2)	$2.83x10^{-3}$	100
Volume	(V), (m^3)	$1.13x10^{-3}$	600
L/D		6.66	0.5
Superficial velocity (u_s), (m/h)		$5.54x10^{-3}$	$8.3x10^{-2}$
Recirculation ratio[(1)]	(R)	88	5
Specific gas production or gas velocity ($m^3/m^2.h$)	[(2)]	0.08	1.12

[(1)] u_s=0.5 $m.h^{-1}$. [(2)] COT removed 90%, F_{gas}=0.5 m^3/kg COD_{rem}.

According to the L/D ratio the geometric similarity criterion is evidently violated. The ratio $(L/D)_{FULL}/(L/D)_{LAB}>12$ indicates that reactors are very different from a geometric point of view.

The liquid superficial velocity (u_s) calculated as the quotient (influent flow rate / free cross area), is a hydraulically significant parameter. For both reactors (Table 2) the value of the superficial velocity obtained on the managed influent flow rates is far away from the design recommended values ($0.5<u_s<1.5$ m.h^{-1}). Nevertheless the superficial velocity of the full scale plant is almost twenty times higher than the one of the laboratory reactor. To obtain an adequate liquid up-flow velocity a recirculation stream must join the influent. (Fig. 1). Assuming a constant value of $u_s=0.5$ m.h^{-1}, the ratios recirculation/feed are 88 and 5 for the lab and full scale plants. The differences in possible dilution effects, caused by the recirculation stream, are evident, particularly if any toxics are present in the feed or are generated as degradation products. As a conclusion, data from lab-scale experimentation cannot be directly extrapolated to full-scale design.

An important parameter related with the mixing quality is the specific biogas production per square metre of area or superficial velocity of the gas phase. Even though the gas production per unit volume of reactor is identical for both reactors, the up-flow velocity of gas can be different. Accepting that COD removal efficiency is 90% and biogas production is 0.5 m^3/kg COD_{REM}, the gas up-flow velocities are 0.08 and 1.12 m.h^{-1}. These results indicate that the laboratory reactor is poorly mixed by the gas while in the industrial plant the mixing rate is significant. Even the flow model can change from nearly plug flow to nearly completely mixed. A summary of differences between lab and full scale plants is shown in Table 3.

Table 3. Qualitative comparison between laboratory and industrial UASB reactors (Wastewater COD = 30 g/l)

	Laboratory	Industrial
L/D ratio	+	-
Recirculation ratio	+	-
Feed dilution	+	-
Mixing by biogas	-	+

+ High -Low

Another main difference between research and full scale operation is related with the start-up period. Usually lab reactors are inoculated with big amounts of very active granular sludge leading to very short start-up periods, furthermore the parameter reported in papers is volumetric loading rate (kg COD/m^3.d) instead of mass loading rate (kg COD/kg VSS.d). Many times the inoculation conditions for industrial reactors are not comparable, producing severe troubles during the start time.

Full scale plant

Following the lab-scale experimental results an industrial UASB reactor was built in 1997 by AREMA in the "Catalana de Polimers" factory in Barcelona. The reactor dimensions are 11.5x8.5x6.5 m, it has 6 inlet pipes with holes assuring a perfect influent distribution. The solid-liquid-gas separation is provided by 4 double bells equipped with baffles. The design flow rates were 108 m^3.d^{-1} for the esterification stream (COD =30,000 mg/l) and 96 m^3.d^{-1} for the textile one (4.500 mg/l). The total organic load was 3,700 kg COD.d^{-1}, with organic loading rate of 9.5 kg COD/kg VSS.d based on working volume and 6.3 kg COD/m^3.d assuming the total liquid volume. The reactor was inoculated in April 1997 with anaerobically digested sludge from a domestic sewage treatment plant. This flocculent sludge had low methanogenic activity (< 0.2 g COD/g VSS.d) and bad settling characteristics. After seven months of operation in spite of the mass organic loading rate of 0.4 kg COD/kg VSS.d with COD removal efficiencies larger than 90%, the biomass growth and accumulation was very poor, leading to only 1.5 kg COD/m^3.d of volumetric loading rate. One month after a new inoculation with 40 m^3 of good and active granular sludge (60 g VS/l) the reactor can operate with 0.6 kg COD/kg VSS.d (5 kg COD/m^3.d.) maintaining efficiencies larger than 90%.

CONCLUSIONS

The feasibility of the anaerobic treatment of polyethylene terephthalate (PET) has been proved performing discontinous biodegradabilty tests and operating a lab-scale UASB reactor.

The scale up of the process is mainly limited by the impossibility of maintain geometrical similarity. The important differences in recirculation ratio, feed dilution and mixing effect of biogas must be taken into account for the design.

The start up period of the industrial plant was characterized by the very low growth and accumulation of anaerobic sludge in spite of the good removal efficiencies.

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