

ACIDITY, BIODEGRADABILITY AND SOLIDS LIMITATIONS IN AN ANAEROBIC REACTOR FEED WITH AROMATIC ACIDS AS COD SOURCE

Varela-Fuentes Fernando ^(a), Macarie/Hervé ^(b), Marcelo-Valencia
Roberto ^(a), Ramirez-Aguilar Guillermo ^(a), González-Aleu Francisco J
^(a), Pérez-Vidal Adolfo ^(a)

^(a) Tereftalatos Mexicanos, Predio Buena Vista de Torres, CP 96340, Cosoleacaque
Veracruz, México, ^(b) invited researcher from ORSTOM, France, to Department
Biotecnología, Universidad Autónoma Metropolitana, A.P. 55-532, 09340,
Iztapalapa D.F., México. Email communications to fvarela@petrotemex.com,
herve@xanum.uam.mx

ABSTRACT.

The Terephthalic acid effluents are considered as a difficult to treat stream and this aromatic acid itself has been reported as inhibitory to anaerobic sludge activity. Usually the difficulty is overcome by the use of special reactor designs and/or neutralization reagents. In this work, we focus on clarify the real limitations for anaerobic treatment imposed by acidity, solubility and biodegradability restrictions. Our findings indicate the treatment is not straightforward but possible, particularly if some considerations are taken. The critical control parameters are the reactor pH, and operate at or above a minimum percentage of COD removal. The organic acid solubility is not a limitation.

KEYWORDS

Anaerobic digestion, Terephthalic acid, biodegradability, neutralization, solids, reactor design.

Fonds Documentaire IRD

Cote : B * 21 436 Ex : 1

INTRODUCTION

The Polyester world production has been continually increasing for several decades now, due to the diversity in applications for this thermoplastic. The Monomers for the production of this material are ethylenglicol and terephthalic acid, this last obtained from p-xylene oxidation with a ternary catalytic mixture containing transition metals salts (Cobalt and Manganese) and Bromine, the oxidation being conducted in acetic acid as solvent.

There exist several different commercial configurations, some purifying the obtained raw material in water with some kind of precious metal catalyst and hydrogen, some other by a post-oxidation of the relatively impure organic acid obtained previously.

In any case, there are some waste streams that contain in different amounts aromatic organic acid like 1,4 benzenedicarboxylic, (terephthalic acid or TA) 1,4 methylbenzoic, (p-toluic acid or p-Tol) 1,4 carboxybenzaldehyde, (4cba); benzenedicarboxylic acid (benzoic acid), 1,3 benzenedicarboxylic, (isophthalic acid); 1,2 benzenedicarboxylic, (orthophthalic acid) 1,3,4 benzenetricarboxylic (trimellitic acid), methylcarboxylic acid

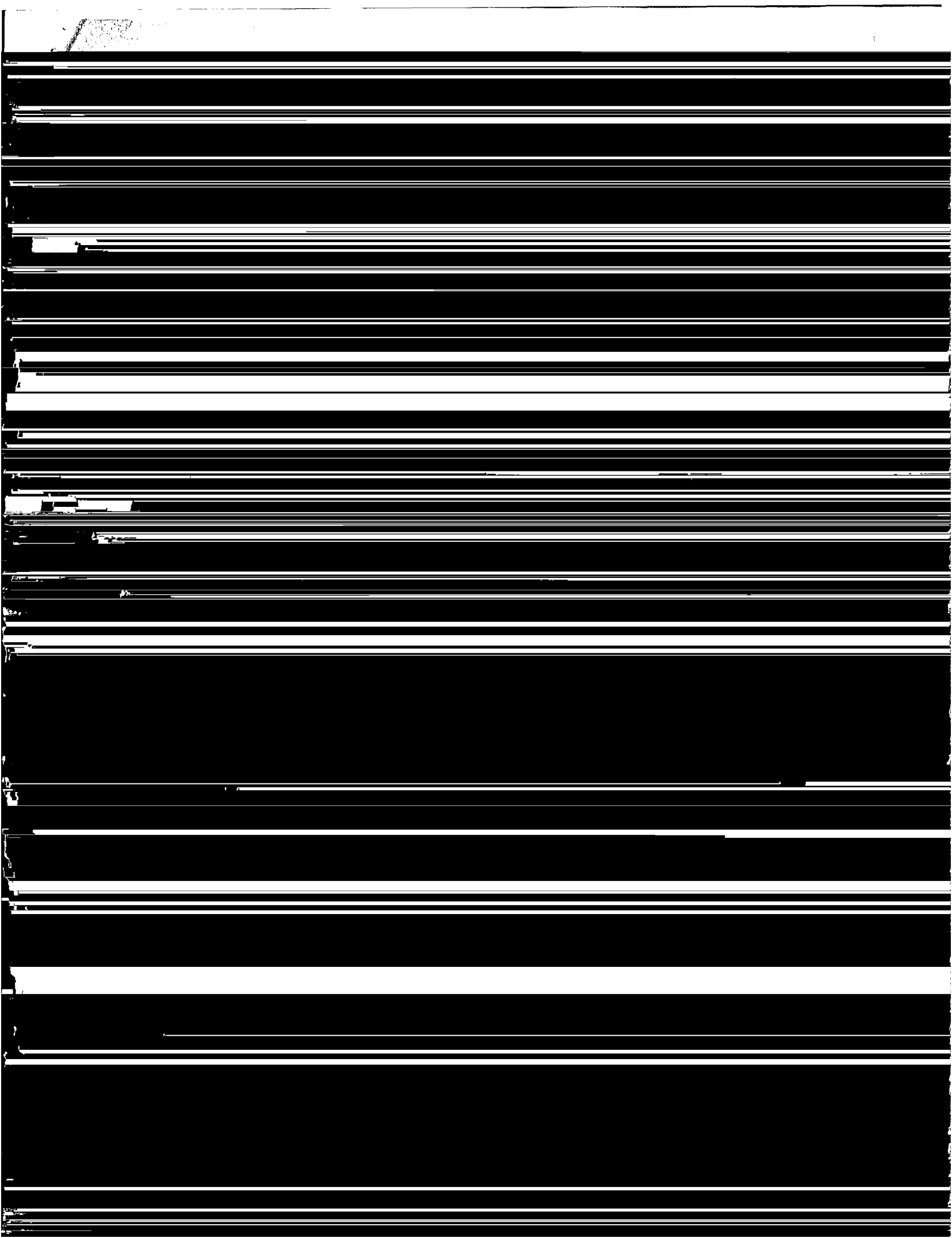


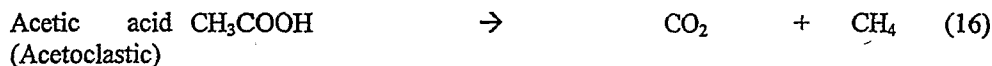
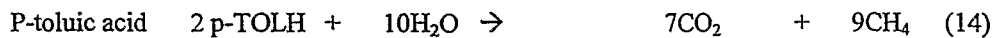
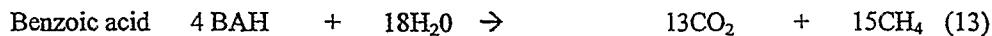
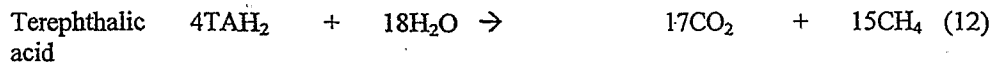
(acetic acid); and others, with some of the catalyst lost and corrosion metals like Iron, Chromium, Nickel and others from pipes, vessels and general equipment.

Aerobic processes have treated this waste stream for long time now. The lower operating cost and continuing development of anaerobic technologies has promoted a re-orientation of the traditional approach towards a pre-treatment by anaerobiosis followed by polishing by aerobic means. Macarie, H. (1996)

Currently there are reported a number of industrial reactors treating this effluent. There persist, however, the perception about some limitations that impose special design requirements, this increasing substantially the initial investment cost, due mainly to the high solids content and the reported limited biodegradability of this stream. In some cases the limitations have been solved by extensive use of additives as caustic soda for neutralization, but ~~increasing significantly the operating cost therefore reducing the incentive for switching to anaerobic processes. In~~

other cases, as reported by by Ely, S. R. Et al.(1989), Shelley, S. (1991), special designs have been developed to





The equations for anaerobic degradation show that the aromatic acid or acetic acid degraded generates the right amount of carbonate, to neutralize its acidity. This is an idealized condition, and for an anaerobic reactor to perform without pH problems would be necessary: (1) To reach 100% degradation efficiency; (2) To use reactor buffer capacity with 100% efficiency.

Those concepts in fact support the cautious approach and the special design considerations to treat this kind of wastewater assuming the problem comes from pH control and knowing the fact anaerobiosis and particularly methanogenic bacteria are sensitive to reactor pH.

Solubility considerations.

To overcome the solids handling problem, several approaches have been applied: reactor design capable of handling solids, (Table 1), NaOH dissolution and pretreatment by solids decantation.

The solubility for terephthalic acid is 19 mg / lt. at ambient temperature. This data does not indicate the pH. If we build the graph 1 of the estimated molar concentrations for the different species of terephthalic acid, TAH_2 , TAH^- and TA^{2-} using the following equations (Data from Bernis, A.G et al (1982)

$$[\text{TAH}_2] = \frac{T}{(1 + 10^{(\text{ph}-\text{pka}_1)} + 10^{(\text{ph}-\text{pka}_2)})} \quad (17)$$

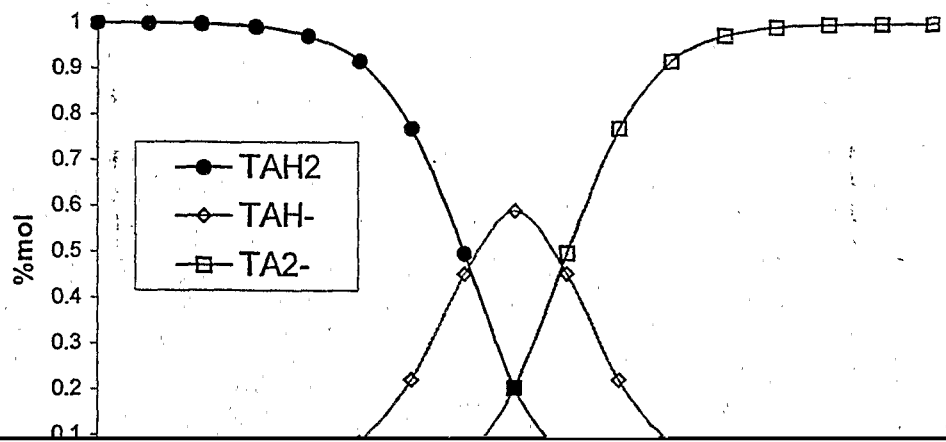
$$[\text{TAH}^-] = \text{TAH}_2 * 10^{(\text{ph}-\text{pka}_1)} \quad (18)$$

$$[\text{TA}^{2-}] = \text{TAH}^- * 10^{(\text{ph}-\text{pka}_2)} \quad (19)$$

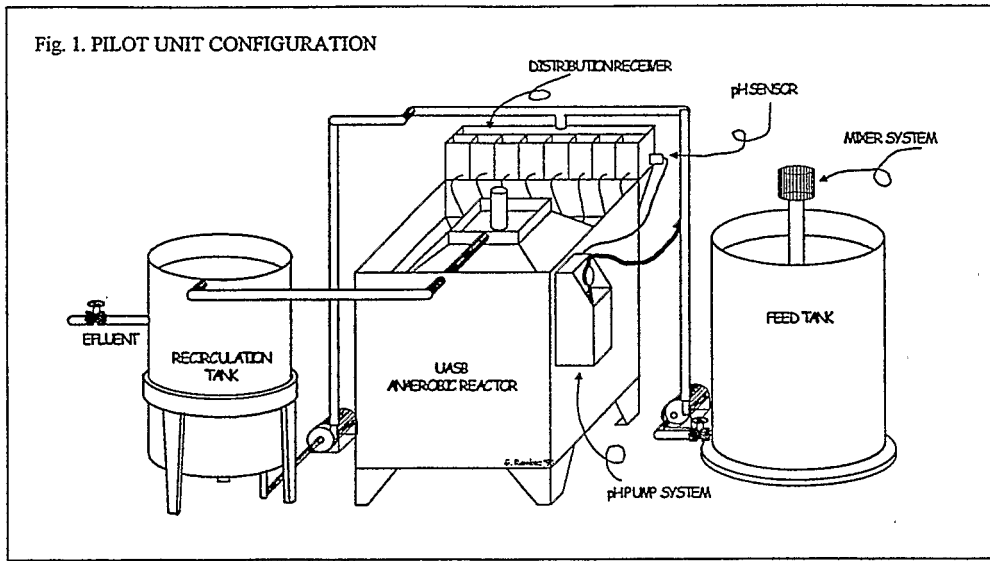
$$T = [\text{TAH}_2] + [\text{TAH}^-] + [\text{TA}^{2-}] \quad (20)$$

$$\text{PKa}_1 = 3.54, \quad \text{pKa}_2 = 4.46$$

graph 1, TAH2, TAH- and TA2- %Mol as pH function



gas collection, as shown. The wastewater feed was controlled with a variable speed peristaltic Cole Palmer pump. The feed and recycle was sent to distributor main box using a standard ½ HP centrifugal pump. The outlet from the reactor was received in a drum from which recycle was taken and excess was discharged. The pH was monitored continuously with a glass electrode set in the distributor main box, connected to a pH-meter and controller, (barnant Company, Italy) which on reaching the low pH value set point, activated a diaphragm pump dosifying 5% caustic solution for pH control. This system was used as safeguard against overloads that could lower the reactor pH.



Biomass: The sludge used for pilot unit inoculation came 3 parts from the existing purge of an existing aerobic industrial facility degrading effectively the waste stream of interest, stabilized for some weeks in an anaerobic digestion pond. 1 part from an industrial anaerobic reactor treating dimethylterephthalate waste water

Reactor feed: The waste water, was kept in a 2500 drum, mixed with a ½ HP 440 V standard motor controlled with an ABB industrial frequency-based speed controller, and a four spades home-made mixer. The feed was enriched with N, P S (200:1, 1000: 1 and 2000:1 COD: nutrient) and micronutrients, Mg (2 ppm) K (10 ppm) Zn, (0.1 ppm) Cu, (0.1 ppm) Ni (0.2 ppm) and Mo 0.1 ppm) other metals were not added, as some were found present already. Periodically the vessel was refilled and any variation in COD or solids content was registered to adjust the nutrients dose and reactor feed flow, but kept unchanged any other way, following the criteria that the pilot reactor should be able to absorb those variations, usual in industrial operation

Waste Water composition. The wastewater contains a variable amount of suspended solids, and a relatively constant dissolved COD, that oscillates around 4500 ppm. The averaged organic compositions are:

Table 2. TYPICAL WASTEWATER ORGANIC COMPOSITION					
Composition	Pilot unit Feed (1)	Pilot Unit Output (2)	Filtered Water (3)	Solids (3)	Total Water (3)
BENZOIC ACID	3.7%	0.1	7%	0.2%	2.2%
P-TOLUIC ACID	18.8%	30.3%	34%	11.2%	11.2%
4-CARBOXIBENZOIC A	0.6%	1.4%	1%	0.3%	0,3%
TEREPHTHALIC ACID	66.9%	68.1%	40%	95%	80%
ACETIC ACID	5.0%	N.D	9%	ND	3%
OTHER ACIDS	5.0%	0.2%	9%	4%	3%
TOTAL SOLIDS	5000 PPM	2000(3200)	2800	5800	8600
TOTAL COD	8000 PPM	3000	5000	8000	13000

Note (1): Correspond to pilot unit feed and output characterized for 31/07/96 to 15/08/96, same period when activity test were performed.

Note (2): total solids in output includes biological solids from reactor, estimated in 1200 ppm, organic acid solids content obtained from COD in filtered sample and organic GC analysis.

Note (3): Corresponds to a plant operating period with high solids content in feed. Filtered water to total water should represent the extremes in operating conditions.

Solubility Curves for Terephthalic and solids in waste stream. Performed at ambient temperature with process water (DI water 2 Mohms) alternate addition of NaOH and Terephthalic acid. / Waste stream solid (comp. As of col. 5 Table 1 by water evaporation: this waste solid does not contain acetic acid) until desired stable pH measured with a glass combination electrode and a metrom 682 automatic titration unit, with saturation shown as visible not dissolved organic material.

Activity test: 150 ml sludge from the reactor bottom was extracted, decanted and washed twice with 300 ml buffer phosphate 0.2M pH 7.0 discarding the liquid. (Conditions in the pilot unit: 31/07/96, 10,000 ppm COD in feed, 88% efficiency removal 4.5 days HRT 2.0 Kg/m³-day load). The volume/mass relationship was estimated by SSV Ten 1000-ml flasks were prepared with 2 gr./lt. of ssv, and two of each 2.0 gr./lt. of Benzoic acid, p-toluic acid, terephthalic acid, acetic acid and industrial waste sample (composition as that of column three in Table 1). The flasks were stoppered, with continuous N₂ flow regular mixing and sampled daily.

Analytical procedures. For organic composition in waste stream analysis was used a Varian 3600 gas chromatograph with a DB-1 30 Mts. 0.5 mm ID 0.25 microns capillary column, and a commercial mixture for derivatizing (bis(trimethylsilyl)trifluoroacetamide) using the standard procedure. For peak identification and quantification was used an internal standard method, reagent grade spiking for each aromatic acid with a spectrophysics automatic area integration.

For COD analysis was prepared a calibration curve using terephthalic acid 99.95% as source, and as reagent 75% conc. Sulfuric acid with 0.02 molar K₂Cr₂O₇ / 0.04M AgSO₄, 0.015M HgSO₄ solution. The prepared samples are treated under total reflux for 4 hrs at 150 °C and the final absorbance read at 760 nm with a Hach 4000 spectrophotometer.

For all other analysis (SSV, ST, metal content, alkalinity, pH, ORP, etc) were used standard methods as of APHA, AWWA and WPCF. (1992).

Experimental results

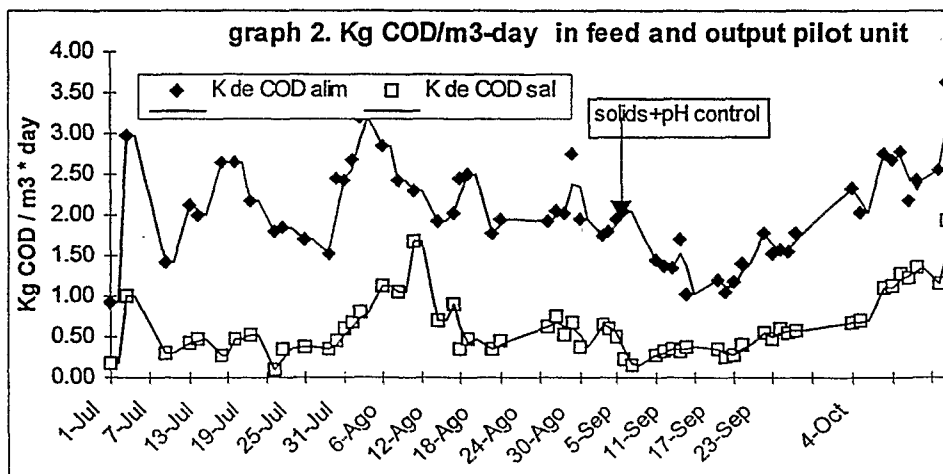
Pilot unit operation following are operating conditions for the pilot unit from 1/07/96 to 17/11/96 in graph 2 can be observed an overload in feed, with a peak at 05/08/98. An excess of confidence generated this condition: we used for flow adjustment pH measurement in feed. As can be seen in graph 3, by the end of July we had a high pH in the reactor that we interpreted as sign of excess capacity. We increased feed, overreached in the adjustment and a week later we had lost control of the reactor, evidenced by: a fall in reactor pH, graph 3, a loss in %efficiency removal, graph 5; and a drastic increase in output COD: The recovery of the system was fast. Table 3 shows main operating conditions for the 31/07 to 15/08, which comprises the upset period.

The efficiency averaged is about 62% removal. Operating with no problem, as in the period from 10/07/96 to 31/07/96, we get an 80% efficiency removal. From Table 3, individual organic efficiency removal is not the same. Toluic acid and 4CBA remain essentially the same whilst acetic and Benzoic acid are removed 100%. About half of TA, that represents 43% of total COD, is removed.

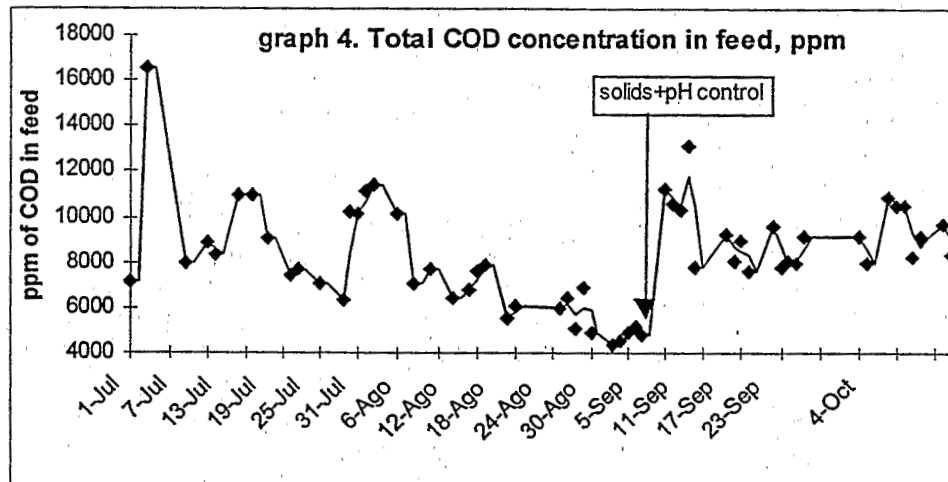
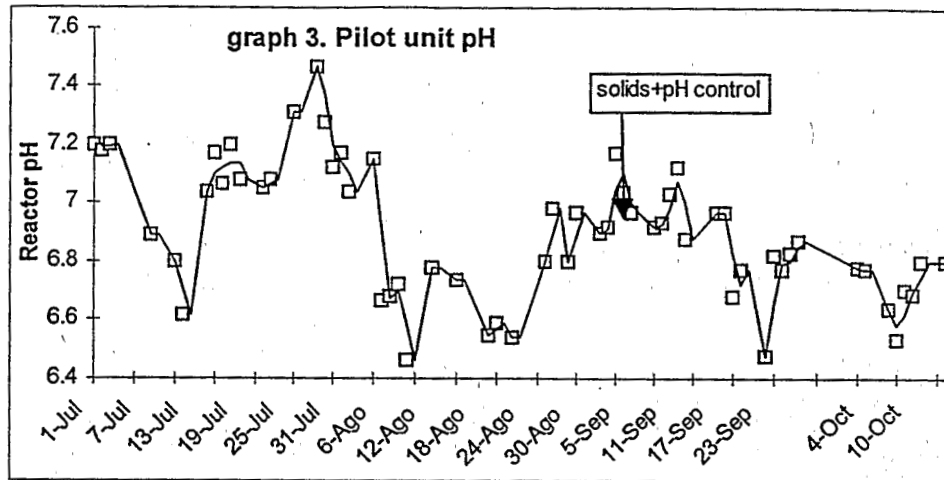
Parameter	st, ppm	cod, ppm	Bz, ppm	Tol, ppm	4-cba, ppm	OTHERS	TA, ppm	Hac, ppm	pH
FEED	5100	8200	300	1000	40	250	3500	250	4.3
OUTPUT	3200	3100	2	800	40	50	1800	N.D.	6.9
%Effic. Rem	37%	62%	99%	20%	0%	80%	49%	100%	

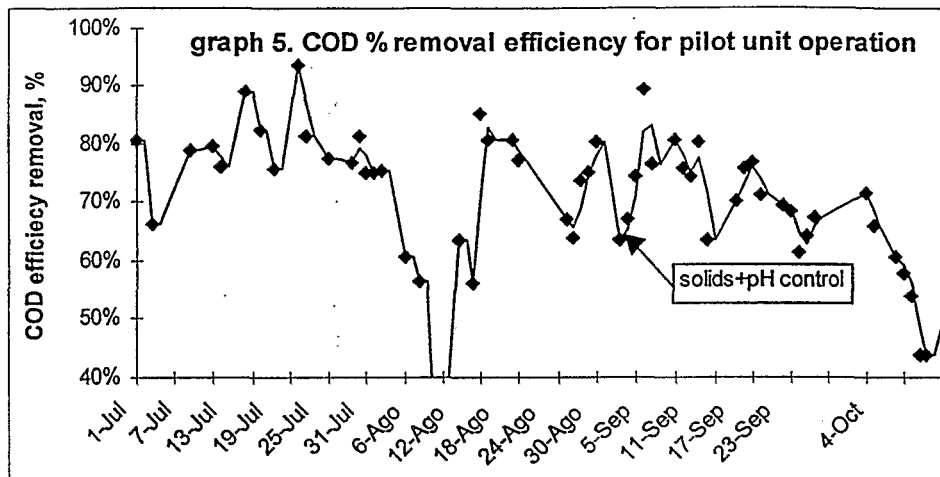
NOTE: Avg 64% COD Removed @ 300 LT/Day Feed (3.4 Day HRT) and 2.5 KG/M³-Day COD.

As we wanted to reach the maximum COD removal rate feasible with this system, we kept pushing feed load as far as possible. As the capacity limitations was always evidenced first by a fall in pH, we implemented the pH control loop as described in reactor design, the 06/09/98 and simultaneously increased solids concentration in Feed, as can be seen in graph 4. After that, the pH trend was somewhat more stable and we were able to increase load as shown in graph 2.



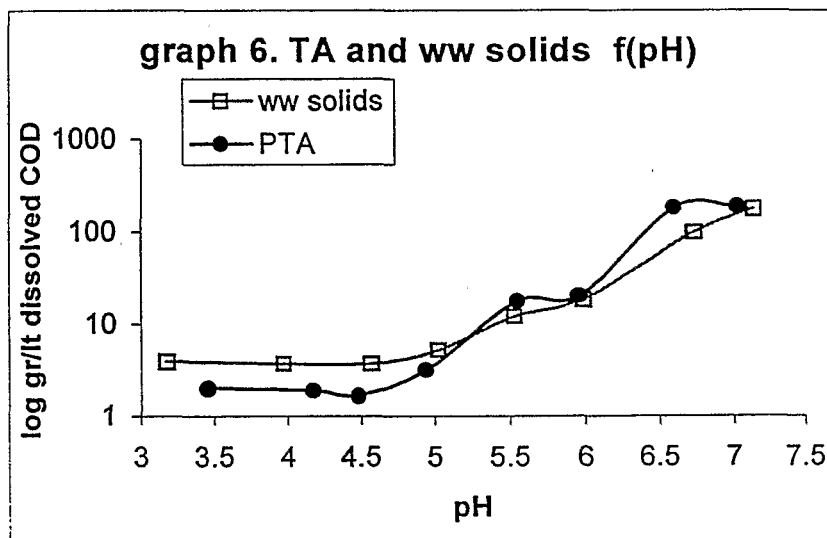
In the same graph, however, can be seen that output COD kept also rising with a constant differential, The efficiency removal kept going down. All those trends show that we reached a maximum load to the system and any additional load just passed through the reactor without more effect than the increasing caustic consumption to kept the pH controlled.



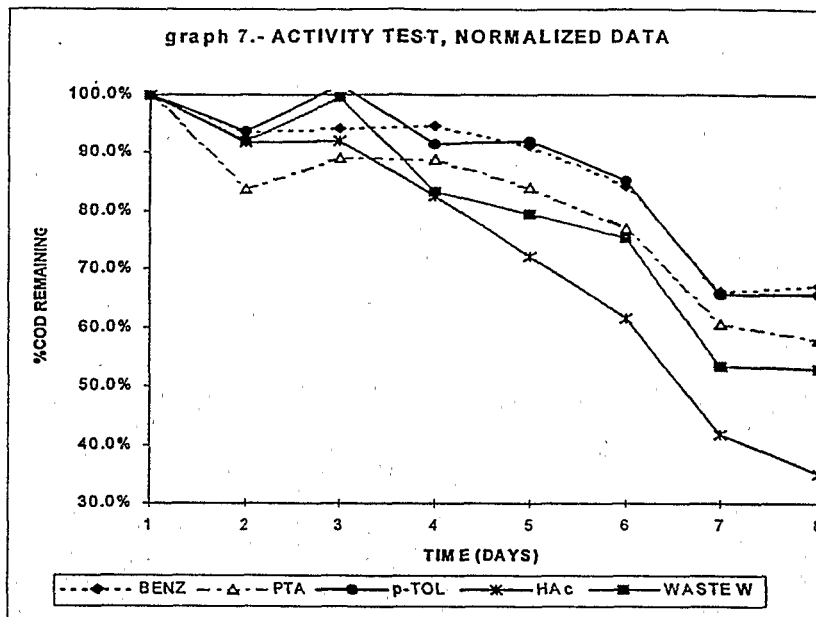


The removed load for this system, averaging 10/07/96 to 31/07/96, 15/08/98 to 05/09/96 (without caustic) and from 10/08/96 to 15/09/96 (with caustic addition) were 1.64 and 1.15 kg/m³-day, with 2.09 and 1.80 Kg/m³-day in feed (COD); 7200 and 9350 ppm concentration. The estimated COD as TA in feed is 58% and 66% respectively.

Solubility data. The graph shows that the general solubility trend as pH function for pure terephthalic acid and waste water solid is similar (see column 5 Table 1 total water composition: this contains a high amount of terephthalic acid). At pH 4.5 and lower, solubility for PTA is lower than ww solid. Above this pH solubility shoots up (Y-axis is logarithmic). This is consistent with the species concentration curve in graph 1, about this pH TA²⁻ concentration rises sharply. At pH 7.0 all solids present in this waste stream are fully dissolved.



Activity tests. They were performed from 01/08/98 onwards. (Graph 7) to obtain data about individual substances degradation. The initial COD conc. was 3200 +/- 750 STD dev. We found no significant difference between replicates, except for acetic acid, with a constant diff. of 260-ppm COD probably originated at replicate preparation. There are three different groups: p-toluic and Benzoic acid were degraded at 50 gr./Kg biomass-day. Terephthalic acid and wastewater at 60 gr./Kg biomass-day And acetic acid at 90 gr./Kg biomass-day. As far as this activity test show, all main organic substances are degraded individually even as the degradation rate is low.



RESULT AND DISCUSSION

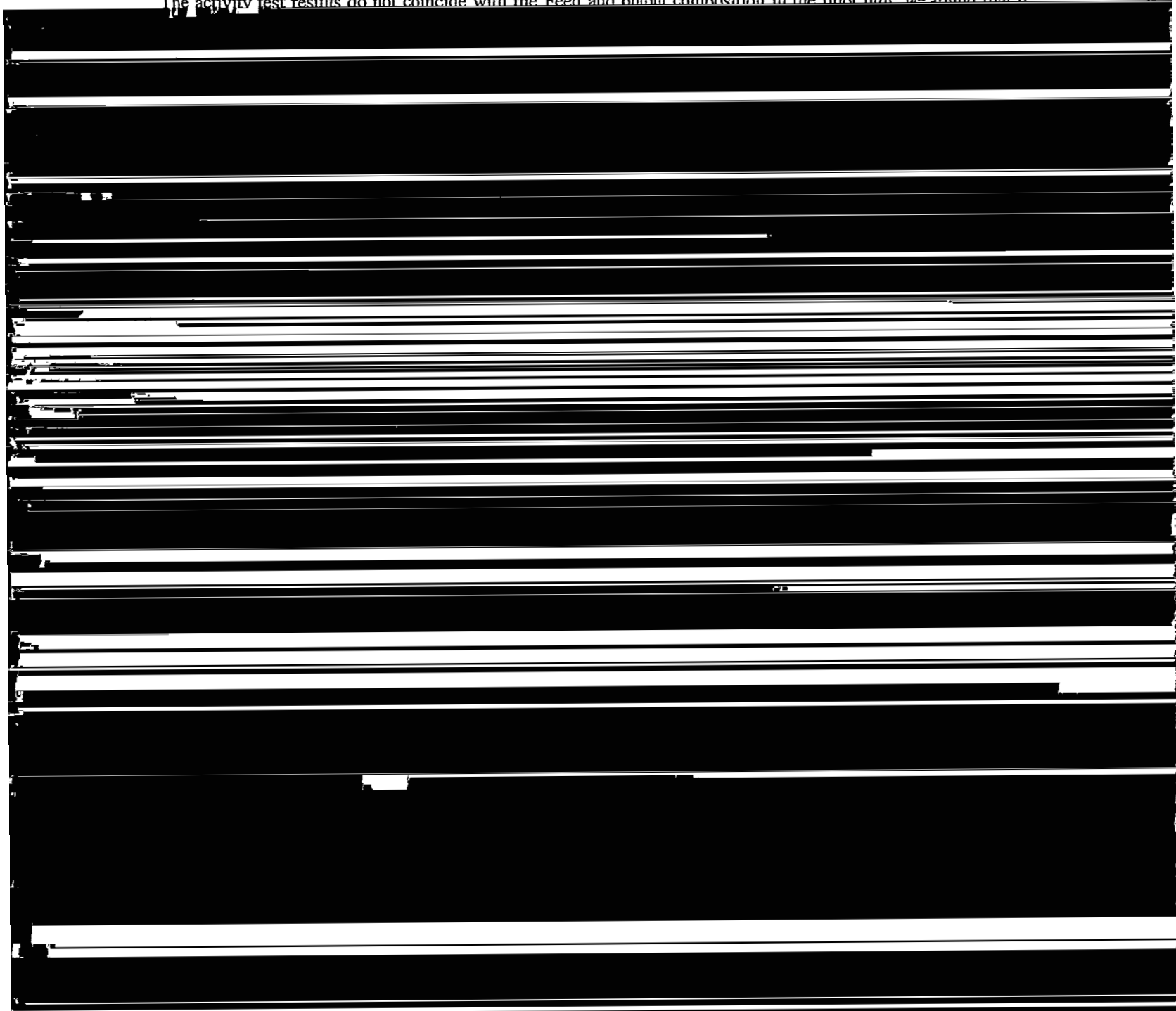
We initiated this work focusing on three main points: Acidity, solubility and biodegradability considerations that impose special design requirements for industrial anaerobic treatment of High aromatic acid content. In the next paragraphs we resume our results.

The Acidity limitation: from a purely conceptual standpoint it seems evident that for pH control is required some neutralization agent, as usually 100% efficiency is not reached. In fact, under stable conditions we reached in the pilot unit operation about 80% degradation. Very important, however, we did not add any neutralization agent as

Solubility Considerations. At the typical pH in the reactor with an efficiency removal of 80%, about 7.0, we did not observe organic solids accumulation in the reactor biomass. Sometimes in the distribution box some solids accumulated in the corners, but usually dissolve themselves after some time. Considering graph 1, that indicate conceptually that at pH 7.0 all terephthalic is in the form TA^{2-} , highly soluble; and this solubility is confirmed experimentally in graph 6, that shows a typical COD loading of about 10,000 ppm is dissolved by an ample margin. So, we do not expect solids accumulation, and the activity problems in works were this accumulation is reported as in Kuang, X. and Wang, J. (1994); could be explained in terms of insufficient reactor pH control.

Biodegradability considerations. We found the degradation rates for organics present in this stream are low. Our activity tests do not show big differences in activity between the main compounds measured individually.

The activity test results do not coincide with the Feed and output composition in the pilot unit; we found that n



Pereboom, J. H. F., De Man, G. and Su, Y. T. (1994). Start-up of full scale UASB reactor for the treatment of terephthalic acid wastewater. In: *Poster Papers, 7th Int. Symp. on Anaerobic Digestion*, January 23-27, Cape Town, South Africa, pp. 307-312.

Vandufel, J. (1993). Anaerobe behandeling van organische zuren. In: *Proc. Symp. on Pretreatment of Petrochemical Effluent*, Breda, The Netherlands.

Ely, S. R. and Olsen, G. P. (1989). Process for treatment of wastewater. *US Patent no 4 826 600* (assigned to

