Pergamon

Wat. Sci. Tech. Vol. 36, No. 2–3, pp. 237–248, 1997.

Printed in Great Britain.
0273–1223/97 $17·00 + 0·00

PII: S0273-1223(97)00393-4

ANAEROBIC PRE-TREATMENT OF PETROCHEMICAL EFFLUENTS: TEREPHTHALIC ACID WASTEWATER

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ABSTRACT

During petrochemical production of purified terephthalic acid (PTA, 1,4-benzene dicarboxylic acid), a large quantity of concentrated effluent is produced. Main polluting compounds in this wastewater are terephthalic acid, acetic acid and benzoic acid in decreasing order of concentration. Acetic acid and benzoic acid are known to be rapidly degraded in high rate anaerobic treatment systems, such as Upflow Anaerobic Sludge Bed (UASB) reactors. Concerning the kinetics of anaerobic mineralization of terephthalic acid, however, no information is available in literature. Therefore our work focused on the anaerobic degradation of neutralized terephthalic acid (disodium terephthalate) in laboratory scale UASB-reactors and batch reactors. It was found that high rate anaerobic treatment of terephthalate was difficult to obtain due to the low growth rate ($\mu \approx 0.04$ day^{-1}) of the terephthalate mineralizing mixed culture. The maximum removal capacity of a lab-scale UASB-reactor was found to be 3.9 g $COD.l^{-1}.day^{-1}$ at a loading rate of 4.5 g $COD.l^{-1}.day^{-1}$ and a hydraulic retention time of 24 hours. Terephthalate was used as sole carbon source during these experiments. Addition of small amounts of sucrose (co-substrate) to the influent, as a source of reducing equivalents, was found to have a negative influence on the anaerobic degradation of terephthalate. Also benzoate was found to inhibit the mineralization of terephthalate. Batch-toxicity experiments showed that terephthalate is not toxic to any of the species involved in its mineralization. Based on these observations, a staged anaerobic reactor system is suggested for the anaerobic pre-treatment of PTA-wastewater. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Anaerobic treatment; benzoic acid; petrochemical wastewater; terephthalic acid; UASB.

INTRODUCTION

Until recently the anaerobic treatment process was considered to be not feasible for pre-treatment of complex wastestreams originating from the petrochemical industry, as a result of presumed toxicity and poor biodegradability of aromatic compounds present in these wastestreams. Recently, however, microbiologists have shown that many aromatic compounds are biodegradable under methanogenic conditions, which has led to an increased interest in anaerobic treatment of these wastestreams. In this work the feasibility of anaerobic treatment for pre-treatment of purified terephthalic acid (PTA) wastewater was studied.

Production and application of PTA. PTA (1,4-benzenedicarboxylic acid) is among the top 50 chemicals manufactured in the world. The total amount of PTA produced was estimated to be 8.7 million tonnes in

1989 (Savostianoff, 1990). Production of PTA is generally based on the well-established process developed by the American Amoco group (Bemis *et al.*, 1982; Franck and Stadelhofer, 1988). This process consists of two steps. In the first step crude terephthalic acid (CTA) is produced through wet-oxidation of para-xylene with air. Acetic acid is used as solvent and the catalytic system consists of Co and Mn acetates and a bromine-based promoter. CTA is separated from the liquid broth by centrifugation and acetic acid is recovered by distillation and dehydration. The second step in the PTA production process is upgrading of the CTA through hydrogenation of impurities, using water as a solvent. The most well known application of PTA is in polyethylene terephthalate (PET) bottles, which are widely used for carbonated drinks. Other applications of PTA are polyester films, used in audio-visual, photographic and packaging fields and textile fibres.

Wastestreams produced during production of PTA. Both in the first and second step of the production process of PTA, wastestreams are produced. During recovery of the acetic acid solvent in the production of CTA, a concentrated wastewater containing mainly acetic acid is produced. Furthermore a solid wastestream (residue), containing mainly terephthalic acid, is produced through sedimentation in the liquid fraction of the centrifuge effluent. During purification of CTA a relatively large wastestream is produced with a low contamination level. In general the residue is dissolved in the wastewater through addition of base. Herewith, per ton of PTA, approximately 3-10 m^3 wastewater is produced with 5-20 $kgCOD.m^{-3}$. The raw wastewater has a pH of 3-5 and a temperature of 40-50°C. Main components in the wastewater are terephthalic acid, acetic acid, benzoic acid and p-toluic acid (4-methylbenzoic acid) in decreasing order of concentration. Minor components that can be present are 4-formylbenzoic acid, methylacetate, and p-xylene (Duffel, 1993; Liangming *et al.*, 1991; Macarie *et al.*, 1992; Pereboom *et al.*, 1993). After neutralization (and dissolution of terephthalic acid) with NaOH, all acids will be present as sodium salts, and are therefore referred to as acetate, benzoate and terephthalate. Structural formulas of the aromatic compounds present in PTA-wastewater are presented in Figure 1

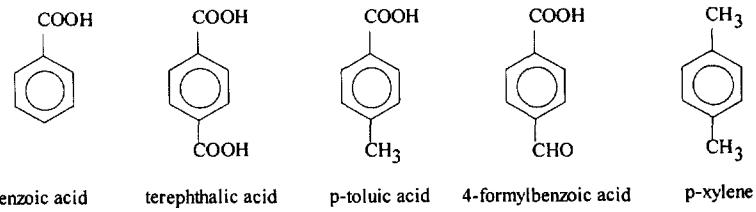

Figure 1. Aromatic compounds present in PTA-wastewater.

Anaerobic pre-treatment of PTA-wastewater. Traditionally PTA-wastewaters are treated using the activated sludge process (Lau, 1978). Advantages of aerobic treatment of PTA-wastewater are high purification efficiencies (>90 %), high process stability and rapid aerobic biodegradability of all compounds present in the wastewater. Disadvantages are high hydraulic retention times due to the high strength of the wastewater, high nutrient requirements due to total absence of nutrients in the raw wastewater, high surplus sludge production and high energy requirements due to aeration.

Combined anaerobic-aerobic treatment may be an interesting alternative to the conventional activated sludge system. Advantages of anaerobic pre-treatment of PTA-wastewater are less surplus sludge production, energy production through the formation of methane instead of energy consumption, and lower nutrient requirements. Furthermore, the high temperature and the high COD-concentration of PTA-wastewater are beneficial for anaerobic pre-treatment.

Considering the composition of the wastewater, a distinction can be made between compounds that are anaerobically easily degradable (benzoate and acetate) and compounds whose anaerobic biodegradability is unclear (terephthalate and p-toluate). Acetate is the main precursor of methane in anaerobic bioreactors and can be converted directly into methane and bicarbonate by methanogenic organisms. Benzoate can be degraded by syntrophic cultures consisting of acetogenic organisms and hydrogenotrophic and acetoclastic

methanogens (Schink *et al.*, 1992). Benzoate was shown to be not toxic to acetoclastic methanogenic activity (Sierra and Lettinga, 1991). Anaerobic degradation of acetate and benzoate can be performed at high rates (volumetric loading rates higher than 20 $kgCOD.m^{-3}.day^{-1}$) in anaerobic bioreactors, as has been shown on lab scale as well as full scale (Frankin *et al.*, 1994).

Only a very limited amount of microbiological research has been performed on the biodegradability of terephthalate and p-toluate under methanogenic conditions. Horowitz (1982) showed that p-toluate can be mineralized under methanogenic conditions by fresh-water sediment. Macarie (1992) showed that p-toluate as sole carbon source could be degraded in a UASB-reactor. Anaerobic biodegradability of terephthalate has only been shown by Lixian *et al.* (1992). Anaerobic biodegradability of the ortho-isomer of terephthalate, phthalate, was shown using inocula from fresh-water sediments and digested sewage sludge (Battersby and Wilson, 1989; Shelton and Tiedje, 1984). No kinetic data were found for anaerobic mineralization of terephthalate and p-toluate.

Table 1. Operational data from anaerobic bioreactors treating PTA-wastewater as described in literature

reference	full/lab scale	reactor type[1]	VLR[2] [$kgCOD.m^{-3}.d^{-1}$]	SLR[3] [$kgCOD.kgVSS^{-1}.d^{-1}$]	efficiency [%]	degradation of terephthalate[4]
Liangming et al. (1991)	lab	UASB	15	1.4	90	NA
	lab	hybrid	22	0.73	90	NA
Macarie et al. (1992)	lab	UASB	2.6	0.29	46	NA
	lab	DFF	1.9	0.09	74	NA
Pereboom et al. (1993)	full	UASB	10	1.1	55	-
	lab	UASB	4.5	0.4	80	+
Van Duffel (1993)	full	DFF	4.0	NA[4]	80	+

1) UASB: Upflow Anaerobic Sludge Blanket reactor; DFF: Downflow Fixed Film reactor, Hybrid: UASB reactor with packing material in top of the reactor instead of a three phase seperator.
2) VLR: Volumetric Loading Rate
3) SLR: Sludge Loading Rate
4) NA: data Not Available, - : no degradation observed, + : significant degradation observed.

Technological data on anaerobic treatment of PTA-wastewaters are available from lab-scale as well as full scale experiences. The obtained results, however, are very unclear and the maximum applicable loading rates reported vary between 2 and 22 $kgCOD.m^{-3}.d^{-1}$, as shown in Table 1. Straight forward comparison of the data in Table 1 is not possible. The described results are of course influenced by the reactor type applied, the source of the inoculum of the reactors, the composition of the wastewater as well as environmental factors as pH and temperature. But it is evident that from the available information in literature it is impossible for engineers to decide if anaerobic treatment of PTA-wastewater is an economically and technologically feasible alternative to conventional aerobic treatment.

MATERIAL AND METHODS

Continuous experiments. Continuous experiments were performed in UASB-type reactors with a total volume of 2.5 or 1.4 l. The reactors were equipped with an external three-phase separator as shown in Figure 2. Biogas produced was led through a 20% NaOH solution for removal of CO_2, and a column filled with soda lime pellets for removal of rest-amounts of CO_2 and water vapour. Methane production was measured using wet-test gas meters (Meterfabriek Dordrecht, The Netherlands). The reactors were seeded with methanogenic granular sludge from a wheat starch processing factory (Latenstein, The Netherlands). The initial specific methanogenic activity on acetate of the granular sludge amounted to 0.67 $gCOD.gVSS^{-1}.day^{-1}$. The reactors were placed in a temperature controlled room at 30±1°C. Artificial substrate and nutrients were fed from separate containers using a multichanel peristaltic pump. Substrate was placed in a refrigerator at 4°C to avoid microbial growth inside the container. Terephthalate, benzoate, butyrate and

acetate were dosed as sodium salts. The composition of the nutrient solution applied was (in $mg.l^{-1}$ influent): NH_4Cl (1040), KH_2PO_4 (170), $(NH_4)_2SO_4$ (170), $MgCl_2.6H_2O$ (150), KCl (270), yeast extract (18). Trace elements were dosed from a stock solution (Huser *et al.*, 1980) (1 $ml.l^{-1}$ influent). $NaHCO_3$ was added to the influent in a concentration of 3.0 $g.l^{-1}$ to avoid a pH-drop inside the reactor. All solutions were prepared in tap water.

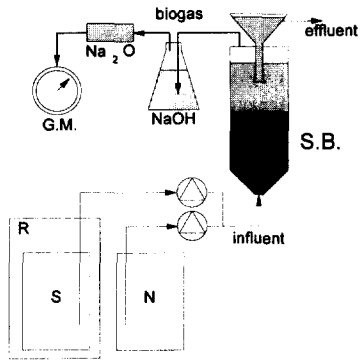

Figure 2. Set-up used for continuous experiments (S.B.: sludge bed; G.M.: gas meter, S: substrate, R: refrigerator (4°C), N: nutrient solution).

Batch experiments. Batch experiments were performed in 1000 ml serum bottles sealed with butyl rubber septa, using a liquid volume of 200 ml. The reactors were inoculated with approximately 1.5 $gVSS.l^{-1}$ of sludge from the continuous experiments. The basal medium used in the batch experiments contained the following (in $mg.l^{-1}$ liquid volume): $NaHCO_3$ (4000), NH_4CL (280), K_2HPO_4 (250), $MgSO_4.7H_2O$ (100), $CaCl_2.2H_2O$ (10), yeast extract (18) and one millilitre of a trace element stock solution (Huser *et al.*, 1980). Substrate was dosed from a neutralized stock solution. The headspace of the reactors was flushed with a mixture of N_2/CO_2 in a ratio of 70:30. After flushing the reactors, 1 ml of a 30 $g.l^{-1}$ $Na_2S.7\text{-}9H_2O$ stock solution was dosed to the reactors. The reactors were incubated at 30±1°C in an orbital-motion shaker.

Analyses. The methane content of the headspace of the batch reactors was measured according to Donlon *et al.* (1995). Determination of the concentration and composition of volatile fatty acids in batch and continuous experiments were performed as described by Visser (1995). The concentrations of terephthalate and benzoate were determined by high pressure liquid chromatography (HPLC). Centrifuged liquid samples were diluted to concentrations smaller than 50 $mg.l^{-1}$ using a Meyvis Dilutor (type no. 401) and a volume of 10 l was injected by autosampler (Marathon). Separation of the peaks was obtained using a Chromospher 5C18 column (100*3 mm). The solvent used as a carrier was a mixture of methanol and a 1% acetic acid solution in water, applied in a methanol-acetic acid ratio of 40-60, at a flow rate of 0.3 $ml.minute^{-1}$. The separated components were detected by a UV-detector (Spectroflow 773) at a wavelength of 230 nm. Chromatograms were stored and integrated using the software package Minichrom. Effluent COD-concentrations were determined using the micro-method as described by Jirka and Carter (1975). The pH of the reactor liquid was determined immediately after sampling of the reactor with a pH-meter (Knick model 511, Berlin, Germany), equipped with a combined electrode (Schott Gerate type N61, Hofheim, Germany). The VSS-content of the sludge was determined according to Standard Methods for Examination of Water and Wastewater (1985).

RESULTS AND DISCUSSION

Continuous experiments

Preliminary experiments. During the preliminary continuous experiments, three 2.5 l UASB-reactors were operated for a period of 120 days. The reactors were inoculated with 70 gVSS per reactor, resulting in a

sludge concentration in the reactor of 28 gVSS.l^{-1}. In Table 2 the applied concentrations of different substrates in the influent and the operational parameters of the reactors are presented.

Sucrose was supplied to reactor 2 (and later butyrate to reactor 3) in order to study if the addition of co-substrate to the influent could enhance the anaerobic biodegradation of the aromatic substrates. In literature the positive effect of co-substrates has been attributed to the generation of reducing equivalents (as hydrogen-gas), resulting in enhancement of reductive steps in the combined oxidative and reductive degradation of aromatic compounds. Enhanced biodegradation through addition of glucose or sucrose has been shown for benzaldehyde (Todini and Hulshoff Pol, 1992), catechol (Hwang and Cheng, 1991) and terephthalate (Pereboom *et al.*, 1993). Benzoate was excluded from the influent from reactor 3 in order to avoid inhibition of the degradation of terephthalate. Inhibition of the degradation of terephthalate by benzoate will be discussed during the batch experiments section.

Table 2. Operational parameters of the UASB-reactors used during the preliminary experiments

	Reactor no.:	1	2	3
acetate	[mgCOD.l^{-1}]	1070	1070	1070
benzoate	[mgCOD.l^{-1}]	980	980	-
terephthalate	[mgCOD.l^{-1}]	1450	1450	1450
sucrose	[mgCOD.l^{-1}]	-	1120	-
butyrate	[mgCOD.l^{-1}]	-	-	(1800)[1]
total COD	[mgCOD.l^{-1}]	3500	4620	2520
HRT	[hour]	20	20	20
VLR	[gCOD.l^{-1}.day^{-1}]	4.20	5.50	3.02
SLR	[gCOD.gVSS^{-1}.day^{-1}]	0.15	0.20	0.11

1) butyrate was dosed to the influent from reactor 3 from day 75.

Within one week after start-up of the reactors, acetate was removed by more than 95% by reactor 1 and 3. Minor amounts of acetate (10-30 mgCOD.l^{-1}) remained in the effluent, which can probably be attributed to mass transfer limitations occurring in the sludge bed. In reactor 2 more than 95% of acetate and sucrose removal was obtained within 3 weeks. Benzoate was removed completely in reactor 1 and 2 within 40 days of operation. Since then no benzoate could be detected in the effluent (detection limit for benzoate amounts 1 mgCOD.l^{-1}). Terephthalate removal was not observed throughout the total experiment (120 days). Measured influent concentrations of terephthalate corresponded well at all times to effluent concentrations, suggesting that neither biodegradation, nor adsorption of terephthalate occurred. The absence of adsorption of terephthalate on the sludge was confirmed by measuring the concentration of terephthalate in the sludge, after washing with a 5% sodium hydroxide solution. Identified components in the effluent corresponded to more than 90% of the centrifuged effluent COD. This suggests that hardly any unidentified intermediates accumulated in the effluent. The measured methane production could account for 80 to 100% of the COD-material removed.

On day 120 feeding of the reactors was stopped. From this day, reactor 2 was operated as a recirculated batch for a period of one week. During this week 40% of the terephthalate present in the reactor was degraded. This suggests that the sludge had a very low activity for terephthalate. The terephthalate removal rate was too low to be observed during continuous operation. During batch incubations with sludge from reactor 1 and 3, significant mineralization of terephthalate could be observed as well, within one week of incubation.

Continuous experiments focusing on the anaerobic degradation of terephthalate. Sludge from reactor 2 of the preliminary experiments was used to inoculate 2 UASB-reactors of 1.4 l (reactor 2A and 2B). Reactor 2A was fed with terephthalate as sole carbon source and reactor 2B was fed with a mixture of terephthalate and sucrose (co-substrate). Initial influent concentrations and operational parameters are presented in Table 3. Acetate and benzoate were removed from the influent to avoid inhibition of the degradation of

terephthalate. Based on the effluent concentration of terephthalate, the loading rate was increased by increasing the concentration in the influent.

Table 3. Operational parameters of the UASB-reactors used during the experiments focused on the anaerobic degradation of terephthalate

	Reactor no.:	2A	2B
terephthalate	[mgCOD.l^{-1}]	720	720
sucrose	[mgCOD.l^{-1}]	-	1120
total COD	[mgCOD.l^{-1}]	720	1840
HRT	[hour]	24	24
VLR	[gCOD.l^{-1}.day^{-1}]	0.51	1.31
SLR	[gCOD.gVSS^{-1}.day^{-1}]	0.057	0.15

In Figure 3 the volumetric loading rate and removal capacity from reactor 2A are presented. From this figure it can be seen that the volumetric loading rate could slowly be increased with time. The maximum loading rate that could be applied was 4.4 gCOD.l^{-1}.day^{-1} for a terephthalate removal efficiency of 89%. Throughout the whole experimental period no acetate or hydrogen could be detected in the effluent. Even though the reactor had been in operation for 160 days, the loading rate could still be increased, indicating that no steady state was obtained. The COD-removal capacity as observed through measurement of the effluent concentration terephthalate was confirmed by COD-measurements and the methane production.

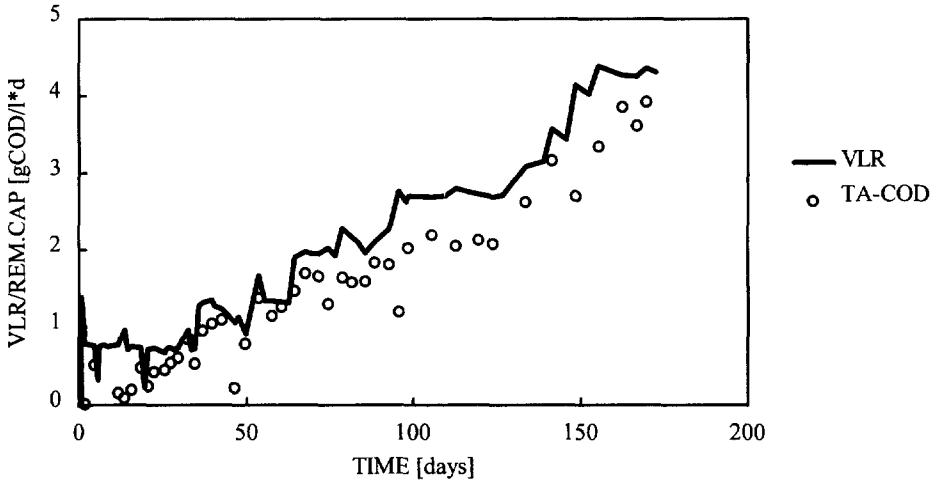

Figure 3. Volumetric loading rate (VLR-TA) and removal capacity based on influent and effluent concentrations terephthalate (RC-TA) of reactor 2A. Terephthalate was used as sole carbon source in this reactor.

From Figure 3 can be seen that after removal of acetate, benzoate and sucrose from the influent, significant degradation of terephthalate was obtained within two weeks of operation. This suggests that degradation of terephthalate was completely inhibited during the preliminary experiments, due to the presence of these other substrates in the influent. Wash-out of the terephthalate degrading culture during the preliminary experiments cannot explain the absence of terephthalate degradation, because the sludge age at the low loading rates applied, is very high (> 100 days).

The volumetric loading rate and removal capacity from reactor 2B are presented in Figure 4. From this figure it can be seen that the terephthalate removal capacity remained very low during the time sucrose was dosed to the reactor. After sucrose was removed from the influent (day 104), the removal capacity of

terephthalate increased rapidly, suggesting that the low removal capacities during the first 104 days of operation were a direct result of the presence of sucrose in the influent. Due to the presence of sucrose in the influent the hydrogen content of the biogas was initially approximately 800 ppm and dropped during 3 months of operation to 80 ppm, which is still much higher than in reactor 2A (less than 20 ppm). Acetate concentrations in the effluent dropped from approximately 300 to 30 mgCOD.l^{-1} after 104 days. From these observations it was concluded that sucrose did not enhance the anaerobic biodegradation of terephthalate, which is in contradiction with observations made by Pereboom *et al.* (1993). Probably the slightly higher concentrations of acetate and/or hydrogen in the reactor have lead to inhibition of the terephthalate degradation.

From the increase of the terephthalate removal capacity after removing sucrose from the influent, the growth rate of the terephthalate degrading culture was estimated (see Figure 4). Assumptions made for calculation of the growth rate are that no biomass was washed out from the reactor (1) and that the substrate concentrations were high enough to avoid mass transfer limitations and substrate depletion in the sludge bed (2). Both assumptions were sufficiently fulfilled during the period of calculation. The growth rate was estimated to be 0.04 day^{-1}, which is an extremely low value. This low growth rate explains the long start-up time required for reactor 2A. In the batch experiments section of this paper the growth rate of the terephthalate degrading sludge will be discussed further.

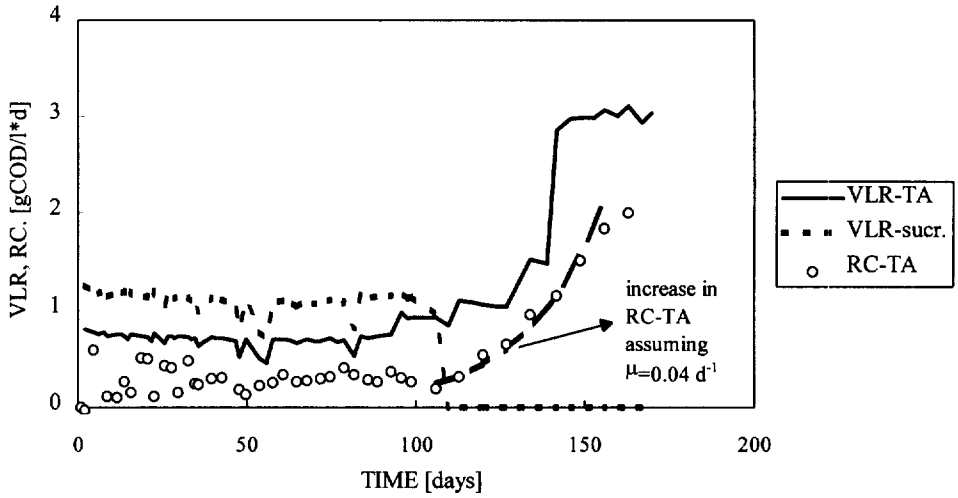

Figure 4. Volumetric loading rate based on sucrose (VLR-sucr.) and terephthalate (VLR-TA) and the terephthalate removal capacity in reactor 2B. On day 104 sucrose was removed from the influent.

Batch experiments

Degradation of acetate, benzoate and terephthalate by terephthalate degrading sludge. In order to study the specific activity of the sludge for acetate, benzoate and terephthalate, batch experiments with sludge from reactor 2A were performed. Sludge was withdrawn from reactor 2A after 110 days of operation and the initial sludge concentration in the batch reactors amounted to 1.73±0.04 gVSS.l^{-1}. The specific activity on benzoate was measured because benzoate was considered to be the first intermediate in the anaerobic biodegradation pathway of terephthalate (Aftring *et al.*, 1981; Taylor and Ribbons, 1983). To study the influence of benzoate on the degradation of terephthalate, an experiment was performed with a mixture of terephthalate and benzoate. The initial concentrations of acetate, benzoate and terephthalate were 1000, 1000 and 800 mgCOD.l^{-1} respectively. In the experiment fed with a mixture of terephthalate and benzoate, a second feeding of benzoate was dosed after 3.8 days, when the concentration of benzoate had dropped to 120±20 mgCOD.l^{-1}. In time the concentrations of terephthalate, benzoate, acetate and methane were

measured. All experiments were performed in duplicate. In Table 4 the specific activities obtained for the various substrates are summarised.

Table 4. Specific activity data for sludge from continuous reactor 2A

substrate	spec. activity [mgCOD.gVSS^{-1}.day^{-1}]
acetate	428 ± 23
benzoate	117 ± 1
terephthalate	33.6 ± 3.1
benzoate & terephthalate	119 ± 2 (7.4 ± 0.1) 33.4 ± 0.3[(1)]

(1) Specific degrading activity for terephthalate in presence of benzoate ( ), and after benzoate is completely degraded

The degradation curve from terephthalate, and its corresponding methane production curve are presented in Figure 5. Throughout the experiment no acetate, benzoate or hydrogen were detected. Furthermore, the sum of the measured concentrations of terephthalate and methane correspond well, suggesting that no unknown intermediates have accumulated in the reactor. Based on these observations it was concluded that the initial step in anaerobic mineralization of terephthalate (probably decarboxylation of terephthalate, under formation of benzoate) is the rate limiting step. From the increase in the rate of degradation of substrate and/or product formation, the growth rate of a culture can be estimated (Visser, 1995). In Figure 5 the optimised curves for growth rates of 0.0 and 0.1 day^{-1} are displayed. Using a growth rate of 0 day^{-1} yields a considerably better fit of the measured data, suggesting that the actual growth rate in the reactor is smaller than 0.1 day^{-1} under the studied conditions. Herewith the very low growth rate observed in the continuous experiments (0.04 day^{-1}) was confirmed. Furthermore, selective washout from the terephthalate degrading culture in the continuous experiments cannot explain the observed low growth rates in the continuous reactors.

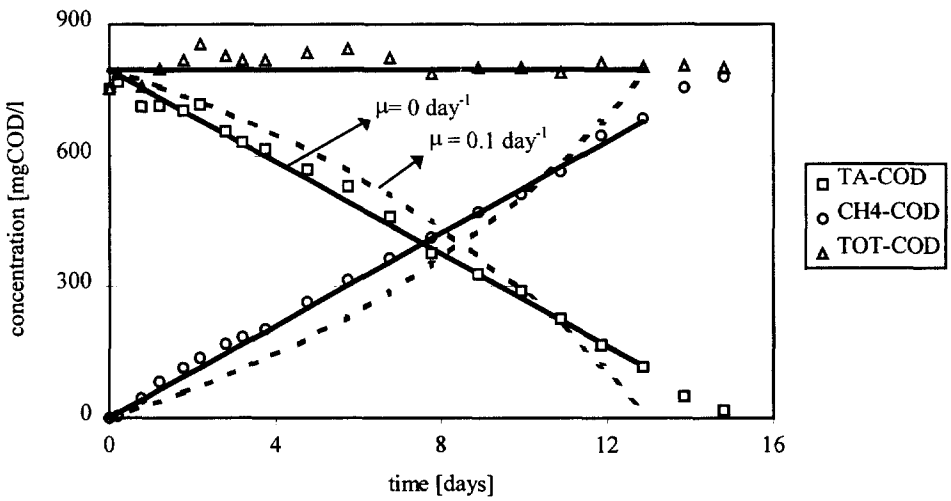

Figure 5. Batchwise degradation of terephthalate by sludge from reactor 2A (TA-COD: terephthalate concentration, CH4-COD: methane concentration, TOT-COD: sum of the measured concentration terephthalate and methane). All measured concentrations were recalculated to COD-equivalents per litre liquid volume. Markers indicate measured data; the solid lines represent a linear fit of the measured data (assuming no growth); dotted curves represent fitted data-points assuming a growth rate of 0.1 day^{-1}. Incorporation of substrate into biomass was neglected during these calculations (biomass yield = 0).

From Table 4 it can be seen that the specific activities of the sludge obtained for terephthalate are very low. The activity values obtained are considerably lower than can be expected from the removal capacity from reactor 2A at the moment of sampling the sludge (day 110 of operation of reactor 2A). This suggests that part of the activity was lost during sampling of the sludge from the reactors.

Benzoate was degraded by the sludge from reactor 2A without a lag period, at much higher rates than terephthalate as shown in Table 4. This observation suggests that benzoate is an intermediate in the degradation of terephthalate. However, since the sludge from reactor 2A had been fed with benzoate, before feeding for 110 days with terephthalate as sole carbon source, no definite conclusions can be drawn from this observation. No influence of the presence of terephthalate on the degradation of benzoate was observed.

Degradation curves from terephthalate in presence and absence of benzoate are presented in Figure 6. From these curves it can clearly be seen that degradation of terephthalate is almost completely inhibited by benzoate. After complete consumption of benzoate, terephthalate is consumed at the same rate as in the experiments performed with terephthalate as sole carbon source. Whether inhibition from the degradation of terephthalate is a result of product inhibition, or diauxic activity, can not be concluded from this experiment.

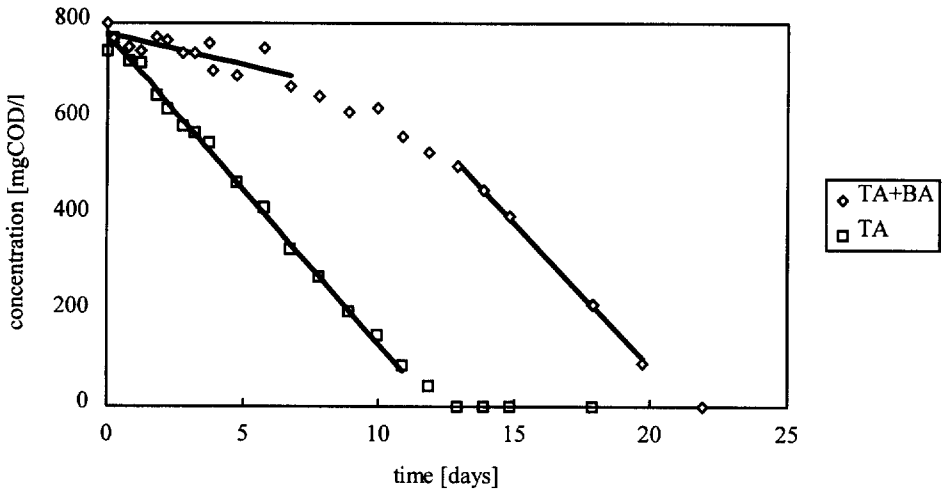

Figure 6. Degradation of terephthalate in reactors fed with terephthalate (TA) and with a mixture of terephthalate and benzoate (TA+BA). The benzoate concentration in the reactors fed with benzoate and terephthalate is 0 after 7.8 days. Markers indicate measured data; lines indicate the linear fit of the data, resulting in the activity values presented in Table 4.

Toxicity of high terephthalate concentrations for a terephthalate degrading culture. Sludge from continuous reactor 2A (2.0 $gVSS.l^{-1}$) was incubated with different concentrations of terephthalate. The concentrations of terephthalate applied were 500, 1000, 2000 and 5000 $mgCOD.l^{-1}$. Over time the concentrations of terephthalate, volatile fatty acids, hydrogen gas and methane gas were followed.

No differences in the methane production rate and the terephthalate consumption rate were observed during this experiment. Furthermore, the concentration of acetate in the medium remained under the detection limit (5 $mgCOD.l^{-1}$) and the concentration of hydrogen gas in the headspace amounted to less than 30 ppm. Anaerobic mineralization of terephthalate involves at least three different species: an organism that converts terephthalate into acetate, carbon dioxide and hydrogen gas (1), an acetoclastic methanogen (2) and a hydrogenotrophic methanogen (3). The obtained results imply that none of the species involved in anaerobic mineralization of terephthalate were inhibited at the terephthalate concentrations applied. Since the applied concentrations of terephthalate in the continuous experiments were at all times lower than the concentrations

applied during this experiment, it was concluded that toxicity of terephthalate played no role during the continuous experiments.

The observation that terephthalate is not toxic to the acetoclastic methanogenic activity of granular sludge is confirmed by Pereboom *et al.* (1993). On the contrary, Macarie *et al.* (1992) observed toxicity of terephthalic acid to acetoclastic methanogens. Kuang and Wang (1994) concluded from their work that the concentration of terephthalic acid should be lower than 750 mgCOD.l^{-1} to avoid inhibition of anaerobic degradation of terephthalic acid. These researchers, however, used terephthalic acid in its particulate form. Based on the pK_a values of terephthalic acid (pK_{a1} and pK_{a2} values of terephthalic acid are 3.5 and 4.8 (Solomons, 1983), they assumed terephthalic acid to be rapidly dissolved within their system. Dissolution of terephthalic acid at neutral pH, however, is a very slow process. Taking this into acount, observed toxic effects may be attributed to the presence of particulate terephthalic acid in their systems. Since in our experiments only dissolved disodium terephthalate was applied, toxicity of particulate terephthalic acid could be excluded.

Influence of additional substrates on the anaerobic degradation of terephthalate

All results obtained during this work indicate that anaerobic mineralization of terephthalate is strongly inhibited by easily degradable substrates. No, or only limited degradation of terephthalate was observed in reactors fed with benzoate, acetate, sucrose or butyrate as additional substrates. Substantial mineralization of terephthalate was only found in reactors fed with terephthalate as sole carbon source.

Benzoate, acetate and hydrogen are intermediates in the anaerobic degradation pathway of terephthalate, suggesting that product inhibition is responsible for the observed inhibition. If benzoate and terephthalate are degraded by the same organism, diauxic activity may play a role as well. Due to the low loading rates in reactors fed with additional substrates, only very low amounts of benzoate, acetate and hydrogen were detected in the effluent. This implies that already at very low concentrations of these compounds in the reactor, anaerobic degradation of terephthalate is inhibited. If the loading rate for additional substrates is sufficiently low and the sludge age is sufficiently high, growth of the terephthalate degrading culture is possible. These observations are in agreement with Pereboom *et al.* (1993), who described that terephthalate (and p-toluate) was only degraded in lab-scale reactors, and not in the full-scale UASB-reactor. Probably this can be attributed to the lower sludge loading rates in the lab-scale reactor (Table 1), leading to lower concentrations of acetate, benzoate and hydrogen inside the reactor. Under these conditions, growth of a terephthalate degrading culture is favoured.

Liangming (1991) showed that PTA-wastewater could be treated at high loading rates (Table 1). The artificial wastewater, however, contained only 600 mgCOD.l^{-1} terephthalate and had a pH of 4.5. No other aromatic compounds were present in the influent. Due to an effluent COD concentration of 400 mg.l^{-1} it was concluded by the authors that terephthalate was degraded in the reactor. At the applied influent pH of 4.5, however, terephthalic acid dissolves very poorly. Even at a pH around 7 inside the reactor this might have led to precipitation of terephthalic acid on the sludge due to the low dissolution kinetics of terephthalic acid at this pH. From these observations it can be concluded that probably no or only limited conversion of terephthalate to methane was obtained in the reactor. Herewith the observed high removal rates can be attributed solely to the conversion of easily degradable substrate.

Macarie (1992) performed laboratory studies in UASB and fixed film reactors. No component analyses were performed and therefore no conclusions can be drawn concerning the removal of specific compounds from the influent. Despite the low loading rates of the UASB reactors only limited COD-conversion was observed (Table 1). These results indicate that only limited conversion of aromatic compounds (terephthalate and p-toluate) has occurred. Higher COD-removal efficiencies were observed in the fixed film reactor. The observed higher removal efficiency in the fixed film reactor can probably be attributed to the higher sludge concentration in the reactor, resulting in lower concentrations of easily biodegradable material inside the reactor and a higher sludge age. Herewith growth of a terephthalate degrading population was favoured in this reactor.

Practical implications

The results obtained during this study, as well as information from literature, imply that PTA-wastewater can only be treated at low loading rates. Complete removal of acetate and benzoate should be obtained, before growth of the terephthalate degrading culture can be expected. Due to the low growth rate of the terephthalate degrading culture, a long start-up period and a high sludge age are required. Despite these drawbacks, anaerobic pre-treatment of PTA-wastewater can still be economically feasible, as shown by Amoco Petrochemicals Inc. (Duffel, 1993). This company has built four full scale downflow fixed film reactors for the anaerobic pre-treatment of PTA-wastewater. The applied loading rates of these reactors are low (4.0 $kgCOD.m^{-3}.day^{-1}$), and therefore the reactor volume is very big (15,200 m^3). Due to the low loading rate applied, high removal efficiencies can be obtained in this reactor. The high investment costs for this reactor are compensated by the lower operational costs due to lower nutrient requirements, less surplus sludge production and lower energy requirements.

Anaerobic pre-treatment of PTA-wastewater may be enhanced by pre-removal of benzoate and acetate in a staged reactor system. Due to the absence of growth on benzoate and acetate, the sludge age in the latter stages of the system will be increased, leading to increased removal capacities for terephthalate, as was shown during our work. Theoretically this approach will lead to a significant increase of the applicable overall loading rate of the treatment system. Therewith smaller reactor volumes will be required. Staged reactor systems can be obtained through application of anaerobic bioreactors in series, or through application of reactor systems in which plug-flow is enhanced. Several concepts of staged anaerobic reactors have been described in literature. (Grobicki and Stuckey, 1991; Lier *et al.*, 1994; Mulligan *et al.*, 1993; Nachaiyasit and Stuckey, 1995).

CONCLUSIONS

Terephthalate can be degraded by methanogenic granular sludge. The maximum removal capacity of a UASB-reactor, fed with terephthalate as sole carbon source, was found to be 3.9 $gCOD.l^{-1}.day^{-1}$ at a volumetric loading rate of 4.4 $gCOD.l^{-1}.day^{-1}$ and a hydraulic retention time of 24 hours. A start-up period of 160 days was required to obtain this removal capacity, which can be attributed to the low growth rate of the terephthalate degrading culture ($\mu \approx 0.04$ day^{-1}).

Dissolved terephthalate is not toxic to any of the species involved in its mineralization. Anaerobic mineralization of terephthalate was found to be strongly inhibited by small amounts of acetate, hydrogen or benzoate in the reactor. To avoid inhibition by these compounds a staged anaerobic reactor system is suggested for the anaerobic pre-treatment of PTA-wastewater.

ACKNOWLEDGEMENT

This research was funded by IOP Milieubiotechnologie (Innovative Research Program Environmental Biotechnology, The Netherlands). Erwin J. A. Smoes is acknowledged for performing part of the experimental work and Hervé Macarie for valuable disussions and supply of literature.

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