Overview of 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 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 1970s and 1980s, 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. 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 developments at lab-scale and discusses some important concepts to consider before the implementation of an anaerobic treatment. In particular a table is presented with the main characteristics of 65 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 owing to its low cost compared with other technologies available: physicochemical and aerobic biological treatments. Its apparent initial drawbacks (very slow growth rate of the biomass, susceptibility to toxic compounds etc.), which translated into huge reactor volumes and operation upsets, were overcome by the development of a new generation of reactors. In these reactors, the problem of slow growth rate was overcome 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-rate reactors constructed in the world (Table 1) anaerobic digestion is considered to have reached technological maturity. Another inventory even indicates 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 and related industries (bakery, brewery, cannery, dairy, distillery, fish and potatoes processing,

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 and 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 and seafood 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 and 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.

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 on the anaerobic treatment of this type of wastewater started at the beginning of the 1970s. 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. A 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 was only in 1981 that the two 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 by 1989, as so far investigated, only 19 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 65 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 and from the chemical and petrochemical industries), postulating that anaerobes, particularly methanogens, contrary to aerobes, were too sensitive to deal with these type of wastewaters (supposedly highly toxic). In fact, a comparative study of tolerance to toxicity between aerobes and anaerobes has shown that such an 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 two 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 in the form of non-toxic metallic sulfides, allowed the first effluent to degrade directly within the anaerobic stage and by modifying the chemical structure of the polyols, transformed them into compounds biodegradable in the aerobic post-treatment unit (Harvey and Rubiano, 1983).

Nature of 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, 13), methanol (4, 10) and glycols (11) also found in more classical effluents for AD. If we except the case of Shell in 1986 with 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 benzene series was treated (reactor 17). Moreover, it should be noted that it is one of the few effluents that 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

Table 2 Full-scale anaerobic digesters treating chemical and petrochemical wastewaters (*)

Reactor number	Year of construction	Company and location	Industrial production generating the wastewater	Type of reactor	Reactor volume m³	Water COD g O_2/L	Organic load kg COD/ m³.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
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	Bio-mechanics[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	–	–	–	–	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, Japan	Chemical processing	UAF	–	–	–	–	Badger
16	1988	GLI corp. Newport, TN, USA	Artificial sweetener (sucralose)	BVF	26500	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]

Table 2 *Continued*

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 (**)
21	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}
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	Light 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
30	1992	Dae Han Ulsan, Korea	Diethylene glycol	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	Formaldehyde	EGSB	275	40	17	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	Enviro Systems Inc^{16}
35	1993	Amoco Co. Geel, Belgium	Purified terephthalic and 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	Hoechst Celanese Calisbury, NC, USA	Polyester resin	UAF	–	–	–	–	Badger
39	1994	Robertet Grasse, France	Perfumes	FB	92	8.4	27.7	94	Degrémont
40	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}
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	1994	Aussapol, Italy	PET	Hybrid	750	12	1.6	77.5	Biotim
44	1994	Tuntex, Thailand	Purified terephthalic acid	UASB	3 x 3000	10	6	–	Hepe^{18}
45	1995	Tae Kwang Korea	Polyesters	Hybrid	500	20	10	80	ADI
46	1995	TNT Thailand	Nylon and PET fibers	BVF	2700	9	1	80	ADI
47	1995	Castagna Unilevel Italy	Ethyl acetate recovery from rotagravure printing	UASB	16	5	4.7	98	Biothane
48	1995	DuPont de Nemours Dordrecht, Netherlands	Thermoplastics	EGSB	550	7.5	10	90	Biothane^{19}
49	1996	SBI - Sanofi Grasse, France	Perfumes	AC	900	–	4.4	90	OTVKruger^{3}
40	1996	BKC Indonesia	Purified terephthalic acid	AC	4000	6–13	1.7–2.3	> 80	Purac

Table 2 *Continued*

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 (**)
51	1996	Eastman Chemical Argentina	PET	UASB	144	12	12	90–95	Biothane
52	1996	Volos PET Industry S.A., Greece	PET	EGSB	250	25	18	90	Biothane
53	1996	Technoparco Valbasento, Italy	Epichlorohydrin	UAF	110	14–16	8	83	Enricerche[20]
54	1996	SK Chemicals Korea	Polyesters and purified terephthalic acid	hybrid	800	15.6	9	80	ADI
55	1996	Garware Chemicals Aurangabad, India	DMT and films	UASB	1088	–	7	–	Paques
56	1996	Rhône Poulenc Chalampé, France	Nylon	UASB	990	16	8	80	Paques[21]
57	1997	Reliance Industries Patalganga, India	Purified terephthalic acid	hybrid	800	8	5.4	52	ADI[22]
58	1997	Catalana de polimers Barcelona, Spain	PET	UASB	635	30	10	90	Arema[23]
59	1998	Dupont Far Eastern Petroch. Ltd, Taiwan	Purified terephthalic acid	hybrid	1 x 5000	6.5	5.6	65	ADI
60	1998	Eastman Chemical Malaysia	Ethylene glycol	hybrid	2 x 33	6 45	2.6	87	ADI
61	1998	Kosa, Vlissingen Netherlands	DMT	EGSB	550	33.8	13.2	–	Biothane
62	1998	Sasa, Turkey	DMT and PET	EGSB	2 x 1000	6 5	13	–	Biothane
63	1998	Toray Plastics Europe France	PET	DSFF	400	5	5	70–80	Proserpol
64	1998	Temex Mexico	Purified terephthalic acid and PET	Upflow pond	20000	6–12	2–3	60–70	IBtech[24]
65	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], Anon. (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.

biodegradable by methanogenic fermentation (Table 4). Consequently we may expect to see the application of anaerobic digestion to a growing number of chemical wastewaters.

Necessity of pre-treatments

Even if several chemical and petrochemical effluents cannot be methanised directly, because they contain organic compounds difficult to treat anaerobically, toxic substances or an inadequate environment (i.e. 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. High salinity can be eliminated by a selective filtration through membranes permeable to organic substances but not mineral salts (Brookes and Livingston, 1994).

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
Plasticizer 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], Goedertz *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

Without going to such sophisticated systems, which are moreover mostly 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 (100°C) 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).

Another example of a simple solution is that selected for the effluents of PTA production. This type of wastewater, characterised by a pH of 4.5 and a temperature of 56°C, 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 25°C, 400 mg/L at 100°C) and has a high density (1.5 g/mL at 25°C) (Macarie *et al.*, 1992; Fajardo *et al.*, 1997). These characteristics indicate that because of its particulate form, TA cannot be degraded significantly in high-rate 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 of withdrawing it from the wastewater by primary settling without treating it in the anaerobic unit (reactor 20 in Table 2), and the second of transforming it by a simple neutralisation (a minimum pH of 5.5 is necessary to avoid precipitation; Kleerebezem, 1999) into its much more soluble sodium salt (140 g/L at 25°C, Merck 1999/2000 catalogue of chemical products) and to treat it in the biological phase (reactors, 17, 25 and 35 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 a 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 56) 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 53). 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, in turn, through hot alkaline hydrolysis. The resulting effluent unfortunately contains 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 (Anon., 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 three reactors of this type have been constructed so far (Table 2, reactor 16, 46, 64). The situation is similar for the anaerobic contact digesters (Table 2, reactors 6, 21, 49, 50). 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 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 (63%, 12 on 19) of the installed reactors.

During the same period, only two UASB reactors (10.5% of the reactors) were built when this system was already the leading anaerobic 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 the majority (43.5% of the reactors). This situation does not appear to be related to sludge granulation difficulties. During the last eight years, one fluidised bed and five EGSB reactors have also been applied. Their small number is probably due to the fact that these technologies have reached commercialisation only recently.

In contrast to what happens in the other industrial sectors, for chemistry and petrochemistry, the types of high rate reactors are not all 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 TA efficiently, 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). With 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 22, 42) compared to a minimum of 75–80% for the others (i.e. reactors 17, 20, 21, 25, 35 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 owing to the fact that acetic and benzoic acids have been shown to inhibit the methanisation of TA (Fajardo *et al.*, 1997; Kleerebezem *et al.*,

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 (b-resorcylate)
  - 2,5-dihydroxy (gentisate)
  - 2,6-dihydroxy (g-resorcylate)
  - 3,4-dihydroxy (protocatechuate)
  - 3,5-dihydroxy (a-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 and 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- and i-butyric
  - 3-hydroxybutyric

Aliphatic compounds

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

- Aldehydes
  - acetaldehyde
  - butyraldehyde
  - crotonaldehyde
  - formaldehyde
  - propionaldehyde

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

- Amines
  - butylamine
  - trimethylamine
  - triethanolamine

- Ketones
  - acetone
  - methyl ethyl ketone

- Esters
  - ethyl, methyl and vinyl acetate
  - butyl, ethyl and methyl acrylate
  - methyl butyrate
  - methyl propionate

- Ethers
  - ethylene glycol monoethyl ether
  - methyl butyl ether

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 to eliminate the benzoic and acetic acids and thus 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 for DSFF reactors owing 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 in 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 33 and 48). 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 61 and 62).

Owing 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 (i.e. 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 reach practical application.

Conclusions

Although anaerobic digestion is already applied in at least 80 chemical and petrochemical companies, its development in this industrial sector has remained limited until now. The capacity of growth is, however, very high and there has been more interest in its application in these last four years. An expansion similar to that met for terephthalic acid is indeed possible for all the effluents already treated this way on an industrial scale (Table 2) and further for all the effluents which contain the molecules mentioned in Table 4. The still low growth rate of anaerobic digestion in this industry seems to be related to a lack of adequate promotion. It is surprising for instance, that while a UASB reactor has been 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 the result only of a study undertaken with rigour. In particular, 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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References

Anonym (1996). Anaerobes tackle industrial effluent. *Water Quality International*, January/February, p. 34.

Araya, P., Aroca, G. and Chamy, R. (1999). Anaerobic treatment of effluents from an industrial polymers synthesis plant. *Waste Management*, **19**, 141–146.

Bekker de, P., Jans, T. and Piscaer, P. (1983). Anaerobic treatment of formaldehyde containing waste water. *Proc. of the European Symposium AWWT*, W.J. van den Brink (ed.), 23–25 November 1983, Noordwijkerhout, TNO Corporate Communication Department, The Hague, the Netherlands, pp. 449–463.

Blum, D.J.W. and Speece, R.E. (1991). A database of chemical toxicity to environmental bacteria and its use in interspecies comparisons and correlations. *Res. J. WPCF*, 63, 198–207.

Borghans, A.J.M.L. and van Driel, A. (1988). Application of the biothane® UASB reactor to a chemical waste water, containing phenol and formaldehyde. *Poster-Papers, 5th Int. Symp. Anaerobic Digestion*, Bologna, Italy, A. Tilche and A. Rozzi (eds.), Monduzzi Editore, Bologna, Italy, pp. 627–630.

Boulenger, P., Driessen, W., van de Werfhorst and Tielbaard, M. (2000). Anaerobic effluent treatment by a pilot and full scale plant at a chemical industrial complex. *Wat. Sci. Tech.*, **42** (5–6) 283–287 (this issue).

Brookes, P.R. and Livingston, A.G. (1994). Biotreatment of a point-source industrial wastewater arising in 3,4-dichloroaniline manufacture using an extractive membrane bioreactor. *Biotechnol. Prog.*, **10**, 65–75.

Chou, W.L., Speece, R.E. and Siddiqi, R.H. (1978). Acclimation and degradation of petrochemical wastewater components by methane fermentation. *Biotech. Bioeng. Symp.*, **8**, 391–414.

Constable, S.W.C. and Kras, R. (1998). Selection, start-up and operation of an anaerobic pretreatment system for wastewater from a thermoplastic production facility. *Proc. 71st Annual Water Environment Federation Conf.*, 3–7 October 1998, Orlando, Florida, USA, 10 pages.

Dangcong, P., Xingwen, Z., Qiting, J., Liangkui, X. and De, Z. (1994). Effects of seed sludge on the performance of UASB reactors for treatment of toxic wastewater. *J. Chem. Tech. Biotechnol.*, **60**, 171–176.

Dohányos, M, Zábrabska, J. and Grau, P. (1988). Anaerobic breakdown of acrylic acid. *Proc. 5th Int. Symp. Anaerobic Digestion*. E.R. Hall and P.N. Hobson (eds.), Pergamon Press, New York, USA, pp. 287–294.

Ely, S.R. and Olsen, G.P. (1989). Process for treatment of wastewater. US Patent. 4,826,600 (assigned to Amoco Co). 10 pages

Fajardo, C., Guyot, J.P., Macarie, H. and Monroy, O. (1997). Inhibition of anaerobic digestion by terephthalic acid and by products. *Wat. Sci. Tech.*, **36**(6–7), 83–90.

Fdz-Polanco, Hidalgo, M.D., Fdz-Polanco, M. and García Encina, P.A. (1999). Anaerobic treatment of polyethylene terephthalate (PET) wastewater from lab to full scale. *Wat. Sci. Tech.*, **40**(8), 229–236.

Ferguson, J.F., Brian, J.E. and Benjamin, M.M. (1984). Neutralization in anaerobic treatment of an acidic waste. *Wat. Res.*, **18**, 573–580.

Ferrel, N.J. and Young, J.C. (1993). Biological treatment of natural gas plant wastewater. *Proc. 48th Purdue Ind. Wast. Conf.*, Lewis Publishers, Chelsea, Michigan, USA, pp. 455–468.

Fueillette, C. (1996). Inventory of the industrial anaerobic reactors in France. Mémoire des Journées Industrielles sur la Digestion Anaérobie, 17–19 June 1996, Narbonne, France, INRA, pp. 1–9 (in French).

Frankin, R.J., Koevoets, W.M.A. and Versprille, A.I. (1994a). Application of the Biobed® system for formaldehyde containing dimethylterephthalate (DMT) waste water. *Poster-Papers. 7th Int. Symp. Anaerobic Digestion*, 23–27 January 1994, Cape Town, South Africa, pp. 244–247.

Frankin, R.J., van Gils, W.M.A. and Wermeling, R.J.P. (1994b). Full scale anaerobic treatment of Shell wastewater containing benzoate with the Biothane® UASB process. *Poster-Papers. 7th Int. Symp. Anaerobic Digestion*, 23–27 January 1994, Cape Town, South Africa, pp. 248–251.

Gardner, D.A., Suidan, M.T. and Kobayashi, A. (1988). Role of GAC activity and particle size during the fluidized-bed anaerobic treatment of refinery sour water stripper bottoms. *J. WPCF*, **60**, 505–513.

Goedertz, J. G., Weber, S. and Ying, W. (1990). Startup and operation of an activated carbon (AnBAC) process for treatment of a high strengh multicomponent inhibitory wastewater. *Environ. Progress*, **9**, 110-117.

Gonzalez-Gil, G., Kleerebezem, R., van Aelst, A., Zoutberg, G. R., Versprille, A. I. and Lettinga, G. (1999). Toxicity effects of formaldehyde on methanol degrading sludge and its anaerobic conversion in Biobed® expanded granular sludge bed (EGSB) reactors. *Wat. Sci. Tech.*, **40**(8), 195–202.

Harvey, L.M. and Rubiano, J.C. (1983). The anaerobic approach: a better answer. *Ind. Waste*, **29**, 22–25.

Henry, M. and Varaldo, C. (1988). Anaerobic digestion treatment of chemical industry waste-waters at the Cuise-Lamotte (Oise) plant of Société française Hoechst. *Proc. 5th Int. Symp. Anaerobic Digestion*, E.R. Hall and P.N. Hobson (eds.), Pergamon Press, New York, USA, pp. 479–486.

Hirata, Y.S. (1994). Experiences and perspectives of industrial wastewater anaerobic treatment in Brazil. *Proc. III Taller y Seminario Latinoamericano Tratamiento Anaerobio de Aguas Residuales*. M. Viñas, M. Soubes, L. Borzaconi, L. Muxi (eds.), 25–28 October 1994, Montevideo, Uruguay, pp. 281–291 (In Portuguese).

Hovious, J., Conway, R. and Ganze, C. (1973). Anaerobic lagoon pretreatment of petrochemical wastes. *J. WPCF*, **45**, 71–84.

Kleerebezem, R. (1999). *Anaerobic Treatment of Phthalates. Microbiological and Technological Aspects*. PhD thesis, University of Wageningen, The Netherlands (ISBN 90-5808-127-3).

Kleerebezem, R., Hulshoff Pol, L.W. and Lettinga, G. (1999a). The role of benzoate in anaerobic degradation of terephthalate. *Appl. Environ. Microbiol.*, **65**, 1161–1167.

Kleerebezem, R., Ivalo, M., Hulshoff Pol, L.W. and Lettinga, G. (1999b). High rate treatment of terephthalate in anaerobic hybrid reactors. *Biotechnol. Prog.*, **15**, 347–357.

Koyama, O., Kamagata, Y. and Nakamura, K. (1994). Degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge. *Wat. Res.*, **28**, 895–899

Macarie, H. (1992). *Anaerobic Treatment of the wastewater of a petrochemical plant producing an aromatic compound, terephthalic acid (1,4-benzenedicarboxylic acid)*. PhD thesis, Université de Provence, France.

Macarie, H., Noyola, A. and Guyot, J.P. (1992). Anaerobic treatment of a petrochemical wastewater from a terephthalic acid plant. *Wat. Sci. Tech.*, **25**(7), 223–235.

Marx, F.T.I. (1994). Mossgas reaction water treatment plant. *Poster-Papers. 7th Int. Symp. Anaerobic Digestion*, 23–27 January 1994, Cape Town, South Africa, pp. 279–282.

Monroy, O., Famá, G., Meraz, M., Montoya, L. and Macarie, H. (2000). Anaerobic digestion for wastewater treatment in Mexico: state of the technology. *Wat. Res.*, **34**, 1803–1816.

Nemer, R., Zaloum, R., Gehr, R. and Guiot, S.R. (1994). Evaluation of available techniques for assessing anaerobic treatability of chemical effluents. *Proc. 17ème Symp. Int. sur le Traitement des Eaux Usées*. 15–17 November 1994, Montréal., Collection Environnement, Université de Montréal, 2, 32–45.

Noyola, A., Macarie, H., Varela, F., Landrieu, S., Marcelo, R. and Rojas, M.A. (2000). Upgrade of a petrochemical wastewater treatment plant by an upflow anaerobic pond. *Wat. Sci. Tech.*, **42**(5–6) 269–276 (this issue).

Page, I.C., Cocci, A.A., Grant, S.R., Wilson, D.R. and Landine, R.C. (1999). Single stage anaerobic hybrid treatment of a polyester-intermediate production wastewater. *Prepint. Int. Conf. Waste Minimisation and End of Pipe Treatment in Chemical and Petrochemical Industries*, 14-18 November, 1999, Merida, Yucatan, Mexico, pp. 529–532.

Page, I.C., Wilson, D.R., Cocci, A.A. and Landine, R.C. (1998). Anaerobic hybrid treatment of terephthalic acid wastewater. *Proc. 71st Annual Water Environment Federation Conf.*, 3-7 October 1998, Orlando, Florida, USA, 3, 575–586.

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

Pulgarin, C. Adler, N., Péringer, P. and Comninellis, C. (1994). Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment. *Wat. Res.*, **28**, 887–893.

Roy, M.A. and Durand, M.B. (1994). The methanisation at French Company Hoechst. Journées Techniques Méthanisation des Effluents Industriels et Valorisation Energétique, 10 Ans d'Expériences. 11 October 1994, Compiègne, ATEE, France, 7 pages (in French).

Seyfried, C.F. and Austermann-Haun, U. (1997). Full scale experiences with the anaerobic pre-treatment of industrial wastewater in Germany. *Proc. 8th Int. Conf. Anaerobic Digestion*, 25–29 May 1997, Sendai, Japan, **1**, 75–82.

Shelley, S. (1991). The company's innovative biodegradation technique-using anaerobic bacteria to degrade chemical waste-wins the 1991 Kirkpatrick chemical engineering achievement award. *Chem. Eng.*, 98(12), 90–93.

Szewzyk, U. and Schink, B. (1989). Methanogenic degradation of hydroquinone in an anaerobic fixed-bed reactor. *Appl. Microbiol. Biotechnol.*, 32, 346–349.

Todini, O. and Hulshoff Pol, L. (1992). Anaerobic degradation of benzaldehyde in methanogenic granular sludge: the influence of additional substrates. *Appl. Microbiol. Biotechnol.*, 38, 417–420.

Totzke, D.E. (1999). 1999 anaerobic treatment technology overview. *Course on Anaerobic Treatment of High Strength Agricultural and Industrial Waste*, 20–21 September 1999, University of Wisconsin, Milwaukee, WI, USA, 14 pages..

Vanduffel, J.M. (1993). *Anaerobic treatment of organic acids*. National Conference on Anaerobic Treatment of Complex Wastewaters, Breda, The Netherlands (in Dutch).

Wang, Y.T. (1990). Methanogenic degradation of ozonation products of biorefractory or toxic aromatic compounds. *Wat. Res.*, **24**, 185–190.

Wilson, G.J., Suidan, M.T., Maloney, S.W and Brenner, R.C. (1997). The biodegradation of 2,4-D industrial wastewater utilising a pilot-scale anaerobic GAC-FBR in Eastern Europe. *Proc. 70th Annual Water Environment Federation Conf.*, 18–22 October 1997. Chicago, Illinois, USA, 9 pages.

Wirtz, R.A. and Dague, R.R. (1993). Anaerobic treatment of a waste furfural production wastewater. *Waste Management*, **13**, 309–315.

Yi, Q., Yibo, W. and Huiming, Z. (1994). Efficacy of pretreatment methods in the activated sludge removal of refractory compounds in coke-plant wastewater. *Wat. Res.*, **28**, 701–707.

Young, J.C. (1991). Factors affecting the design and performance of upflow anaerobic filters. *Wat. Sci. Tech.*, **24**(8), 133–155.

Young, J.C., Kim, I.S., Page, I.C., Wilson, D.R., Brown, G.J. and Cocci, A.A. (2000). Two stage anaerobic treatment of purified terephthalic acid production wastewaters. *Wat. Sci. Tech.*, 42(5–6), 277–282 (this issue).

Young, J.C. and Young, H.W. (1991). Full scale treatment of chemical process wastes using anaerobic filters. *Res. J. WPCF*, **63**, 153–159.

Zoutberg, G.R. and de Been, P. (1997). The Biobed® EGSB (expanded granular sludge bed) system covers shortcomings of the upflow anaerobic sludge blanket reactor in the chemical industry. *Wat. Sci. Tech.*, **35**(10), 183–188.

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