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Thermophilic anaerobic treatment of sulphur rich forest industry wastewater

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Abstract

Thermophilic anaerobic treatment of sulphur-rich paper mill wastewater (0.8-3.1 gCOD/l, 340–850 mgSO_4/l; COD:SO_4 3.4-5.3) was studied in three laboratory-scale, upflow anaerobic sludge blanket (UASB) reactors and in bioassays. The reactors were inoculated with non-adapted thermophilic granular sludge. In the bioassays, no inhibition of the inoculum was detected and about 62% COD removal (sulphide stripped) was obtained. About 70 to 80% of the removed COD was methanised. In the reactors, up to 60–74% COD removal (effluent sulphide stripped) was obtained at loading rates up to 10–30 kgCOD/m^3d and hydraulic retention times down to 6 to 2 hours. The effluent total sulphide was up to 150–250 mg/l. Sulphide inhibition could not be confirmed from the reactor performances. The results from bioassays suggested that both the inoculum and sludge from the UASB reactor used acetate mainly for methane production, while sulphide was produced from hydrogen or its precursors.

Introduction

Anaerobic processes have gained wide popularity in industrial wastewater treatment during the last decades: up to about 1000 full-scale applications were reported in 1997 (Hulshoff Pol et al. 1997). Also pulp and paper industry wastewaters, especially those from mechanical pulping and secondary fibre pulping, as well as condensates from chemical and semichemical pulping, are increasingly treated applying anaerobic processes (Rintala & Puhakka 1994).

Sulphur compounds have caused problems in the methanogenic anaerobic treatment of some industrial wastewaters, including some pulp and paper industry wastewater streams, as reviewed by Rinzema & Lettinga (1988). Sulphur compounds are used as a principal agent in pulping or in bleaching the pulp. In chemical pulping, sodium sulphate is used in the kraft process and sulphur dioxide in the sulphite process, while sodium sulphite is used in chemi-thermomechanical pulping. Dithionite is used in bleaching mechanical pulp. In pulp and paper mill wastewaters, inorganic sulphur can appear as sulphate, sulphite or dithionite. In anaerobic treatment of sulphur containing wastewaters, sulphate reducing micro-organisms compete with methane producers and acetogenic micro-organisms for available substrates such as hydrogen and acetate or propionate, respectively. Additionally, sulphur compounds and especially unionised hydrogen sulphide may inhibit anaerobic micro-organisms, of which methanogens are the most sensitive. Furthermore, hydrogen sulphide in the effluent reduces the removal efficiency measured as chemical oxygen demand (COD) as well as the methane yield.

Biological-both anaerobic and aerobic-wastewater treatment is applied to industrial wastewaters almost exclusively under mesophilic conditions, although in many modern manufacturing industries the process waters and wastewaters are hot. The elevated water temperatures are caused by high temperature manufacturing processes, low water consumption, heat recovery, and increased separation of hot and cool process water streams. The hot waters usually contain high concentrations of organic compounds due to enhanced dissolution of organic material at elevated temperatures. The current practice is to combine hot streams with cooler and more dilute streams and subsequently further cool and treat them in mesophilic aerobic or anaerobic systems. On the other hand, intensive laboratory studies as well as some pilot-scale studies have shown that reliable and efficient thermophilic high-rate anaerobic treatment of industrial wastewaters is feasible at 55 °C (reviewed e.g. Rintala 1992; Ahring 1994; van Lier & Lettinga 1995) and probably even at 80 °C (Lepistö & Rintala 1996).

Anaerobic high-rate treatment of sulphur rich wastewaters, as well as factors affecting the competition between sulphate reducers and methanogens, has been studied intensively in mesophilic processes (reviewed e.g. by Rinzema & Lettinga 1988). Lower undissociated sulphide concentrations are expected under thermophilic conditions than in the mesophilic processes, because high temperature decreases the fraction of undissociated hydrogen sulphide in the liquid while increasing the partitioning of hydrogen sulphide from liquid to gas (Rintala & Puhakka, 1995). In thermophilic anaerobic reactors, sulphate reduction has been studied mainly with model compounds, while experiences with industrial wastewaters are few. In anaerobic reactors, sulphate reduction has been shown to occur also under thermophilic conditions with acetate at 55 °C (Rintala & Lettinga 1992; Visser et al. 1992; Rintala 1997), and at 70 °C (Rintala 1997). In thermophilic (55 °C) anaerobic treatment of thermomechanical pulping (TMP) process water, sulphate reduction was partial with apparently hydrogen as the electron donor, while acetate was used for methane production (Rintala et al. 1991).

This work focuses on thermophilic anaerobic treatment of sulphate rich paper mill wastewaters. Wastewaters were obtained from a mill using dithionate for pulp bleaching. The temperature of the wastewaters at the mill site was up to 60 °C. Experiments were conducted to determine anaerobic treatment potential to decrease the load of the paper mill to an existing activated sludge plant treatment level. The thermophilic process was chosen because it could obviate cooling of the wastewater before treatment. Furthermore, the hot anaerobically treated wastewater would increase the temperature in subsequent combined activated sludge treatment of sewage and paper mill wastewater, and thus stimulate temperature dependent nitrification during low temperature periods.

Table 1. The paper mill wastewater characteristics

	N	Average	Std	Range
pH	12	3.9	0.6	3.0–4.8
CODtot (mg/l)	11	1921	633	830–3100
CODsol (mg/l)	11	1683	567	710–2800
BODtot (mg/l)	9	728	267	340–1100
BODsol (mg/l)	9	710	265	320–1000
SS (mg/l)	12	167	87	41–340
VSS (mg/l)	12	142	78	27–280
Ntot (mg/l)	8	2.9	1.1	1.5–4.8
Ptot (mg/l)	11	1.2	0.3	0.55–1.9
SO_4^{2-} (mg/l)	5	572	241	340–850
Stot (mg/l)	3	163	35	130–200
BODtot/CODtot*100 (%)	9	41	4.5	33–48
BODsol/CODsol *100 (%)	9	45	6.3	36–55

N = number of samples.

Materials and methods

Reactors

The experiments were conducted with three upflow anaerobic sludge blanket (UASB) reactors R1 (experimental days 1–113), R2 (days 1–57), and R3 (days 58–93), with liquid volumes of 1.9, 1.3, and 0.22 l, respectively (R1 and R2 inner diameter was 74 mm; R3 40 mm). Reactors R1 and R2 were started simultaneously to study the effects of nutrient additions on the process performances. The reactors were run at 55 °C in a temperature controlled waterbath. Methane production (in reactor R1) was measured with a wet-test gas meter (Ritter KG, model TG-1) after the evolved biogas passed through a 5 M NaOH solution to remove CO_2 and H_2S. Samples to determine biogas composition were taken from the gas tubes in front of the NaOH solution.

Wastewater

The wastewaters were obtained from a pulp and paper mill, which manufactures newsprint from mechanical pulp. A new wastewater batch was obtained from the mill every 1–2 weeks and stored in darkness at 4 °C. The wastewater characteristics are shown in Table 1.

To prevent clogging of the feed tubes by solids, the wastewater was settled for 30 minutes and screened (1 mm pore size) before being used as feed. New feed was prepared 1–2 times per week. Ammonium chloride and phosphoric acid were added to the feed to obtain a COD:N:P ratio of 500:5:1. The feed for reactors R1 and R3 was supplemented with nutrients from the beginning of the runs and that for reactor R2 from experimental day 44 onwards. The pH of the feed was adjusted between 7.5 and 8.0 with 5 M NaOH. From day 16 on, sodium bicarbonate (3 g $NaHCO_3$/l) was added to the feed as buffer. The feed was stored at 4 °C under nitrogen gas.

Inoculum

Reactors R1 and R2 were inoculated with thermophilic granular sludge from laboratory- and pilot-scale UASB reactors treating vegetable processing wastewaters (Lepistö & Rintala 1997; Rintala & Lepistö, 1997). Before being used in the experiment, 63% of the seed sludge was adapted to the paper mill wastewater for 12 days in a 55 °C UASB reactor. Reactor R3 was inoculated with sludge from reactor R2 at the end of its run. The inocula in reactors R1, R2, and R3 amounted to 13.2 g volatile suspended solids (VSS) /l, 13.5 gVSS/l, and, 19.0 gVSS/l, respectively.

Bioassays

Two sets of assays were run. In the first set, the assays were run in triplicate in 118 ml glass serum vials with a liquid volume of 63 ml. 3 ml of thermophilic granular sludge (inoculum of the UASB reactors) was transferred directly into the vials containing a volatile fatty acid (VFA) solution (1.6 gCOD/l; 74:22:4, acetic acid: propionic acid: butyric acid on COD basis), undiluted paper mill wastewater, or wastewater diluted to 60% with distilled water. Besides the substrate, nutrients (Rintala & Lepistö 1992), $NaHCO_3$(3 g/l) and distilled water to obtain liquid volume of 63 ml were added to the media.

pH was adjusted to 7.0-7.3 with either 1 M NaOH or 1 M HCl. The vials were then flushed with N_2 and sealed with butyl rubber stoppers and aluminium crimps. Finally, $Na_2S^*9H_2O$ was injected into the vials to a final concentration of 0.25 g/l to ensure anaerobic conditions.

The assays comprised two consecutive feedings. Before the second feeding, the supernatant was carefully decanted and the liquid replaced with new media (VFA, undiluted wastewater, wastewater diluted to 60%). The vials were then flushed and sealed as described above except for the final addition of $Na_2S^*9H_2O$.

The second bioassay set consisted of a triplicate test with 60 ml vials with 32 ml liquid volume and 2 ml of inoculum (sampled from R2; day 57) for each

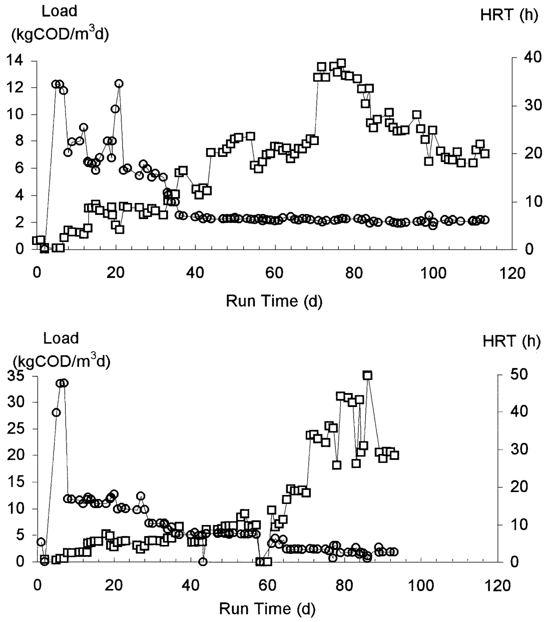

Figure 1. Loading rates (□) and hydraulic retention times (○) in thermophilic UASB reactors (above: R1; below: R2 days 1–57 and R3 days 58–93) treating paper mill wastewater.

substrate. The substrates were sodium acetate (1.8 gCOD/l), undiluted wastewater, wastewater diluted to 60%, and a mixture of sodium acetate (1.8 gCOD/l) and sodium sulphate (2.9 gSO_4/l). pH was adjusted to 6.9-7.2 and nutrients (Rintala and Lepistö 1992), and $NaHCO_3$ (1 g/l) were added to the media, whereat the vials were sealed, flushed (mixture of 80% N_2 and 20% CO_2), and injected with $Na_2S^*9H_2O$, as above.

In all the bioassays, the vials were incubated in static cultures at 55 °C. The gas phase and liquid total sulphide were sampled with a lure lock and an ordinary syringe. The media without substrates were used in control vials. The methane production from the inoculum in the controls was subtracted from that in the test vials.

Analyses and Calculations

COD, biological oxygen demand (BOD), suspended solids (SS), VSS and sulphate (gravimetrically) were analysed according to *Standard Methods* (APHA 1985). The effluent COD samples were filtered and flushed (pH adjustment <2 and N_2 stripping for 20 min) to eliminate the interference of S^{2-}. The pH of the anaerobic effluent was measured with an Orion model SA 720 (Orion research, model SA 250 electrode) immediately after sampling in order to avoid pH

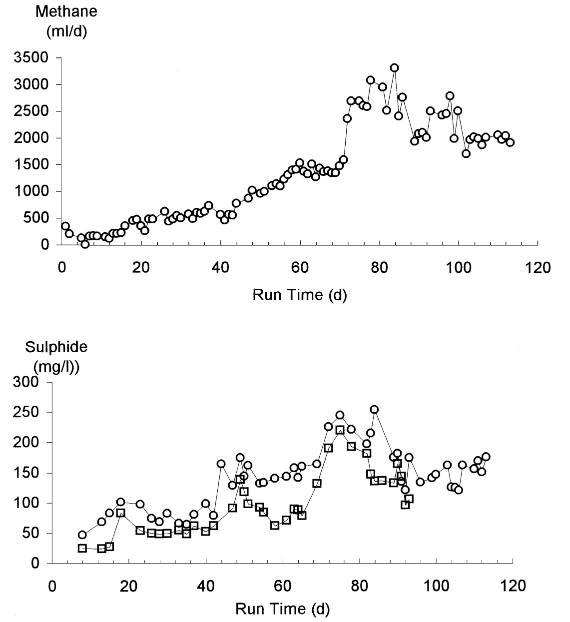

Figure 2. Effluent sulphide concentrations (R1, ○; R2 days 1–57 and R3 days 58–93, □) and methane production (R1, ○) in thermophilic UASB reactors treating paper mill wastewater.

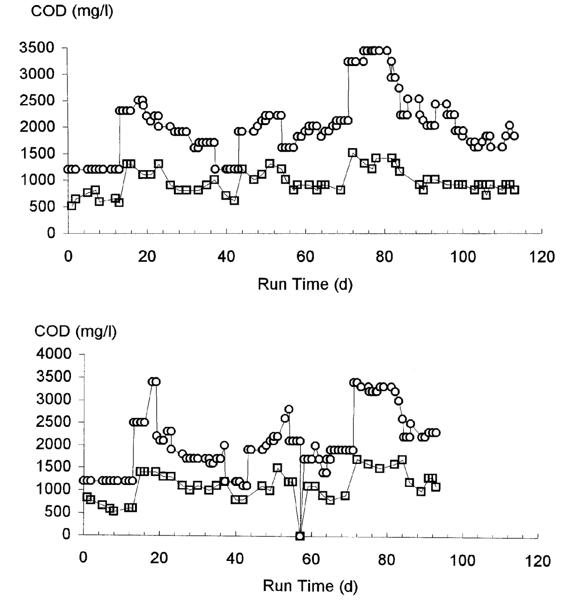

Figure 3. Feed (○) and effluent CODs (□) of thermophilic UASB reactors (above: R1; below: R2 days 1–57 and R3 days 58–93) treating paper mill wastewater.

changes. The samples for soluble COD and BOD, and sulphate were filtered with Whatman GF/A glass-fibre filters. The soluble values are presented if otherwise not stated.

Total nitrogen (N_{tot}) was determined by a modified sulfateperoxide oxidation-distillation method (SFS standard 5505 1988) and phosphorus according to the Finnish Standards (SFS standard 3026 1986). Sulphide was analysed by the spectrophotometric method of Trüper and Schlegel (1964). The hydrogen sulphide in the liquid and in the gas phase was calculated as previously described (Rintala et al. 1991).

Results

Reactor Studies

Reactors R1 and R2 were started simultaneously with loading rates of less than 4 kgCOD/m^{3}d and hydraulic retention times (HRTs) of 7-15 h (from day 8 onwards; Figure 1). Methane production started immediately (measured only in R1; Figure 2). On day 15, pH in all reactors dropped to 6.0 to 6.4 (data not shown), but after buffer addition to the feed (3 g $NaHCO_3$ /l), the effluent pH increased to 6.9 −7.2, being afterwards in the range 7.0 to 8.0. From day 36 onwards, HRT was decreased to 5–8 h in both R1 and R2, and maintained for the remainder of the runs.

The R1 loading rate ranged up to 13.4 kgCOD/m^{3}d in accordance to the influent COD (from 1.1 up to 3.1 g/l; Figure 3). COD removal varied between 50 and 74% calculated on the sulphide stripped effluent samples, and between 40 to 65% on the non-stripped effluent samples (Figure 4). The COD removals were clearly unaffected by the loading rate or the feed COD. When no nutrients were added into R2 influent, its removal efficiency was slightly less than that of R1 in the beginning of the runs (until day 43; Figure 4), indicating a nutrient deficiency limitation of the growth of the active thermophilic consortium.

Reactor R3 (days 58–93) was started with R2 sludge and was run in parallel with R1 (days 58–113) with higher loading rates and shorter HRTs (down to 2–3 h; Figure 1). The higher loading rate imposed on R3 did not markedly affect its process performance, as evinced by the COD removal comparison between R3 and R1 (Figure 4).

The feed COD/SO_4 -ratio ranged from 3.4 to 5.3 (n=5). About 40 to 80% of sulphate was reduced (data not shown). Effluent sulphide increased in the beginning of the runs in both R1 and R2 being achieved up to about 150 mg/l in R1 (Figure 2). Between days 70-85, sulphide was up to 200-250 mg/l, with exceptionally high COD values in the feed but decreased

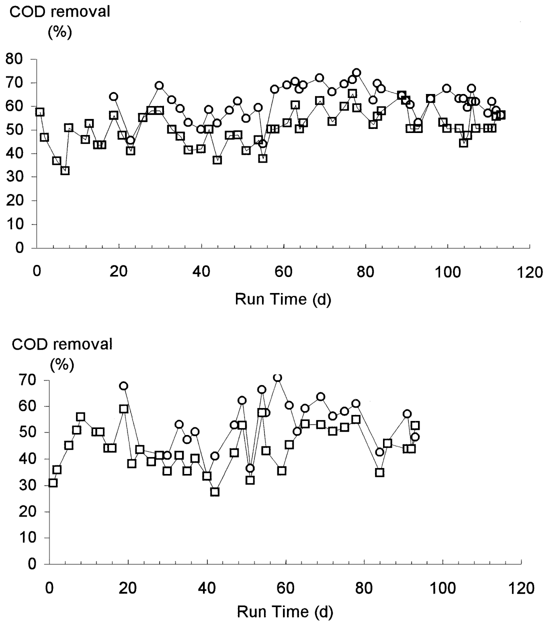

Figure 4. COD removal (effluent sulphide stripped, ○; effluent sulphide not stripped, □) in thermophilic UASB reactors (above: R1; below: R2 days 1–57 and R3 days 58–93) treating paper mill wastewater.

to about 150 mg/l when the feed COD dropped with a new batch. Furthermore, the R3 sulphide concentrations were slightly less than those of R1 during a comparative period. The highest total sulphide concentration measured was 250 mg/l in R1. At pH 7.0 and 7.5, this corresponds to about 70 and 30 mg/l of undissociated hydrogen sulphide in the effluent, respectively.

Methane production in R1 increased in the course of the run together with improved COD removal, indicating the enhancement of methanogenic activity (Figure 2). The biogas methane content varied between 40 and 55%, barring about day 70, when increased sulphide production apparently raised the H_2S level in the biogas.

BOD removal ranged from 74 to 77% in reactor R1 (days 57–113, n= 6) and from 61 to 69% in R3 (days 66–93, n=4), with concomitant COD removal of 67-70% in R1 and 40–67% in R2. At its lowest, the effluent BOD was 250–300 mg/l, corresponding to 800–1000 mgCOD/l (sulphide stripped). A 49-day BOD test for residual aerobically degradable material was run on R1 effluent (sampled day 84; Table 2). BOD_7 accounted for 61% of BOD_{49} and the anaerobically-aerobically biodegradable COD was about 75% of feed COD.

Bioassays

The paper mill wastewater was assayed in two consecutive feedings for methane and sulphide production before the reactor experiments with the thermophilic inoculum started (Table 3). The wastewater samples produced methane at initial rates (0.2 gCH_4-COD/gVSSd) comparable to control assays with VFA (data not shown) and some sulphide. The sulphide production increased in the second feeding, probably due to acclimation of the sulphate reducers and/or to increased sulphate reducing population in the sludge, or to residual sulphur in the vial from the first feeding. The undissosiated hydrogen sulphide in the liquid phase was less than 20 to 30 mg/l, and in the gas phase less than 20 mg/l. Methane production accounted for 73 to 88% of the COD removal. The COD balances were apparently affected by the inaccuracies in the COD and sulphide measurements and some residual sulphur from the first feeding of the first bioassay.

The sludge from R2 (sampled on day 57) was assayed for methane and sulphide production with wastewater, acetate, and acetate plus sulphate (Table 3). With R2 sludge both the undiluted wastewater and the wastewater diluted to 60% produced sulphide in amounts comparable to those from the first feeding with inoculum (first bioassays) indicating that the reactor run had little or no effect on the sulphidogenic activity of the sludge. In the bioassay with acetate and sulphate, sulphate addition slightly increased the sulphide concentration but had no significant effect on methane production (data not shown), as compared to the assays with acetate as sole substrate (no sulphate addition).

Discussion

The results show that paper mill wastewaters rich in sulphur can be treated under anaerobic thermophilic conditions at relatively high loadings (10 to 30 $kgCOD/m^3d$) and with hydraulic retention times down to 6 and even to 2 hours. Also previous studies (Minami et al. 1991; Rintala et al. 1991) have suggested the feasibility of thermophilic anaerobic treatment for treating hot, sulphur-rich pulp and paper mill wastewaters. The applied loading rates are comparable to those reported for mesophilic processes treating TMP wastewaters (e.g., Jurgensen et al. 1985; Rintala & Vuoriranta 1988; Sierra-Alvarez et al. 1990) and for thermophilic treatment of sulphur rich TMP whitewater (Rintala et al. 1991). The process performances

Table 2. Biodegradation of paper mill wastewater in anaerobic treatment and subsequent BOD tests (R1 effluent sampled on day 89)

	BOD (mg/l)	COD (mg/l)
Feed, paper mill wastewater	1300	2700
Anaerobic effluent	300 (as BOD_7)	1150
Anaerobic effluent, a 49-day BOD test	560 BOD_{49}	670 (sampled after 49-day test)
Removal in 49-day BOD test	260 (BOD_{49}–BOD_7)	480

Table 3. Bioassays with thermophilic inoculum (1st bioassay) and reactor R2 sludge (sampled on day 57; 2nd bioassay)

Bioassay/ Substrate	COD initial (mg/l)	COD removal (%)	Final sulphide (mg/l)	CH_4-COD/COD removed* 100 (%)	Sulphide-COD/ COD removed* 100 (%)
1st Bioassay 1st feeding[1]					
100% wastewater	1700	62	64	82	16
60% wastewater	1100	63	60	73	22
1st Bioassay 2nd feeding[2]					
100% wastewater	1600	58	114	88	32
60% wastewater	1100	59	83	77	33
2nd Bioassay[3]					
Acetate	1800	97	<5	96	<1
Acetate + SO_4	1750	93	43	93	7
100% wastewater	1750	59	96	60	24
60% wastewater	1150	63	73	50	26

incubation periods: 11[1], 12[2], and 9[3] days.

(COD removal, effluent sulphide) varied slightly also after the start-up period, which might be due to either changes in feed characteristics and loading rates or to slight inhibition. Possible inhibition could be caused by unionised sulphide, wood extractives (mainly resin acids) or by chemicals used in paper manufacturing. However, the UASB reactor performances did not show any severe disturbances.

In the present study, the highest effluent sulphide concentrations in the reactors were up to 150–250 mg/l at a pH of 7.0 to 7.5, corresponding to about 15 to 70 mg/l undissociated sulphide. In batch assays at a pH of 7.1–7.2, 75 mg/l of unionised H_2S caused 50% inhibition of the aceticlastic methanogenesis of a granular sludge from an acetate- and sulphate-fed 55 °C UASB reactor (Visser et al. 1993). The effect of undissociated H_2S was highly pH dependent: at pH 7.8-8.0, as low as 24 mg/l caused 50% inhibition (Visser et al. 1993). On the other hand, with dispersed biomass from a 55 °C reactor no pH effect on undissociated hydrogen sulphide inhibition was observed (Visser et al. 1993). Thus, the sulphide concentrations in the present UASB reactors were at the level that inhibited methanogenesis in a study by Visser et al. (1993). However, the inhibitory concentration in each case may be affected by factors, such as microbial composition, and substrate. Thus, no definite conclusion could be drawn about the reactor inhibition.

Wood extractives, probably the cause of the BOD in the anaerobic effluent, are hardly degradable under anaerobic conditions but are readily degradable in aerobic treatment (e.g. Rintala & Puhakka 1994). The effluent volatile acids were measured randomly; the highest value was 300 mg/l, while with 50 to 60% COD removal the volatile acids were less than 40 mg/l (data not shown). Previous studies with TMP whitewater have shown that low (<25 – 50 mg/l) VFA concentration can be obtained in 55 °C UASB reactors (Rintala & Lepistö 1992).

In the present study, sulphate reduction was partial both in the assays and in the reactors, in accordance with the results obtained with sulphur-rich

TMP whitewater (Rintala et al. 1991). In the assays, sulphide was produced from paper mill wastewater, while only very low amounts were produced from acetate plus sulphate medium. This could mean that with cultivated sludge, mainly hydrogen or its precursors (e.g., propionate) and not acetate was used for sulphate reduction. On the other hand, in the thermophilic process, the fate of acetate may be more complex than in the mesophilic process. At 55 °C, besides the aceticlastic reaction, acetate oxidation to hydrogen and carbon dioxide by acetate oxidizing rods has also been observed (Zinder & Koch 1984). Furthermore, sulphate reducers may also oxidise acetate to carbon dioxide. *Desulfotomaculum thermoacetoxidans* and *Desulfotobacterium kuznetsovii* are the main isolated acetate utilizing thermophilic sulphate reducers, while several hydrogen utilizing thermophilic sulphate reducers have been isolated (reviewed by Rintala & Puhakka 1995). Both hydrogen and acetate utilizing sulphate reducers grow also on other substrates.

The sludge from the UASB reactor fed with paper mill wastewater produced mainly methane when bioassayed with acetate and sulphate as substrate suggesting that acetate utilizing sulphate reducers had not out competed acetate utilizing methanogens during the run. This was contradictory to the finding that acetate plus sulphate-cultivated 55 °C sludge from a UASB produced primarily sulphide and simultaneously methane when assayed with acetate and sulphate as substrate (Rintala 1997). Competition between sulphate reducers and methanogens on acetate has been studied intensively in mesophilic processes with contradictory results (e.g., review by Rinzema & Lettinga 1988). Several factors have been proposed to affect the competition for acetate, such as the source of inoculum, substrate concentration, process configuration, and the length of the experiment. However, the outcome of the competition seems unpredictable in mesophilic processes. In the present study the inoculum was from methanogenic thermophilic reactors. Previous studies on acetate fed-systems showed that sulphate reduction dominated over methanogenesis in thermophilic processes even with actively methane producing populations. Sulphate reduction commenced readily following the change from 37 to 55 °C of an acetate-fed, methane-producing UASB reactor (Rintala & Lettinga 1992; Visser et al. 1992), and immediately after the addition of sulphate into the feed of acetate methanising 55 and 70 °C UASB reactors (Rintala 1997).

Conclusions

Anaerobic treatment of sulphur-rich, paper mill wastewater in a high-rate thermophilic reactor is feasible. About 60% COD removal is achievable with short hydraulic retention times. In this study sulphate reduction was partial. The effluent sulphide concentrations were up to 150–250 mgS/l (undissociated H_2S 20 to 70 mg/l). No definite inhibition was observed. According to the batch assays with the paper mill wastewater studied, sulphide was mainly produced by hydrogen-utilizing sulphate reducers, while acetate was preferentially used for methanogenesis.

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