

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

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### 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.

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### 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 Ely, S. R. Et al.(1989), Shelley, S. (1991), special designs have been developed to minimize the problem. Table 1 show information about facilities treating this wastewater anaerobically.

Table 1. Anaerobic treatment systems presently used to treat PTA producer's waste streams

N°	Year	Location	Built by	Pretreatment used for solids	Reactor Type*	Reactor Volume**	Organic load	COD removal
							m <sup>3</sup>	Kg COD/m <sup>3</sup> day
1	1989 <sup>1</sup>	Capco Co., Taiwan	Amoco	NaOH dissolution	DSFF	2*5000	3-4	85***
2	1990	China	Local	Primary settling	Hybrid	4*3000	6.3	80
3	1991 <sup>2</sup>	Tuntex, Taiwan	Grontmij	Primary settling	UASB	7000	10	55
4	1992	Amoco, USA	Amoco	NaOH dissolution	DSFF	8200	3-4	85 ***
5	1993 <sup>3</sup>	Amoco, Belgium	Amoco	NaOH dissolution	DSFF	15200	3.7	80***
6	1994	Sam Nam, Korea	ADI	?	Hybrid	2*1100	10	75
7	1994	Reliance Ind., India	ADI	?	Hybrid	2*3200	6	70
8	1996	ATV Petroch., India	Paques	?	UASB + AF	1330	10-12	65
9	1997	Reliance Ind., India	ADI	?	Hybrid	560	5	65
10	1997	Reliance Ind., India	ADI	?	Hybrid	7000	5	65

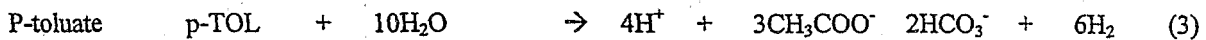
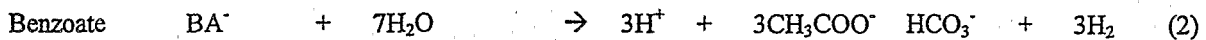
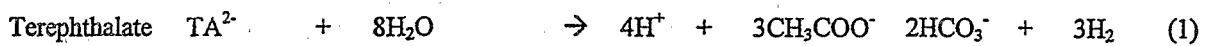
Shelley, 1991<sup>1</sup>, Pereboom *et al.*, 1994<sup>2</sup>, Vandufel, 1993<sup>3</sup>; \* DSFF: Downflow Stationary Fixed Film, UASB: Upflow Anaerobic Sludge Blanket, AF: Upflow Anaerobic Filter; \*\* The reactors of the plants 6, 7 as well as the UASB and the AF of the plant 8 are operated in series; \*\*\* Removal efficiency based on TOC instead of COD

As can be seen, there are not many, and essentially not feeding solids straight to the reactor. The load is generally low and there are only two UASB reactors operating, as far we know. The Table 1 shows that effectively special considerations have been applied to solve the difficulties to treat this waste stream posed by Acidity, biodegradability (DSFF or hybrid reactor are mainly applied for biomass protection to avoid high local concentrations of toxic materials) and solids presence in the feed.

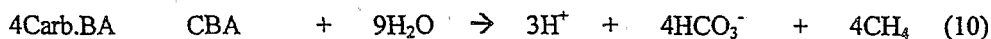
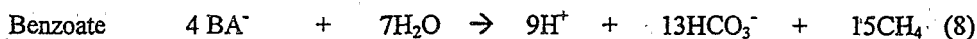
#### Feed stream acidity considerations.

The pH in anaerobic reactor is an important parameter and it should be kept about 7.0 for optimal performance. In this particular waste stream containing form PTA production process, have been applied two approaches for anaerobic treatment: NaOH addition, and special reactor design to optimize buffer capacity utilization combined with reduced NaOH addition.

Let's consider the following equations for organic acid degradation:



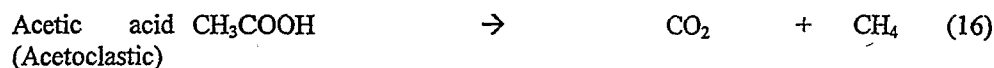
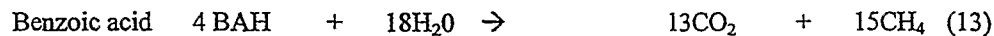
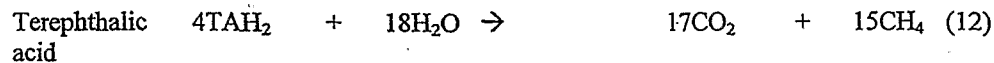
Assuming true this reactions and considering organic acid degradation to methane and bicarbonate, we obtain (combining eq (1) to (4) with (5), (6)).



In the other side, we know the following equilibrium plays a significant role in anaerobiosis:



Combining reaction (7) to (10) with (11), and considering the feed to the reactor is in the acid form an not in neutralized state for each aromatic compound, we obtain:



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,  $\text{TAH}_2$ ,  $\text{TAH}^-$  and  $\text{TA}^{2-}$  using the following equations (Data from Bernis, A.G et al (1982)

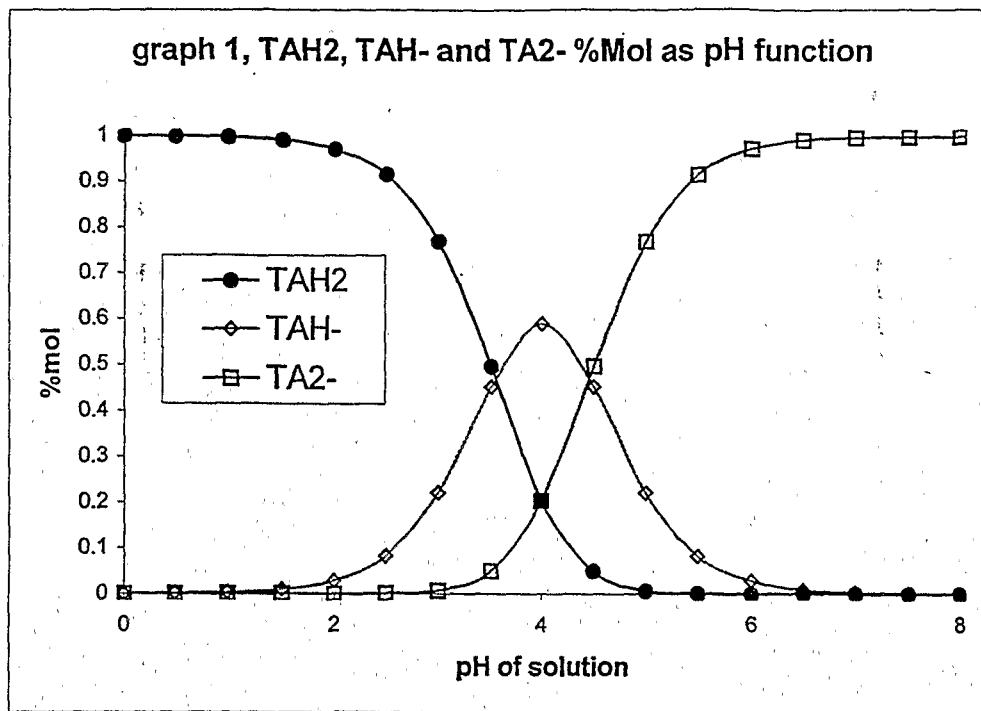
$$[\text{TAH}_2] = \frac{T}{(1 + 10^{(\text{ph}-\text{pka}1)} + 10^{(\text{ph}-\text{pka}2)})} \quad (17)$$

$$[\text{TAH}^-] = \text{TAH}_2 * 10^{(\text{ph}-\text{pka}1)} \quad (18)$$

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

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

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



The TAH<sub>2</sub> is very insoluble but its ionized forms are much more soluble, as happens with the potassium biphthalate salts, We would not expect solids accumulation based on pH equilibrium data, unless solution kinetics were very slow or the reactor design favored inadequate mixing.

#### Biodegradability Considerations.

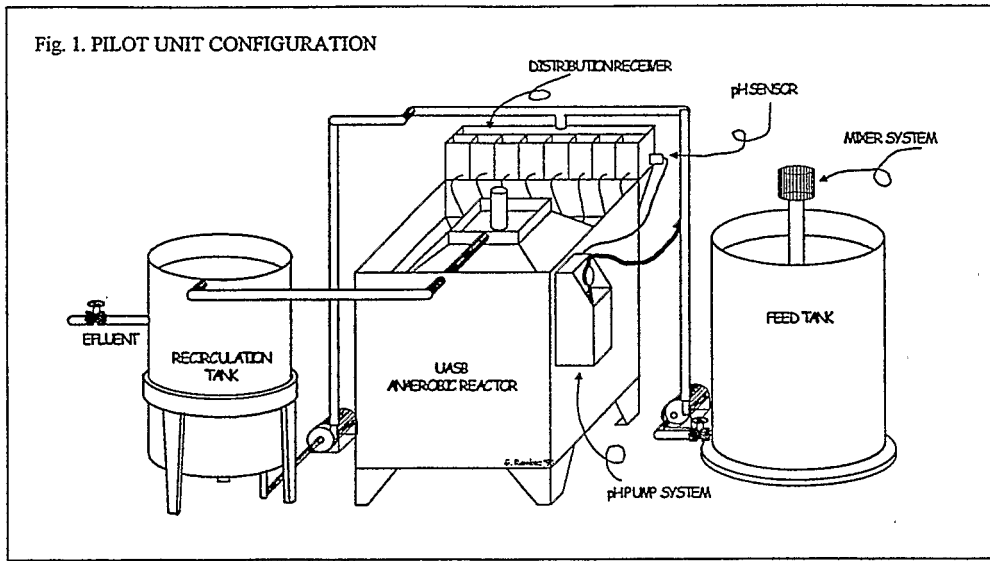
The main component in this waste stream has not been found to be toxic at mutagenic levels (Lerda, D. E.). Inhibitory concentrations for anaerobic activity are reported as IC<sub>50</sub> 0.8, 4.6 and 16.6 g/l for 4-CBA, p-toluic and TA, respectively tested with not pre-adapted sludge (Fajardo, C. et al, (1997)). In the same reference is reported TA degradation inhibition by Benzoic acid and glucose presence. The biodegradation pathway proposed by Lixian, S. et al (1991), considers TA is anaerobically degraded with Benzoic acid as an intermediate step. Tur, M. Y. and Huang, J. C. (1997). reported some experimental results in which was reached a 0.81-0.85 gr. COD /gr. VSS-day specific COD removal for TA acid. In this report is concluded it was not possible to reach higher COD removal rates because of biomass inhibition or HRT limitations. The maximum Specific rate reached by Kleerebezem, et al (1997). was 0.034 gr. COD / gr. VSS-day. It is also concluded that easier to degrade substrates inhibit TA degradation rate. Cheng, S. S. Et al (1997) concluded TA acid has low degradability and P-toluic acid none, Young, J. C. (1997) reports biodegradability for Benzoic and acetic acid, but essentially none for the other acids. Summing up: the references for TA anaerobic indicate TA specific COD removal rates ranging from 1.4 gr. COD / gr. VSS-day to almost no degradation.

We seek to: (1) evaluate the real limitations of solubility, acidity and Biodegradability attributed mainly to terephthalic acid and to a lesser extent to p-toluic acid in this waste stream. (2) Propose options to reduce as much as possible the installation and operating cost associated to technical solutions already applied to this particular stream.

#### MATERIAL AND METHODS

**Anaerobic Reactor design.** In this work was used a 1000 lt. unit as shown schematically in diagram 1, 1.0 Mt. x1.0 Mt. x 1.0 Mt. size carbon steel vessel coated with epoxy resin, a 16 boxes distributor, with lines to equidistant points in the bottom of the vessel. For solid-liquid-gas separation was used a single cover with a central opening for

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/m<sup>3</sup>-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 N<sub>2</sub> 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 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> / 0.04M AgSO<sub>4</sub>, 0.015M HgSO<sub>4</sub> 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**

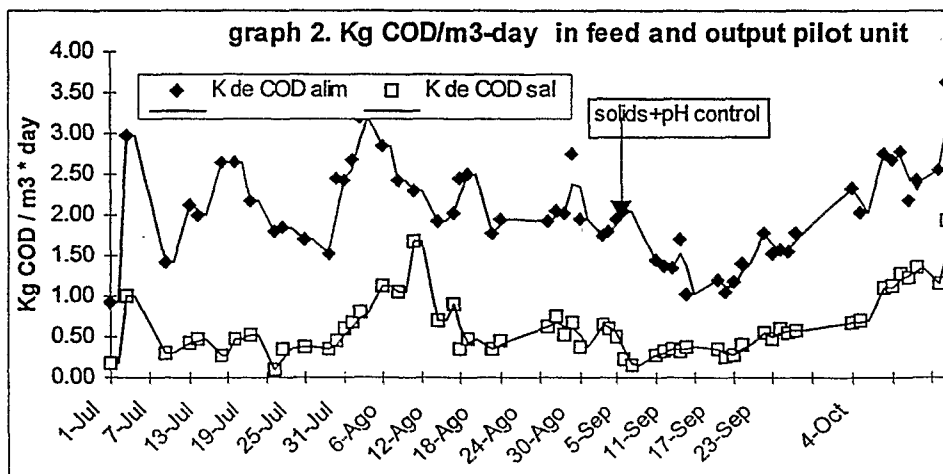
**Pilot unit operation** following are operating conditions for the pilot unit from 1/07/96 to 17/11/96 in graph 2 can be observed an overload in feed, with a peak at 05/08/98. An excess of confidence generated this condition: we used for flow adjustment pH measurement in feed. As can be seen in graph 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%	

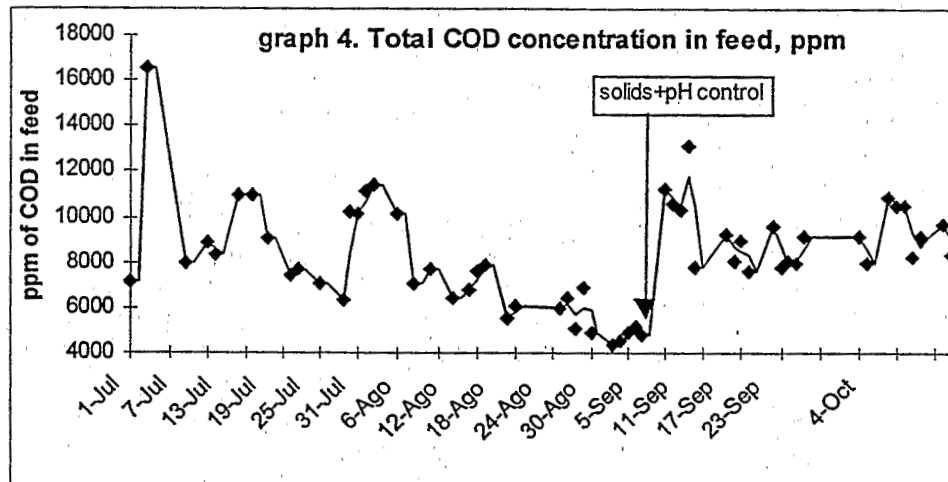
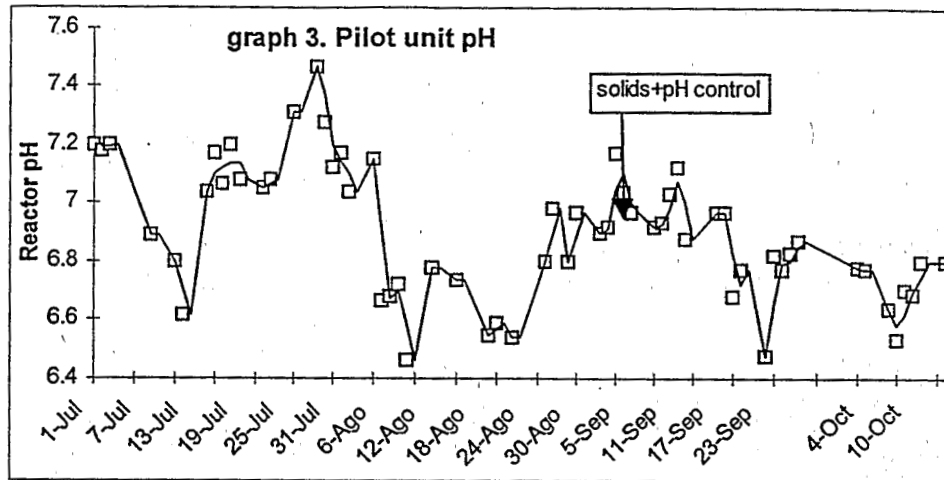
NOTE: Avg 64% COD Removed @ 300 LT/Day Feed (3.4 Day HRT) and 2.5 KG/M<sup>3</sup>-Day COD.

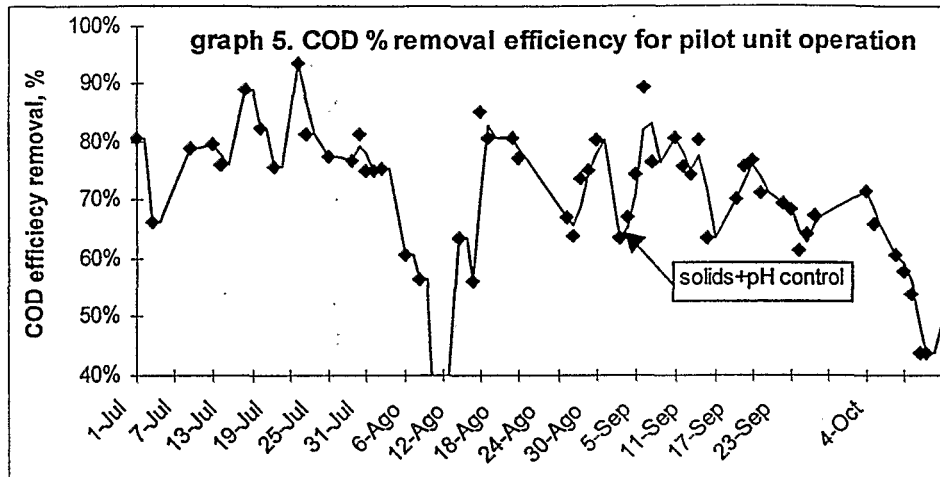
As we wanted to reach the maximum COD removal rate feasible with this system, we kept pushing feed load as far as possible. As the capacity limitations was always evidenced first by a fall in pH, we implemented the pH control loop as described in reactor design, the 06/09/98 and simultaneously increased 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.





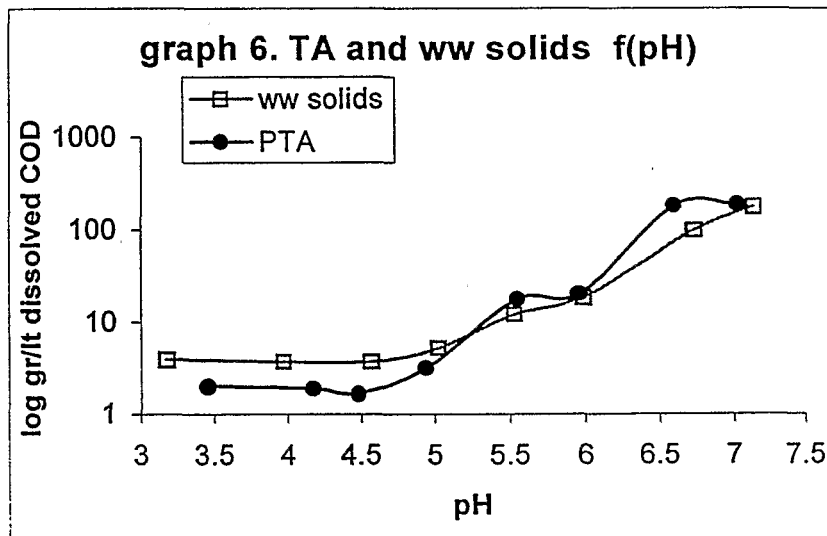
In the same graph, however, can be seen that output COD kept also rising with a constant differential, The efficiency removal kept going down. All those trends show that we reached a maximum load to the system and any additional load just passed through the reactor without more effect than the increasing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



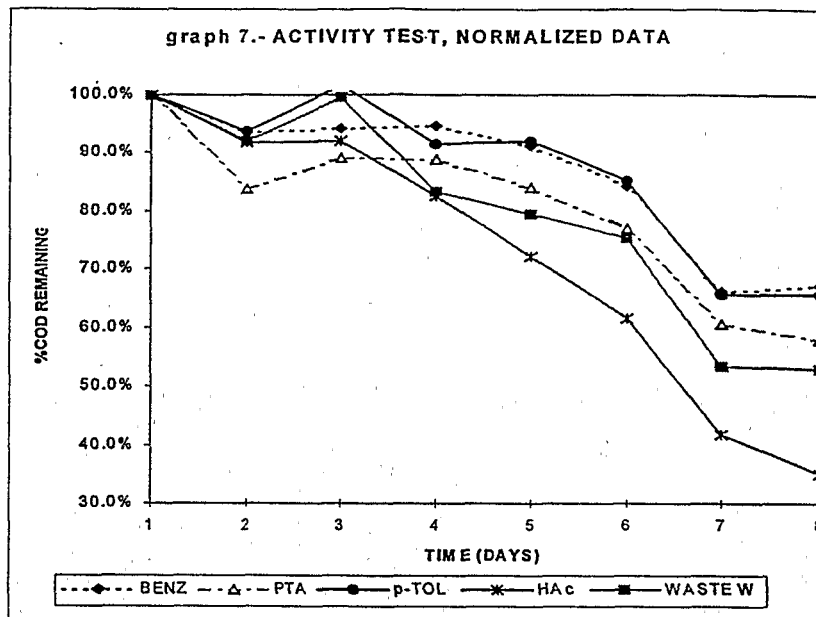


The removed load for this system, averaging 10/07/96 to 31/07/96, 15/08/98 to 05/09/96 (without caustic) and from 10/08/96 to 15/09/96 (with caustic addition) were 1.64 and 1.15  $\text{kg/m}^3\text{-day}$ , with 2.09 and 1.80  $\text{Kg/m}^3\text{-day}$  in feed (COD); 7200 and 9350 ppm concentration. 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  $\text{TA}^{2-}$  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

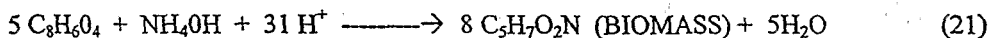
We initiated this work focusing on three main points: Acidity, solubility and biodegradability considerations that impose special design requirements for industrial anaerobic treatment of High aromatic acid content. In the next paragraphs we resume our results.

**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 reagent on this period

This could be explained with one or both of the following:

This kind of facilities usually uses caustic solution for equipment an piping washing in maintenance activity, as this is an efficient way to dissolve and remove accumulated organics. The washings are sent to waste treatment system. The caustic typical consumption would about explain this 80% efficiency with no pH control problems.

The degradation reactions expressed in the introduction to this work are very far from representing the myriad of chemical reactions taking place in the reactor UASB and some of them could very well consume  $H^+$ . Just like an example, if we consider a generic reaction for biomass synthesis from terephthalic, we have:



This reaction indicates a high  $H^+$  requirement for biomass synthesis. An important point is the fact that when we overreached in feed the pH of the reactor descended sharply. The limit for our particular experimental conditions is around 70% efficiency. With 80% or higher the system is on the safe side, with a pH of 6.7 or higher.

The approach observed in industrial facilities already existing, as shown in Table 2, with the use of caustic for neutralization, is justified by system safety but costly. We used a pH control system with caustic feed for pH control, but found it was necessary only when we went to loads in the feed higher that it was possible to treat efficiently. There is no use in neutralizing higher loads than the degradation capacity; just to pass it through the reactor untouched.

**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 p-toluic and 4-carboxibenzaldehyde remains essentially untouched, whilst in the activity test the p-toluic degradation was very similar to benzoic acid. This difference could be explained considering already references authors who concluded the anaerobic removal of difficult to treat substances is inhibited in the presence of easier to remove organics.

We observed a decrement in removal efficiency measured as Kg COD / $m^3$ -day from the moment we started to feed solids (essentially terephthalic acid) and controlling pH with caustic. This partly could be explained considering the increment in  $TA^{2-}$  concentration and assuming there was a limited biomass amount to remove this organic. Taking (1.64 kg/ $m^3$ -day COD removed) \* (58% COD as  $TA^{2-}$  / 100) \* (49%  $TA^{2-}$  specific efficiency) in the low solids feed condition, we get a 0.47 kg/ $m^3$ -day  $TA^{2-}$  capacity removal for this system. When we feed the high solids stream, that contained (1.80 Kg/ $m^3$ -day) \* (66%  $TA^{2-}$  in feed / 100); 1.19 Kg/  $m^3$ -day COD loading as  $TA^{2-}$ , an excess of 0.72 kg/ $m^3$ -day. So, the maximum efficiency we could reach with this feed composition was (1-0.72/1.80) or 1.08 kg/ $m^3$ -day. It Appears the lower %efficiency removal we observe when feeding a high solids stream is generated by a calculation artifact: the specific efficiency as removed  $TA^{2-}$  is the same, with no inhibition effect for higher  $TA^{2-}$  concentration in solution, in the range the system was tested.

## CONCLUSIONS.

We found that: the acidity limitation in the feed is not a critical problem if the %efficiency removal in the reactor is kept above a certain value that could vary for particular conditions. In the development of this work we found 80% adequate.

The solubility limitation is not a problem by itself, but associated to inadequate reactor operation defined by excessive loading referred to specific organic removal capacity and acidification

We observed p-toluic acid degradation inhibition in the presence of other substances in the feed, confirming results already reported, that suggest competing degradation mechanisms

The specific removal rate for  $TA^{2-}$  we reached is intermediate in the range of values reported in literature. Our future work will focus on studying conditions to get higher specific degradation rates considering parameters as nutrients and micronutrients in the feed, biomass conditioning.

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