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This version has been corrected from the published one due to the detection of 3 plants counted twice in the original Table 2.

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

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ABSTRACT

During the last 20 years, as a result of its low cost, anaerobic digestion has turned into a popular wastewater treatment technology. Today, with at least 1330 reactors constructed in the world, it is considered to have reached the technological maturity. Until recently however, it was 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 80 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 characteristics of 62 of the 80 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: physicochemical 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: DSFF) or moving (Fluidised Bed reactors: FB) supports but also by selecting well settling flocculating biomass (Anaerobic Contact: AC, Upflow Anaerobic Sludge Blanket reactors: UASB, Expanded Granular Sludge Bed reactors: EGSB, Internal Circulation reactors: IC). 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 1330 low and high rates reactors constructed in the world (Table 1) anaerobic digestion is considered to have reached the technological maturity. Other inventory indicates, even, a number of anaerobic plants in excess of 2000 (Totzke, 1999). Until today, however, anaerobic treatment has been applied quite exclusively (76% of all the reactors in operation) to the treatment of wastewaters from the food

Table 1. Estimated number of the full scale reactors built in the world for treating several kinds of wastewaters (*)

Type of Wastewater	Type of reactor (**)									
	Low rate & CSTR	AC	UAF	DSFF	Hybrid	UASB	EGSB	IC	FB	**Total number**
Food and related industries										
Brewery and malt	2	-	5	1	-	169	15	33	4	**229**
Distillery & ethanol	25	24	8	24	6	72	1	3	-	**163**
Food and fruit processing	5	7	10	-	1	64	6	4	1	**98**
Sugar production	-	43	1	2	3	31	2	-	1	**83**
Soft drinks and tea beverage	-	-	3	-	7	58	1	1	2	**72**
Potato processing	11	3	3	-	-	44	2	4	-	**67**
Starch production	2	7	7	1	-	36	4	1	2	**60**
Dairy and cheese	12	6	3	2	1	22	-	4	1	**51**
Yeast production	4	3	2	-	3	24	6	-	-	**42**
Candy/Confectionery/Chewing gum	2	-	1	1	1	14	1	1	-	**21**
Slaughterhouse and meat rendering	2	4	4	1	-	5	-	-	-	**16**
Fruit Juice	-	3	-	-	-	12	1	-	-	**16**
Cannery	-	1	2	1	1	8	-	1	-	**14**
Citric acid production	2	2	1	-	-	3	1	2	1	**12**
Wine processing	-	-	-	-	6	4	-	-	-	**10**
Coffee processing	-	-	2	-	5	3	-	-	-	**10**
Vegetable processing	2	1	3	-	-	2	-	-	1	**9**
Fish & Sea food processing	1	4	-	-	-	2	-	-	-	**7**
Ice cream production	-	3	3	-	-	1	-	-	-	**7**
Jam production	-	-	1	3	-	1	-	-	1	**6**
Bakery	-	1	-	-	1	3	-	-	-	**5**
Pectin production	-	4	-	-	-	-	-	-	-	**4**
Fermentation	-	-	-	-	1	1	1	-	-	**3**
Tobacco manufacture	-	-	-	-	-	3	-	-	-	**3**
Chocolate processing	-	-	-	-	-	2	-	-	-	**2**
Store garbage	-	-	-	2	-	-	-	-	-	**2**
Guar gum manufacture	-	-	1	-	-	-	-	-	-	**1**
Cooking oil production	-	-	-	-	-	1	-	-	-	**1**
Non Food Industries										
Pulp and paper	1	14	4	-	2	75	-	7	3	**106**
Petrochemical and chemical	3	4	17	12	11	23	9	-	1	**80**
Leachates	-	-	1	1	1	17	-	-	-	**20**
Pharmacy	4	2	2	1	-	5	3	-	-	**17**
Pig, cow manure & poultry	5	3	3	2	-	1	-	-	-	**14**
Natural rubber	-	-	3	-	-	3	-	-	-	**6**
Sludge liquor	-	-	1	-	1	2	-	-	1	**5**
Textile	-	-	-	-	-	3	-	-	-	**3**
Tannery	-	-	-	-	-	2	-	-	-	**2**
Flue gas desulfurization	-	-	-	-	-	-	1	-	-	**1**
Electronic components manufacture	-	-	-	-	-	1	-	-	-	**1**
Sewage	-	-	2	-	1	58	-	-	-	**61**
Number of reactors per type	**83**	**138**	**91**	**54**	**51**	**772**	**54**	**61**	**19**	**1330**

(*) The data of this table have been compiled from the 1999 reference lists of ADI, Applied Technologies, Biotecs, Biothane, Biotim, Degrémont, Enviroasia, Paques and Proserpol, 1998 of Grontmij, 1994 of Badger and Purac as well as information on reactors built by local companies in Brazil (Hirata, 1994), Germany (Seyfried and Austermann-Haun, 1997) and Mexico (Monroy *et al*., 2000). (**) CSTR: Continuous Stirred Tank Reactor, AC: Anaerobic Contact, UAF: Upflow Anaerobic Filter, DSFF: Downflow Stationary Fixed Film reactor, UASB: Upflow Anaerobic Sludge Blanket reactor, EGSB: Expanded Granular Sludge Bed reactor, IC: Internal Circulation reactor, FB: Fluidised Bed reactor.

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 (4.6% of all the digesters in operation) as well as other industrial sectors such as the pulp and paper (8% 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 pre-treatment 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 2). Three more years passed before a third reactor was built and until 1989 as far investigated, only 16 full-scale reactors were in operation on that type of waste in the world (Table 2). From 1990 to date, the rate of construction of digesters for that industrial sector increased from 2.1 reactors/year for the past decade to 4.6 and presently, at least 80 digesters (6% of all the digesters) are treating chemical waste in the world (Table 1). Detailed information is given about 62 of them in Table 2. No data were available for the others (7 built by Biothane, 5 by Amoco Co., 1 by Biotim and 1 by Enviroasia).

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 and 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 and 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 bacteria, 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 2, 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, 12), 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 (reactor 1), 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 series was treated (reactor 14). Moreover, It should be noted that it is one of the few effluents, which has given rise to the construction of a series of anaerobic plants, 14 until now. In fact, in its case, anaerobic digestion seems, even, to be on the way to become the conventional form of treatment. The other activities which resulted in the construction of more than one reactor are the production of DMT (dimethylterephthalate, 4 plants), PET (polyethylene terephthalate, 6 plants) and aspartame (2 plants). 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 2. Already, several others have been successfully treated anaerobically at pilot or lab scale (Table 3). 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 (Table 4). Then it should be expected to see in the future, the application of anaerobic digestion to a growing number of chemical wastewaters.

Table 2. 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 m^3	Water COD g O_2/L	Organic Load kg COD/m^3.d	COD removal %	Constructor / references (**)
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	Biome-chanics[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, Netherlands	Methylstyrene and Propene oxides	UASB	1430	20 - 45	10 - 20	80 - 95	Biothane[8]
9	1987	Toban Dyeing, Hyogo, Japan	Dyeing wastewater	UAF	-	-	-	-	Shinko Pantec
10	1988	JGC, Kanagawa, Japan	Synthetic resin	UAF	260	10.5	8	75	Shinko Pantec
11	1988	Orient Chemical Osaka, Japan	Dyes	UAF	320	7	7	80	Shinko Pantec
12	1988	Shin Etsu chemical Nigata, Japan	Synthetic cellulose	UAF	2350	12.6	8	65	Shinko Pantec
13	1988	GLI corp. Newport, TN, USA	Artificial sweetener (sucralose)	BVF	26500	8.3	0.83	75	ADI
14	1989	Capco Co. Taiwan	Purified terephthalic acid	DSFF	2 x 5000	10	3 - 4	85 (TOC)	Amoco[9]
15	1989	Cheil Synthetic textiles Gumi, Korea	Polyester resins	UAF	-	-	-	-	Badger
16	1989	Shell oil Co., Deer Park, TX, USA	Chemical processing	UAF	-	-	-	-	Badger
17	1990	China	Purified terephthalic acid	Hybrid	4 x 3000	9	6.3	80	-[10]
18	1990	Sam Nam, Korea (+ extension 1994)	Purified terephthalic acid	AC Hybrid	2000 2 x 1100 In series	12.6 12.4	4.35 9	75 90	Purac[11] ADI[11, 12]
19	1991	Tuntex, Taiwan.	Purified terephthalic acid	UASB	7000	6 - 13	10	55	Grontmij[13]
20	1992	Nigata, Japan	Carboxymethylcellulose	UAF	1210	7.8	7	75	Shinko Pantec
21	1992	Okayama, Japan	Ligth oil from asphalt	UAF	1025	8	6	55	Shinko Pantec
22	1992	Amoco Co Joliet, IL, USA	Purified terephthalic and isophthalic acids	DSFF	8200	-	3.5	85 (TOC)	Amoco
23	1992	Mossref, Mossel Bay South Africa	Synthetic fuels	DSFF	3 x 5000	14.2	8.5	93	Proserpol[14]
24	1992	Unichema, Taiwan	Oleochemicals (glycerine)	DSFF	400	4.4	4.8	70	Proserpol
25	1992	Samyang Co Seoul, Korea	Plastics	UASB	840	15	9.9	-	Biothane
26	1992	Bombay Dyeing Patalganga, India	DMT	UASB	1500	20	8	70	Paques

Table 2. 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 (**)
27	1992	Dae Han Ulsan, Korea	Diethylene glycol	UASB	2 x 82	3.6	7.5	-	Biothane
28	1992	Tonen Chemical Kawasaki, Japan	Maleic acid	UASB	100	13.6	17.8	90	Paques
29	1992	Nutrasweet Co. Univ. Park, IL, USA	Aspartame	UASB	2 x 600	22	7.8	-	Biothane
30	1992	Caldic Europoort Netherlands	Formaldehyde	EGSB	275	40	17	98	Biothane[15]
31	1992	Northwest Pipeline Co. Opal, Wyoming, USA	Natural Gas processing	UAF	2 x 108 in series	13.4	8	90 - 95	EnviroSys-tems Inc[16]
32	1993	Amoco Co. Geel, Belgium	Purified terephthalic & Isophthalic acids	DSFF	15200	16.7	3.7	80 (TOC)	Amoco[17]
33	1993	Exxon Co, Santa Barbara, Ca, USA	Oil well produced water	UAF	-	-	-	-	Badger
34	1993	Petrocel, Mexico	DMT	UASB	2 x 2400	18.5	7.5	95	Biothane
35	1993	Hoechst Celanese Calisbury, NC, USA	Polyester resin	UAF	-	-	-	-	Badger
36	1994	Robertet Grasse, France	Perfumes	FB	92	8.4	27.7	94	Degrémont
37	1994 (ext. 1997)	Reliance Industries Hazira, India	Purified terephthalic acid	Hybrid	2 x 3076 2 x 4190	8.3 6.28	4.8 5.3	66 70	ADI[11]
38	1994	Akso-Nobel Emmen, Netherlands	Aramid fibers	UASB	1400	0.65	3.8	60	Paques
39	1994	ATV petrochemicals Mathura, India	Purified terephthalic acid	UASB+UAF in series	1330 (UASB)	12	10-12	> 60	Paques
40	1994	Aussapol, Italy	PET	Hybrid	750	12	1.6	77.5	Biotim
41	1994	Tuntex, Thailand	Purified terephthalic acid	UASB	3 x 3000	10	6	-	Hepe[18]
42	1995	Tae Kwang Korea	Polyesters	Hybrid	500	20	10	80	ADI
43	1995	TNT Thailand	Nylon and PET fibers	BVF	2700	9	1	80	ADI
44	1995	Castagna Unilevel Italy	Ethyl acetate recovery from rotagravure printing	UASB	16	5	4.7	98	Biothane
45	1995	DuPont de Nemours Dordrecht, Netherlands	Thermoplastics	EGSB	550	7.5	10	90	Biothane[19]
46	1996	SBI - Sanofi Grasse, France	Perfumes	AC	900	-	4.4	90	OTVKruger[3]
47	1996	BKC Indonesia	Purified terephthalic acid	AC	4000	6 - 13	1.7 - 2.3	> 80	Purac
48	1996	Eastman Chemical Argentina	PET	UASB	144	12	12	90 - 95	Biothane
49	1996	Volos PET Industry S.A., Greece	PET	EGSB	250	25	18	90	Biothane
50	1996	Technoparco Valbasento, Italy	Epichlorohydrin	UAF	110	14 - 16	8	83	Eniricerche[20]
51	1996	SK Chemicals Korea	Polyesters and Purified terephthalic acid	hybrid	800	15.6	9	80	ADI
52	1996	Garware Chemicals Aurangabad, India	DMT and films	UASB	1088	-	7	-	Paques
53	1996	Rhône Poulenc Chalampé, France	Nylon	UASB	990	16	8	80	Paques[21]

Table 2. 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 (**)
54	1997	Reliance Industries Patalganga, India	Purified terephthalic acid	hybrid	800 (***)	8	5.4	52	ADI[22]
55	1997	Catalana de polimers Barcelona, Spain	PET	UASB	635	30	10	90	Arema[23]
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
58	1998	Kosa, 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	Toray Plastics Europe France	PET	DSFF	400	5	5	70 - 80	Proserpol
61	1998	Temex Mexico	Purified terephthalic acid & PET	Upflow pond	20000	6 - 12	2 - 3	60 - 70	IBtech[24]
62	1999	Rotapas Italy	Solvents recovery from a print shop	UASB	50	8	8	-	Biothane

(*) The abbreviations are the same as in Table 1, BVF = Bulk Volume Fermenter, TOC = Total Organic Carbon, DMT = Dimethylterephthalate, PET = Polyethylene terephthalate (**) The information comes from the same source as in Table 1 and from the following articles: Harvey and Rubiano (1983)[1], Young (1991)[2], Feuillette (1996)[3], Young and Young (1991)[4], Borghans and van Driel (1988)[5], Roy and Durand (1994)[6], Henry and Varaldo (1988)[7], Frankin *et al*. (1994b)[8], Shelley (1991)[9], Macarie *et al*. (1992)[10], Page *et al*. (1998)[11], Young *et al*. (2000)[12], Pereboom *et al*. (1994)[13], Marx (1994)[14], Zoutberg and de Been (1997)[15], Ferrel and Young (1993)[16], Vanduffel (1993)[17], Kleerebezem (1999)[18], Constable and Kras (1998)[19], Anonym (1996)[20], Boulenger *et al*. (2000)[21], Page *et al*. (1999)[22], Fdz-Polanco *et al*. (1999)[23], Noyola *et al*. (2000)[24]. (***) Refurbished from an existing anaerobic FB reactor designed by Dorr-Oliver.

Table 3. 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 L	Wastewater COD g O_2/L	Organic loading rate kg DCO/m^3.d	COD removal %
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
Synthetic 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
2,4-dichlorophenoxyacetic acid production[9]	FB with GAC(**)	710	2.5-6.3	14-38	85-90
Styrene polymer synthesis plant[10]	UASB	4	2.2	4.3	> 75

(*) 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 and Hulshoff Pol (1992)[7], Dangcong *et al*. (1994)[8], Wilson *et al*. (1997)[9], Araya *et al*. (1999)[10]. (**) GAC: Granular Activated Carbon

Necessity of pre-treatments

Even if several chemical and petrochemical effluents cannot be methanised directly, because they contain organic compounds difficult to be treated anaerobically, toxic substances or an inadequate environment (e.g. high salinity), several pre-treatment systems are in fact available to solve these problems. The techniques of electrochemical (Pulgarin *et al*., 1994), chemical (Koyama *et al*., 1994) and photochemical (Yi *et al*., 1994) oxidation or else ozonation (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 structure) 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 adjustment 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 denature them, transforms spontaneously at high pH (11-12) and temperature (100ºC) in a mixture of sugars, 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 impossible to treat anaerobically unless applying a very high dilution (Bekker *et al*., 1983).

Other example of simple solutions is that selected for the effluents of PTA production. This type of wastewater, characterised by a pH of 4.5 and a temperature of 56ºC, contains a high concentration (1-4 g/L) of terephthalic acid (1,4-benzenedicarboxylic acid, TA), which is poorly soluble in water (19 mg/L at 25ºC, 400 mg/L at 100ºC) and has a high density (1.5 g/mL at 25ºC) (Macarie *et al*., 1992; Fajardo *et al*., 1997). 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 properties 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 17 in Table 2), and the second to transform it by a simple neutralisation (a minimum pH of 5.5 is necessary to avoid precipitation; Kleerebezem, 1999) in its much more soluble sodium salt (140 g/L at 25ºC, Merck 1999/2000 catalogue of chemical products) and to treat it in the biological phase (reactors, 14, 22 and 32 in Table 2). A complete neutralisation with external alkaline compounds is however not necessary since the alkalinity produced within the anaerobic system can be valorised through effluent recirculation. The alkaline power of the recycled effluent may even be increased by stripping of its CO_2 content (Ferguson *et al*., 1984). Such process, which reduces substantially the cost of neutralisation, has lead to the register of a patent (Ely and Olsen, 1989).

Two last examples of simple pre-treatments correspond to those applied at full scale in the case of Nylon wastewaters (Table 2, reactor 53) and effluents containing epichlorohydrin (1-chloro-2,3-epoxypropane), a solvent used in the manufacture of natural and synthetic resins, gums, cellulose esters and ethers as well as several other products (Table 2, reactor 50). Nylon wastewaters contain peroxides, which like oxygen are harmful to anaerobic bacteria. They can be easily eliminated by a combination of heat and catalytic treatment (Boulenger *et al*., 2000). Epichlorohydrin which is also toxic may be removed, from its side, through hot alkaline hydrolysis. The resulting effluent contains unfortunately an increased concentration of NaCl due to chloride liberation during the hydrolysis and must be further desalted with i.e. classical evaporation and crystallisation processes (Anonym, 1996).

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 detailed 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, such as anaerobic lagoons, seems to have found little echo in the (petro)chemical industry since only 3 reactors of this type have been constructed so far (Table 2, reactor 13, 43, 61). The situation is similar for the anaerobic contact digesters (Table 2, reactors 6, 18, 46, 47). This may be due to the fact that chemical industries are familiar of « 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 realisations were based however on the technology of the upflow anaerobic filter and until 1989, they represented the majority (56%, 9 on 16) of the installed reactors.

Table 4. Non exhaustive list of organic compounds biodegradable by methanogenic fermentation and susceptible to be present in the effluents of chemical and petrochemical industries (after Macarie, 1992).

Homocyclic aromatic compounds

Benzene
methylbenzene (toluene)

Benzoate
2-hydroxybenzoate (salicylate)
3-hydroxy
4-hydroxy
2,4-dihydroxy (β-resorcylate)
2,5-dihydroxy (gentisate)
2,6-dihydroxy (γ-resorcylate)
3,4-dihydroxy (protocatechuate)
3,5-dihydroxy (α-resorcylate)
2,3,4-trihydroxy
2,4,6-trihydroxy
3,4,5-trihydroxy (gallate)
3-chloro
4-chloro
3-chloro,4-hydroxy
3,5-dichloro
2-bromo
3-bromo
4-bromo
2-iodo
3-iodo
4-iodo
2-amino (anthranilate)
3-amino
4-amino
2-methyl (o-toluate)
3-methyl (m-toluate)
4-methyl (p-toluate)
2-methoxy
3-methoxy
4-methoxy (p-anisate)
3,4,5-trimethoxy
4-hydroxy-3- methoxy (vanillate)
4-hydroxy-3,5-dimethoxy (syringate)
2-nitro
2-acetyl (acetylsalicylate)

Benzaldehyde
4-hydroxy-3,5-dimethoxy (syringaldehyde)
4-hydroxy-3-methoxy (vanilline)

o, m, p-dicarboxybenzene (o, m, p-phthalate)
dimethyl o-phthalate & p-phthalate
diethyl o-phthalate
di-n-butyl o-phthalate
Butylbenzyl o-phthalate

Nitrobenzene
3-nitrobenzene sulfonate

Hydroxybenzene (phenol)
1,2-dihydroxybenzene (catechol)
1,3-dihydroxy (resorcinol)

Homocyclic aromatic compounds

1,4-dihydroxy (hydroquinone)
1,2,3-trihydroxy (pyrogallol)
1,3,5-trihydroxy (phloroglucinol)
3-hydroxy methyl- (m-cresol)
4-hydroxy methyl- (p-cresol)
2-chlorophenol
3-chloro
4-chloro
2,4-dichloro
3,4-dichloro
3,5-dichloro
pentachloro-
2-amino
2-methoxy
3-methoxy
4-methoxy
2,6-dimethoxy
2-nitro
3-nitro
4-nitro

phenylacetate
phenylpropenoate (cinnamate)
phenylpropionate (hydrocinnamate)
3-methoxy-4-hydroxy cinnamate (ferulate)
4-hydroxyphenylalanine (tyrosine)

Benzyl alcohol
4-hydroxy benzyl alcohol

Heterocyclic aromatic compounds

pyridine
3-pyridine carboxylate (nicotinate)
2,6-pyridinedicarboxylate (dipicolinate)
purine
adenine
xanthine
indole
tryptophane
uracil
quinoline
2-furaldehyde (furfural)

Aliphatic compounds

Hydrogen cyanide

Acids
acetic
acrylic
adipic
4-aminoadipic
n- & i-butyric
3-hydroxybutyric

Aliphatic compounds

caproic
citric
crotonic
formic
fumaric
glutaric
glyoxalic
lactic
maleic
palmitic (sodium salt)
propionic
3-hydroxypropanoic
sorbic
stearic (sodium salt)
succinic
n & i-valeric

Aldehydes
acetaldehyde
butyraldehyde
crotonaldehyde
formaldehyde
propionaldehyde

Alcohols
n & i-butanol
1,2 & 2,3-butanediol
3-methylbutanol
ethylene glycol
di, tri & polyethylene glycol
ethanol & 2-methoxyethanol
glycerol
methanol
octanol
pentanol
propanol & 1-amino-2-propanol
1,2-propanediol

Amines
butylamine
trimethylamine
triethanolamine

Ketones
acetone
methyl ethyl ketone

Esters
ethyl, methyl & vinyl acetate
butyl, ethyl & methyl acrylate
methyl butyrate
methyl propionate

Ethers
ethylene glycol monoethyl ether
methyl butyl ether

During the same period, only 2 UASB reactors (12.5% 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 (34.8% of the reactors), but globally reactors with static packing (UAF, DSFF, hybrid) remained majority (43.5% of the reactors). This situation does not appear to be related with sludge granulation difficulties. During the last 8 years, 1 Fluidised bed and 5 EGSB reactors have been also applied. Their small number is probably due to the fact that these technologies have reached commercialisation only recently.

Contrarily to what happens in the other industrial sectors, for chemistry and petrochemistry, all the types of high rate reactors are not interchangeable. Again, a precise example corresponds to the case of the effluents generated during the production of terephthalic acid. Whereas full-scale DSFF and hybrid reactors are usually able to remove efficiently TA, besides benzoic acid and acetic acid (the two other main organic pollutants present in this type of wastewater), single stage anaerobic contact and UASB reactors are often unable to achieve it, or at least much less efficiently and after a long lag phase (Vanduffel, 1993; Pereboom *et al*., 1994; Young *et al*., 2000). TA representing 7 to 50% of this wastewater COD, the performances of this last class of reactors may be limited to 50-60% COD removal (Table 2, reactors 19, 39) compared to a minimum of 75-80% for the others (e.g. reactors 14, 17, 18, 22, 32 in Table 2). Such difference in behaviour is probably related to an improved retention of biomass. Actually, TA primary degraders are characterised by an extremely low growth rate, which indicates that they should be retained more easily in reactors with some kind of packing as was observed by Kleerebezem *et al*. (1999b) in a study with UASB and hybrid reactors fed with TA as sole carbon and energy source. This explanation however is insufficient due to the fact that acetic and benzoic acids have been shown to inhibit the methanisation of TA (Fajardo *et al*., 1997; Kleerebezem *et al*, 1999a). 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 specialised in the degradation of terephthalic acid. Such a physical separation is possible only when the biomass is distributed on all the height of the digesters and these are operated in a plug flow mode which allows the formation of concentration gradients. This may be the case of 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 single stage perfectly mixed anaerobic contact and UASB reactors.

Another example of the importance of the type of reactor corresponds to the effluents containing formaldehyde. As indicated previously, this last compound is strongly toxic, it is however biodegradable below a certain concentration for which, an equilibrium between biomass growth and decay rates can be reached (Gonzalez-Gil *et al*., 1999). A simple dilution of the wastewater can thus make it possible to eliminate toxicity and by the same way to avoid an expensive chemical pre-treatment such as the one described above. Dilution with river water being prohibited, a dilution in closed loop with the water coming out of the digester is possible. The level of dilution necessary (10 to 30 to reach less than 0.5 g formaldehyde/L) requires however a very high rate of recirculation involving high water upflow velocities that only fluidised 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 formaldehyde and thermoplastics (Table 2, reactors 30 and 45). 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 2, reactors 58 and 59).

Due to the adsorptive properties of activated carbon, several lab-scale experiments (Table 3) have shown also that fluidised bed reactors packed with this type of carrier could deal with wastewaters (e.g. refinery stripper bottoms, phenolic resins, 2,4-D production) containing high concentrations of various toxicants otherwise difficult to treat with more classical anaerobic biological means (Gardner *et al*., 1988; Goedertz *et al*., 1990; Wilson *et al*., 1997). To date however these systems seem not to have reached practical application.

CONCLUSIONS

Although anaerobic digestion is already applied at least in 80 chemical and petrochemical companies, its development in this industrial sector remains limited until now. The capacity of growth is however very high 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

(Table 2) 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. It must be emphasised that the success of a project in this sector will be only the result of a study undertaken with rigour. Particularly the operation of a pilot scale unit on the industrial site is strongly recommended before the implementation of a full-scale unit.

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