OVERVIEW ON THE APPLICATION OF ANAEROBIC DIGESTION TO THE TREATMENT OF CHEMICAL AND PETROCHEMICAL WASTEWATERS

Hervé Macarie

Institut de Recherche pour le Développement (IRD-France, ex-ORSTOM), Ciceron 609, Col. Los Morales, 11530 México D. F., Mexico
Email : herve@xanum.uam.mx, Tel/Fax : (52) (5) 724 47 23

ABSTRACT

Today, with at least 848 reactors constructed in the world, anaerobic digestion is considered to have reach the technological maturity. Until now however, it has been used quite exclusively for the treatment of food industry effluents. It is only during the last 10 years that anaerobic digestion has started to be applied massively to the treatment of sewage and effluents from other industrial activities. During the 70's and 80's, the chemical and petrochemical industries were almost refractory to the introduction of anaerobic digestion. The situation has reversed since 1990 and at least 63 full scale anaerobic plants are nowadays treating this type of waste in the world. Nevertheless, a great amount of promotion is still required before anaerobic digestion can be considered as an accepted technology by this industry. The paper presents the actual situation of anaerobic treatment at full scale in this industrial sector as well as recent development at lab scale and discuss some important concepts to consider before the implementation of an anaerobic treatment. Particularly a table is given with the main characteristcs of the 63 full scale plants identified to date. The probable reasons for the slow initial development of anaerobic treatment are also discussed and it is shown that anaerobic digestion has been the solution to treatment problems for which aerobic systems were inefficient

KEYWORDS

Anaerobic treatment; chemical; petrochemical; wastewater

INTRODUCTION

During the last 20 years, anaerobic digestion (AD), a biological process in which organic matter is converted to CH_4 and CO_2, has grown more and more into an attractive technology for wastewater treatment due to its low cost compared to the other technologies available: physico-chemical and aerobic biological treatments. Its apparent initial drawbacks (very slow growth rate of the biomass, susceptibility to toxic compounds...), translated in huge reactor volumes and operation upsets, were overcame by the development of a new generation of reactors. In these reactors, the problem of slow growth rate was turned by capturing the biomass in the form of biofilms on static (Upflow Anaerobic Filters: UAF, Downflow Stationary Fixed Film Reactors: DSSF) or moving (Fluidized bed reactors: FB) supports but also by selecting well settling flocculating biomass (Anaerobic contact: AC, Upflow Anacrobic Sludge Blanket reactors: UASB, Expanded Granular Sludge Bed Reactors : EGSB). With such modifications, the sludge retention time in these reactors became independent of the hydraulic retention time (HRT) allowing the application of short HRTs (6 h to 1 week) and correspondingly the application of high organic loading rates (4 to 40 kg COD/$m^3_{reactor}$ /day). This resulted in much smaller reactors but also in a much more stable operation than before.

Nowadays, with at least 848 low and high rates reactors constructed in the world anaerobic digestion is considered to have reach the technological maturity. Inventories performed by other authors indicate, even, numbers of anaerobic plants as high as 1000 to 2000 (Hulshoff Pol *et al.*, 1997; Totzke, 1999). Until today, however, anaerobic treatment has been applied quite exclusively (75% of all the reactors in operation) to the treatment of wastewaters from the food and related industries (bakery; brewery; cannery; dairy; distillery; fish and potatoes processing; malting; candy, citric acid, coffee, cheese, chocolate, enzyme, fruit juice, jam, soft drink, starch, sugar, wine and yeast productions) and it is only recently (over the last 10 years) that it started to be applied massively to sewage (3.6% of all the digesters in operation) as well as other industrial sectors such as the pulp and paper (9.7% of the operating digesters). What happened during this time in the chemical and petrochemical industries?

DEVELOPMENT OF AD AMONG (PETRO)CHEMICAL INDUSTRIES

The first studies about the anaerobic treatment of this type of wastewaters started at the beginning of the 70's. In 1973, for instance, Hovious *et al.* demonstrated at pilot scale the possibility to use an anaerobic lagoon as an efficient pretreatment for petrochemical effluents. Few years later, Chou *et al.* (1978) published a list of 41 organic compounds potentially present in petrochemical and chemical industry effluents that they found to be biodegradable by methanogenic fermentation. Despite these early works, it is only in 1981 that the 2 first high rate digesters treating chemical waste were built by the Celanese company in USA (Table 1, reactor 1, 2). Four more years passed before a third reactor was built and until 1989 as far investigated, only 19 full scale reactors were in operation on that type of waste in the world (Table 1). From 1990 to date, the rate of construction of digesters for that industrial sector increased from 2 reactors/year for the past decade to 4.4 and presently, at least 63 digesters (7.4% of all the digesters) are treating chemical waste in the world (Table 1).

The initial slow development of anaerobic digestion in that sector was probably the result of an "*a priori*" (both from the companies dedicated to the design of anaerobic systems than the chemical & petrochemical industries), postulating that anaerobes, particularly methanogens, contrarily to aerobes, were too sensible to deal with this type of wastewaters supposed to be highly toxic. In fact, a comparative study of tolerance to toxicity between aerobes and anaerobes has shown that such assumption is not justified (Blum & Speece, 1991). In some cases anaerobic digestion has even appeared to be the key to the success of the degradation of some molecules. In 1981, for instance, the activated sludge treatment system of the Celanese company at Bishop, Texas, USA, was not able to treat 2 particular effluents. One of them, although composed of readily biodegradable molecules, had a concentration of heavy metals (5-500 mg/L) toxic for the aerobic bacterias, while the second contained polyols (pentaerythritol, trimethylolpropane) refractory to aerobic degradation. The implementation of an anaerobic reactor previous to the aerobic plant, by precipitating the heavy metals under the form of non toxic metallic sulfides, allowed to degrade the first effluent directly within the anaerobic stage and by modifying the chemical structure of the polyols, transformed them into compounds biodegradables in the aerobic post-treatment unit (Harvey and Rubiano, 1983).

Nature of the wastewaters presently treated at full scale or which could be treated.

As indicated in Table 1, the spectrum of wastewaters already treated at full scale results from a large number of very different industrial activities. Nevertheless, on the whole, the first anaerobic digestion installations were set up on relatively simple wastewaters, composed mostly of volatile fatty acids (reactors 2, 4, 5, 6, 7, 10, 13), methanol (4, 10) and glycols (11) also found in more classical effluents for AD. If we except the case of Shell in 1986 which contained a high concentration of benzoic acid (reactor 8) and that of Celanese in 1981, it is only in 1989, with the installation by Amoco of a digester on PTA (Purified Terephthalic Acid) wastewater, that a really unusual effluent containing aromatic compounds from the benzenic serie was treated (reactor 17). Moreover, It should be noted that it is practically the only type of effluent which has given rise to the construction of a serie of reactors, 13 until now. In fact, in its case, anaerobic digestion seems, even, to be on the way to become the conventionnal form of treatment. The other activities which resulted in the construction of more than one reactor are the production of DMT (dimethylterephthalate) (5 reactors), PET (polyethylene terephthalate) (4 reactors) and aspartame (2 reactors). All the other reactors correspond however to single experiences. It is evident, that the chemical and petrochemical effluents treatable by anaerobic digestion are not limited to those presented in Table 1. Already, several others have been successfully treated anaerobically at pilot or lab scale (Table 2). A great number of molecules susceptible to be produced by this type of industrial activity and then to be present in the wastewaters are also known to be biodegradable by methanogenic fermentation. Then it should be expected to see in the future, the application of anaerobic digestion to a growing number of chemical wastewaters.

Necessity of pretreatments

Even if several chemical and petrochemical effluents cannot be methanized directly, because they contain organic compounds difficult to be treated anaerobically, toxic substances or an inadequate environment (i. e. high salinity), several pretreatment systems are in fact available to solve these problems. The technics of electrochemical (Pulgarin *et al.*, 1994), chemical (Koyama *et al.*, 1994) and photochemical (Yi *et al.*, 1994) oxidations or else ozonisation (Wang, 1990), by their ability to modify the structure of the molecules (cleavage of the aromatic nucleus and polymeric linear chains, introduction of oxygen within the stucture) allow for instance to increase the biodegradability and decrease the toxicity of the effluents. On its side, the high salinity can be eliminated by a selective filtration through membranes permeables to organic substances but not mineral salts (Brookes and Livingston, 1994).

Without going to so sophisticated systems which are moreover for most of them still at the experimental stage, a simple adjustement of pH may be the solution to toxicity problems. In this way, formaldehyde which is strongly toxic to microorganisms because of its capacity to react with proteins and denaturate them, transforms spontaneously at high pH (11-12) and temperature in a mixture of sugar, methanol and formic acid. This technique has been applied successfully at pilot scale (UASB reactor of 6 m^3) to detoxify the effluents from the production of DMT (formaldehyde concentration of 2-3 g/L) otherwise not biodegradable anaerobically (de Bekker *et al.*, 1983). Other example of simple solutions is that selected for the effluents of PTA production. This

Table

Reactor number	Year of construction	
1	1981	C B
2	1981	C P U
3	1984	H Fr
4	1985	M A
5	1986	D Ro
6	1986	Ho Lil
7	1987	Ho Cu Fra
8	1987	She Mo
9	1987	Tok Hyc
10	1988	Kan
11	1988	Osa
12	1988	Orie Osal
13	1988	Niga
14	1988	JGC,
15	1988	Shin Niga
16	1988	GLI New
17	1989	Capc Taiw
18	1989	Cheil Gumi
19	1989	Shell Deer I
20	1990	China
21	1990	Sam N (+ ext
22	1991	Tuntex
23	1992	Nigata
24	1992	Okaya
25	1992	Amoco Joliet, I
26	1992	Mossre South A
27	1992	Unichet
28	1992	Samyan Seoul, K
29	1992	Bombay Patalgan

Table 1. Full scale anaerobic digesters treating chemical and petrochemical wastewaters in the world (*)

Reactor number	Year of construction	Company and location	Industrial production generating the wastewater	Type of reactor	Reactor volume	Water COD	Organic Load	COD removal	Constructor / references (**)
					m^3	g O_2/L	kg COD/m^3.d	%	
1	1981	Celanese Bishop, TX, USA	Acetic acid , formaldehyde, methanol, polyols, polyesters	UAF	5682	7.12	3.6	81	Badger[1]
2	1981	Celanese Pampa, TX USA	Acetic, propionic, butyric and anhydride acetic acids Ketones, ethylacetate, Acrylic esters	UAF	5229	13.3	10.4	80	Badger[2]
3	1984	Hercules, Alizay France	Carboxymethylcellulose	-	3000	-	1.7	87	Biomechanics[3]
4	1985	Monsanto Corp Augusta, GA, USA	Aspartame	UAF	2 x 1900 in series	12	3 - 4 6 - 8	90 - 95 85 - 90	-[2,4]
5	1986	DSM Chemicals Rotterdam, Netherlands	Phenol	UASB	1280	30.5	9 - 12	95	Biothane[5]
6	1986	Hoechst Lillebonne, France	Acetaldehyde Glyoxylic acid	AC	3000	43	5.5	98	Degrémont[6]
7	1987	Hoechst Cuise-Lamotte France	Glyoxylic acid and glyoxane Paratertiobutylbenzoic acid Tienylacetic acid, hydantoine	DSFF	2150	45 - 50	7.4	90	Proserpol[6,7]
8	1987	Shell Chemie Moerdijk, Hollande	Methylstyrene and Propene oxides	UASB	1430	20 - 45	10 - 20	80 - 95	Biothane[8]
9	1987	Toban Dyeing, Hyogo, Japan	Dyeing wastewater	UAF	-	-	-	-	Badger
10	1988	Kanagawa, Japan	Synthetic resin	UAF	260	10.5	8	75	Shinko Pantec
11	1988	Osaka, Japan	Dyes	UAF	320	7	7	80	Shinko Pantec
12	1988	Orient Chemical Osaka, Japan	Chemical ink processing	UAF	-	-	-	-	Badger
13	1988	Nigata, Japan	Synthetic cellulose	UAF	2350	12.6	8	65	Shinko Pantec
14	1988	JGC, Kanagawa, Japan	Petrochemical	UAF	-	-	-	-	Badger
15	1988	Shin Etsu chemical Nigata, Japon	Chemical processing	UAF	-	-	-	-	Badger
16	1988	GLI corp. Newport, TN, USA	Artificial sweetener (sucralose)	BVF	26,500	8.3	0.83	75	ADI
17	1989	Capco Co. Taiwan	Purified terephthalic acid	DSFF	2 x 5000	10	3 - 4	85 (TOC)	Amoco[9]
18	1989	Cheil Synthetic textiles Gumi, Korea	Polyester resins	UAF	-	-	-	-	Badger
19	1989	Shell oil Co., Deer Park, TX, USA	Chemical processing	UAF	-	-	-	-	Badger
20	1990	China	Purified terephthalic acid	Hybrid	4 x 3000	9	6.3	80	-[10]
21	1990	Sam Nam, Korea (+ extention 1994)	Purified terephthalic acid	AC Hybrid In series	2000 2 x 1100	12.6 20	4.35 10	75 79	Purac[11] ADI[12]
22	1991	Tuntex, Taiwan.	Purified terephthalic acid	UASB	7000	6 - 13	10	55	Grontmij[13]
23	1992	Nigata, Japan	Carboxymethylcellulose	UAF	1210	7.8	7	75	Shinko Pantec
24	1992	Okayama, Japan	Ligth oil from asphalt	UAF	1025	8	6	55	Shinko Pantec
25	1992	Amoco Co Joliet, IL, USA	Purified terephthalic and isophthalic acids	DSFF	8200	-	3.5	85 (TOC)	Amoco
26	1992	Mossref, Mossel Bay South Africa	Synthetic fuels	DSFF	3 x 5000	14.2	8.5	93	Proserpol[14]
27	1992	Unichema, Taiwan	Oleochemicals (glycerine)	DSFF	400	4.4	4.8	70	Proserpol
28	1992	Samyang Co Seoul, Korea	Plastics	UASB	840	15	9.9	-	Biothane
29	1992	Bombay Dyeing Patalganga, India	DMT	UASB	1500	20	8	70	Paques

Table 1. Full scale anaerobic digesters treating chemical and petrochemical wastewaters in the world (continuation)

Reactor number	Year of construction	Company and location	Industrial production generating the wastewater	Type of reactor	Reactor volume m^3	Water COD g O_2/L	Organic Load kg COD/m^3.d	COD removal %	Constructor / references (**)
30	1992	Dae Han Ulsan, Korea	Diethylenglycol	UASB	2 x 82	3.6	7.5	-	Biothane
31	1992	Tonen Chemical Kawasaki, Japan	Maleic acid	UASB	100	13.6	17.8	90	Paques
32	1992	Nutrasweet Co. Univ. Park, IL, USA	Aspartame	UASB	2 x 600	22	7.8	-	Biothane
33	1992	Caldic Europoort Netherlands	Fiberglass	EGSB	275	40	10	98	Biothane[15]
34	1992	Northwest Pipeline Co. Opal, Wyoming, USA	Natural Gas processing	UAF	2 x 108 in series	13.4	8	90 - 95	EnviroSystems Supply Inc.[16]
35	1993	Amoco Co. Geel, Belgium	Purified terephthalic & Isophthalic acids	DSFF	15200	16.7	3.7	80 (TOC)	Amoco[17]
36	1993	Exxon Co, Santa Barbara, Ca, USA	Oil well produced water	UAF	-	-	-	-	Badger
37	1993	Petrocel, Mexico	DMT	UASB	2 x 2400	18.5	7.5	95	Biothane
38	1993	Hoescht Celanese Calisbury, NC, USA	Polyester resin	UAF	-	-	-	-	Badger
39	1994	Robertet Grasse, France	Perfumes	FB	92	8.4	27.7	94	Degrémont
40	1994	Reliance Industries Hazira, India (+ extension 1997)	Purified terephthalic acid	Hybrid	2 x 3076	8.3	4.8	66	ADI[11]
					2 x 4190	6.28	5.3	70	
41	1994	Akso-Nobel Emmen, Netherlands	Aramid fibers	UASB	1400	0.65	3.8	60	Paques
42	1994	ATV petrochemicals Mathura, India	Purified terephthalic acid	UASB+UAF in series	1330 (UASB)	12	10-12	> 60	Paques
43	1995	Tae Kwang Korea	Polyesters	Hybrid	500	20	10	80	ADI
44	1995	TNT Thailand	Nylon and PET fibers	BVF	2700	9	1	80	ADI
45	1995	Castagna Unilevel Italy	Ethyl acetate recovery from rotagravure printing	UASB	16	5	4.7	96	Biothane
46	1995	DuPont de Nemours Dordrecht, Netherlands	Thermoplastics	EGSB	550	7.5	10	90	Biothane[18]
47	1996	SBI - Sanofi Grasse, France	Perfumes	AC	900	-	4.4	90	OTVKruger[3]
48	1996	BKC Indonesia	Purified terephthalic acid	AC	4000	6 - 13	1.7 - 2.3	> 80	Purac
49	1996	Eastman Chemical Argentina	PET	UASB	144	12	12	90 - 95	Biothane
50	1996	Volos PET Industry S.A., Greece	PET	EGSB	250	25	18	90	Biothane
51	1996	Technoparco valbasento, Italy	Epichlorohydrin	UAF	100	14 - 16	8	83	Enitricerche[19]
52	1996	SK Chemicals Korea	Polyesters and Purified terephthalic acid	hybrid	800	15.6	9	80	ADI
53	1996	Garware Chemicals Aurangabad, India	DMT and films	UASB	1088	-	7	-	Paques
54	1996	Rhône Poulenc Châlampé, France	Nylon	UASB	990	16	8	80	Paques[20]
55	1997	Reliance Industries Patalganga, India	Purified terephthalic acid	hybrid	800 (***)	8	5.4	52	ADI[21]
56	1998	Dupont Far Eastern Petroch. Ltd, Taiwan	Purified terephthalic acid	hybrid	1 x 5000 1 x 4000	6.5	5.6	65	ADI
57	1998	Eastman Chemical Malaysia	Ethylene glycol	hybrid	2 x 33	6.45	2.6	87	ADI

Table 1. Full

Reactor number	Year of construction	
58	1998	H N
59	1998	S
60	1998	C B
61	1998	T F
62	1998	T N
63	1999	E T

(*) The abreviations are t as in table 1 and from t (1988)[5], Roy & Durand (1999)[12], Pereboom *et a* Anonyme (1996)[19]; Boul FB reactor designed by D

Type of wastewate
Production of acry esters[1]
Synthetic wastew hydroquinone[2]
Refinery sour wat
Furfural productic
Production of phe phenol molding c
Platicizer product a resin distillation
Synthethic effluer benzaldehyde anc
Production of sty polymeric resins[8]

(*) Dohányos *et* (1994)[6], Todini &

Table 1. Full scale anaerobic digesters treating chemical and petrochemical wastewaters in the world (continuation)

Reactor number	Year of construction	Company and location	Industrial production generating the wastewater	Type of reactor	Reactor volume	Water COD	Organic Load	COD removal	Constructor / references (**)
					m^3	g O_2/L	kg COD/m^3.d	%	
58	1998	Hoechst, Vlissingen Netherlands	DMT	EGSB	550	33.8	13.2	-	Biothane
59	1998	Sasa, Turkey	DMT & PET	EGSB	2 x 1000	6.5	13	-	Biothane
60	1998	Catalana de polimers Barcelona, Spain	PET	UASB	635	18	5	90	Arema[22]
61	1998	Toray Plastics Europe France	PET	DSFF	400	5	5	70 - 80	Proserpol
62	1998	Temex Mexico	Purified terephthalic acid & PET	Upflow pond	20000	6 - 12	2 - 3	60 - 70	IBtech[23]
63	1999	Rotapas Turkey	Solvents recovery from a print shop	EGSB	50	8	8	-	Biothane

(*) The abreviations are the same as in table 1, DMT = Dimethylterephthalate, PET = Polyethylene terephthalate (**) The information comes from the same source as in table 1 and from the following articles : Harvey & Rubiano (1983)[1], Young (1991)[2], Feuillette (1996)[3], Young & Young (1991)[4], Borghans & van Driel (1988)[5], Roy & Durand (1994)[6], Henry & Varaldo (1988)[7], Frankin *et al.* (1994)[8], Shelley (1991)[9], Macarie *et al.* (1992)[10], Page *et al.* (1998)[11], Young *et al.* (1999)[12], Pereboom *et al.* (1994)[13], Marx (1994)[14], Zoutberg & de Been (1992)[15], Ferrel & Young (1993)[16], Vandufel (1993)[17], Constable & Kras (1998)[18], Anonyme (1996)[19], Boulenger *et al.* (1999)[20], Page *et al.* (1999)[21], Fdz-Polanco *et al.* (1998)[22], Noyola *et al.* (1999)[23]. (***) Refurbished from an existing anaerobic FB reactor designed by Dorr-Oliver.

Table 2. Laboratory studies showing the possibility to apply anaerobic digestion to chemical effluents untreated by this way at full scale until now

Type of wastewater (*)	Type of reactor (**)	Reactor volume	Wastewater COD	Organic loading rate	COD removal
		L	g O_2/L	kg DCO/m^3.d	%
Production of acrylic acid and related esters[1]	UAF	5	19	2.6	97
Synthetic wastewater containing hydroquinone[2]	UAF	0.5	1 - 4	3.2 - 60	47 - 100
Refinery sour water stripper bottoms[3]	FB with GAC	-	1.5	2 - 11	63 - 91
Furfural production[4]	UAF	9.5	10 - 16	23	92
Production of phenolic resins and phenol molding compounds[5]	FB with GAC (**)	30	39	5.6	98
Platicizer production and effluent from a resin distillation column[6]	Hybrid	1	17	12	58
Synthethic effluent containing benzaldehyde and saccharose[7]	UASB	2	-	4.8	84
Production of styrene-divinylbenzene polymeric resins[8]	UASB	6	8-10	4.5	78

(*) Dohányos *et al.* (1988)[1], Szewzyk and Schink (1989)[2], Gardner *et al.* (1988)[3], Wirtz and Dague (1993)[4], Goeddertz *et al.* (1990)[5], Nemer *et al.* (1994)[6], Todini & Hulshoff Pol (1992)[7], Dandcong *et al.* (1994)[8]. (**) GAC: Granular Activated Carbon.

type of wastewater, characterized by a pH of 4.5 and a temperature of 56°C, contains a high concentration (1-4 g/L. 30-40% of the COD) of terephthalic acid (1,4-benzenedicarboxylic acid, TA) which is poorly soluble in water (19 mg/L at 25°C, 400 mg/L at 100°C) and has a high density (1.5 g/mL at 25°C) (Noyola *et al.*, 1999). These characteristics indicate that because of its particulate form, TA cannot be degraded significantly in high rates digesters operated with short hydraulic retention times. Its deposition in tanks and lines would also generate serious plugging problems of the reactor feeding tubes as well as displacement of the active biomass. Two solutions based on its physical properpies are presently used at full scale. The first consists to withdraw it from the wastewater by primary settling without treating it in the anaerobic unit (reactor 20 in Table 1), and the second to transform it by a simple neutralisation in its much more soluble sodium salt 140 g/L at 25°C, Merck 1999/2000 catalog of chemical products) and to treat it in the biological phase (reactors, 17, 25 and 35 in table 1). This last solution lead to the register of a patent on the recirculation of the digester effluent and stripping of CO_2 in the recycle line in order to decrease substantially the cost of neutralization related to TA dissolution (Ely and Olsen, 1989). The previous comments show that anaerobic digestion should not be eliminated straight away at the first problem and that the possibility to apply it to a chemical or petrochemical wastewater must be the result of a detailled evaluation.

Type of reactors applied for the treatment of chemical and petrochemical effluents

Despite the precursory work of Hovious *et al.* (1973), the technology of low rate reactors seems to have found little echo in the (petro)chemical industry since only two reactors of this type have been constructed so far (table 1, reactors 16, 44). The situation is similar for the anaerobic contact digesters (Table 1, reactors 6, 21, 47, 48). This situation may be due to the fact that chemical industries are customed to « high tech » technologies which means that they are probably more attracted by high rate processes. In this last category, all the types of digesters have been applied. The first realizations were based however on the technology of the upflow anaerobic filter and until 1989, they represented the majority (63%, 12 on 19) of the installed reactors. During the same period, only 2 UASB reactors (10.5% of the reactors) were built when this system was already the anaerobic leading technology in other industrial sectors. During the following years, UASB systems progressed (32% of the reactors), but globally reactors with static packing (UAF, DSFF, hybrid) remained majority (46% of the reactors). This situation does not appear to be related to sludge granulation difficulties. During the last 6 years, 1 Fluidized bed reactor and 6 EGSB have been also applied. Their small number is probably due to the fact that these technologies have reached commercialization only recently.

Contrarily to what happens in the other industrial sectors, for chemistry and petrochemistry, all the type of high rate reactors are not interchangeable. Again, a precise example correspond to the case of the effluents generated during the production of terephthalic acid. Whereas DSFF and hybrid reactors are able to degrade the whole effluent after neutralisation and reach COD removal higher than 75% (Table 2, reactors 17, 20, 25, 35), single stage UASB reactors cannot exceed usually 55% COD removal (Table 1, reactors 22 and 42) (Macarie *et al.*, 1992; Pereboom *et al.*, 1994; Shelley 1991). This different behavior lies in the fact that this wastewater contains aromatic acids easily (acid benzoic) and not easily biodegradable (terephthalic and p-toluic acids) as well as acetic acid and that the degradation of terephthalic and p-toluic acids is inhibited in the presence of benzoic and acetic acids (Macarie and Guyot, 1992; Fajardo *et al.*, 1997). The degradation of all the organic compounds in only one reactor thus requires the separation in space of two distinct bacterial populations. The first population has for role to eliminate the benzoic and acetic acids and by the same way, to detoxify the medium for a second population specialized in the degradation of terephthalic and p-toluic acids. Such a physical separation is possible only when the biomass is distributed on all the height of the digesters. This corresponds perfectly to DSFF reactors due to the disposition of the packing available for biomass fixation but also to hybrid reactors for which the biomass is physically separated between a sludge bed at the bottom and a bacterial film on support at the top. This advantage does not exist however in conventional perfectly mixed single stage UASB reactors.

Another example of the importance of the type of reactor, corresponds to the effluents containing formaldehyde. As we saw previously, this last compound is strongly toxic, it is however biodegradable below a certain concentration. A simple dilution of the wastewater can thus make it possible to eliminate toxicity and by the same way to avoid an expensive chemical pretreatment. Dilution with water of river being prohibited, a dilution in closed loop with the water coming out of the digester is possible. The level of dilution necessary requires however a very high rate of recirculation involving high water upflow velocities that only fluidized bed and EGSB reactors are able to tolerate. This scheme corresponds to the solution chosen for the effluents of the companies Caldic Europoort and DuPont both in the Netherlands which manufacture respectively glass fibre and thermoplastics (Table 1, reactors 33 and 46). Such design has been shown also at lab scale as a good option for the treatment of high formaldehyde binding DMT wastewaters (Frankin *et al.*, 1994a), and has been recently implemented at full scale in The Netherlands and Turkey (Table 1, reactors 58, 59).

CONCLUSIONS

Although anaerobic digestion is already applied at least in 63 chemical and petrochemical companies, its development in this industrial sector remains limited until now. The capacity of growth is however very strong and more interest on its application has

pointed out these last 4 years. An expansion similar to that met for terephthalic acid is indeed, possible for all the effluents already treated by this way on an industrial scale and beyond for all the effluents which contain the molecules mentioned in table 4. The still low growth rate of anaerobic digestion in this industry seems related to a lack of adequate promotion. It is surprising for instance, that while an UASB reactor is in operation since 1986 to treat the wastewaters of phenol production, no other reactor has been built to treat the same type of effluent since this date. The success of a project in this sector will be only the result of a study undertaken with rigour. It will be in particular necessary to test several types of reactors in parallel.

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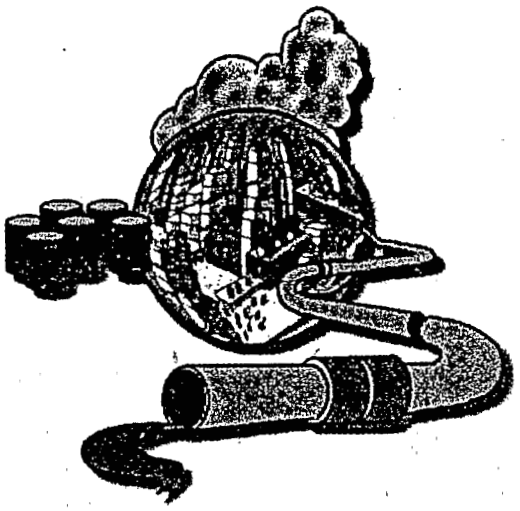

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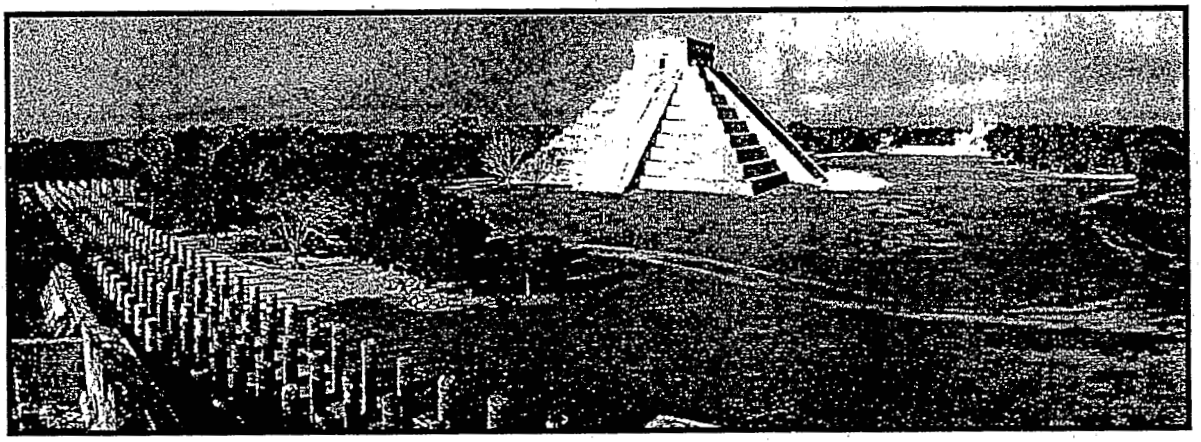

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