Biodegradation **9:** 103–111, 1998.

High rate biological treatment of sulfate-rich wastewater in an acetate-fed EGSB reactor

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Accepted 20 May 1998

Key words: acetotrophic sulfate reduction, calcium precipitation, competition, EGSB bioreactor, sulfide inhibition

Abstract

An expanded granular sludge bed reactor, inoculated with acclimated sulfidogenic granular sludge, was operated at 33 °C and fed with acetic acid as COD source and sulfate as electron acceptor. The bioreactor had a sulfate conversion efficiency of 80–90% at a high sulfate loading rate of 10.4 g SO_4^{2-}-S/l.d after only 60 days of start-up. This was achieved by implementing a dual operational strategy. Firstly acetic acid was dosed near stoichiometry (COD over sulfur ratio = 2.0 to 2.2) which allowed almost complete sulfate removal. Secondly the pH in the bioreactor was kept slightly alkaline (7.9 ± 0.1) which limited the concentration of the inhibitory undissociated hydrogen sulfide H_2S ($pK_a = 7$). This allowed the acetotrophic sulfate reducing bacteria to predominate throughout the long term experiment.

The limitations of the EGSB technology with respect to the sulfate conversion rate appeared to be related to the biomass wash-out and granule deterioration occurring at superficial upflow velocities above 10 m/h. Increasing the recirculation flow caused a drop in the sulfate reduction rate and efficiency, an increase of the suspended sludge fraction and a considerable loss of biomass into the effluent, yielding bare mainly inorganic granules. Elemental analysis revealed that a considerable amount of the granular sludge dry matter at the end of the experiment, at an upflow velocity of 20 m/h, consisted of calcium (32%), mainly in the form of carbonate deposits, while organic matter only represented 7%.

Introduction

Many industrial wastewaters, e.g. from paper mills and potato starch factories, contain considerable amounts of sulfate (in the order of grams per liter) because of the use of sulfuric acid (as a cheap and strong acid) or sulfite (as a bleaching agent) in production processes (Colleran et al. 1995). The biological removal of sulfur from these wastewaters can happen in two steps: firstly sulfate or sulfite is anaerobically reduced to sulfide, which is subsequently partially re-oxidized to elemental sulfur, a recoverable product (Buisman 1989; Visser 1995; Janssen 1996).

Waste gas scrubbing waters originating from flue gas desulphurization units constitute a special problem, since they do not contain organic compounds to support the sulfate-reducing bacteria. In order to biologically treat these wastestreams, an external carbon and energy source has to be supplied. The choice for the appropriate electron donor is based on the following criteria: (i) the suitability for the sulfate reduction process, and the availability (ii) in large enough quantities (iii) at a reasonable cost. Synthesis gas (H_2/CO_2), simple alcohols (e.g. ethanol) and short chain volatile fatty acids (e.g. butyrate, propionate and acetate) are considered to be good electron donors for sulfate-reducing bacteria (Visser 1995; van Houten 1996). There are however only limited literature data showing the ability of these electron donors to support high rates of sulfate conversion. Efficient biological treatment of sulfate-loaded wastewaters strongly depends on the outcome of the competition for common

substrates between sulfate reducers and other groups of bacteria in an anaerobic bioreactor, a process not yet fully understood (Oude Elferink et al. 1994). The COD to sulfur ratio (COD/S) in the influent and the pH in the reactor strongly determine the level and outcome of competition. The former defines whether sulfate or carbon is the limiting substrate (McCartney & Oleszkiewicz 1993; Harada et al. 1994; Uberoi & Bhattacharya 1995), while the latter affects the level of inhibition by sulfide species in solution (McCartney & Oleszkiewicz 1991; Reis et al. 1992; Maillarchervu et al. 1993; Okabe et al. 1995). This is especially true for acetotrophic sulfate-reducing bacteria which are highly sensitive for the undissociated hydrogen sulfide (H_2S) (Stucki et al. 1993; Maillarchervu & Parkin 1996). Acetate metabolism is therefore considered as the critical step in anaerobic degradation processes under sulfate-reducing conditions.

High pH or sulfide removal through stripping equally favored sulfidogenic acetate removal which otherwise accumulated in an ethanol-fed EGSB reactor (De Smul et al. 1997). The aim of the present study is to determine if an EGSB reactor operated with acetate as sole source of carbon and energy under the conditions identified above can efficiently treat sulfate-rich wastewaters.

Materials and methods

Reactor

A 2.3 L glass lab-scale UASB/EGSB bioreactor was used, consisting of a 1.3 L cylindrical tube (length = 66 cm; internal cross-section = 5 cm) topped by a spherical 1 L three phase separator. Liquid recirculation (flow rate = 236 l/d) was applied in order to achieve an initial upflow superficial velocity of 5.0 m/h, creating a continuous granular bed expansion of approx. 100%. On day 117 approximately one third of the sludge was removed from the bioreactor to prevent excessive sludge wash-out, after which the superficial upflow velocity was increased from 5 to 10 m/h by doubling the recirculation flow to approx. 470 l/d.The recirculation flow was further increased on day 150 to approx. 940 l/d corresponding to an upflow velocity of 20 m/h. The synthetical influent was pumped continuously in the recycle stream at the bottom of the reactor at a flow rate of 30 l/d. To enhance biomass retention in the reactor, a deflector was introduced in the recirculation stream. This was basically an upward curving of the effluent tubing to avoid excessive biomass wash-out. The head-space of the reactor was connected with a column filled with an acidic solution to allow monitoring of biogas formation and its composition.

Reagents and media

Sulfate was supplied as its sodium salt Na_2SO_4 and acetate as acetic acid. Nitrogen and phosphorus were supplied as NH_4Cl and KH_2PO_4 respectively in order to obtain a COD/N/P ratio of 100/1.25/0.25 in the tap water based influent solution. Iron sulfate ($FeSO_4$) was dosed at 0.5 ml per liter influent from a 10 g/l stock solution. One ml of a trace element solution was added per liter of influent. This trace element solution was composed of 100 mg/l of resazurin, 500 mg/l of H_3BO_3, $ZnCl_2$, $(NH_4)_6Mo_7O_{24}.4H_2O$, $NiCl.6H_2O$, $AlCl_3.6H_2O$, $CoCl_2.6H_2O$ and $CuSO_4.5H_2O$, 1000 mg/l of $NaSeO_3.5H_2O$, 5000 mg/l of $MnCl_2.4H_2O$ and 5 ml/l of a 37% HCl solution.

Inoculum

The reactor was inoculated with sludge originating from a high-rate sulfate reducing lab-scale EGSB bioreactor that was operated during two months with ethanol as the electron donor (De Smul et al. 1997). The original sources were several full-scale anaerobic UASB reactors. The amount of biomass present in the seed sludge was approx. 10 g VSS/l.

Operational conditions

The EGSB reactor was operated during 180 days. According to the overall acetotrophic sulfate conversion reaction,

$$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$$

one mole of acetate is required for the complete reduction of 1 mole of sulfate. Since 1 g of acetate approximately corresponds to 1.07 g of acetate-COD (or C_2-COD), 2 g of C_2-COD are required for the complete conversion of 1 g of SO_4^{2-}-S. The COD to sulfur ratio was initially maintained at the stoichiometric value of 2 g COD/g S to allow complete COD removal through sulfate reduction. The COD/S ratio was increased to 2.2 after 23 days of operation and kept at this value throughout the experiment. The initial sulfate concentration in the influent was 100 mg SO_4^{2-}-S/l. The influent flow rate was gradually increased from 22.0 to 29.8 $\pm$ 1.8 l/d after 4 days and

then maintained at this value. The hydraulic retention time accordingly decreased from 2.5 to 1.9 ± 0.1 h. Whenever appropriate the sulfate loading rate was increased by increasing the influent sulfate concentration without changing the influent flow rate or the COD/S ratio. The pH on the influent depended on the applied loading rate and was set in order to obtain a pH ranging from 7.5 to 8.2 in the bioreactor (average value: 7.9 ± 0.1). The reactor was installed in a temperature controlled room, thus allowing mesophilic conditions (temperature range: 33–37 °C). The following parameters were routinely monitored during the experiment: effluent sulfate and acetic acid concentrations, reactor pH, biogas production and composition (methane and CO_2 content of the biogas) and influent flow rate.

Analysis

The total dissolved sulfide concentration (TDS) was measured with a sulfide selective electrode (ATI Orion 9416 SC) under the form of HS^-(aq). Prior to sulfate analysis, 2 ml of a 0.25 m $Zn(Cl)_2$-solution were added to the 20 ml-samples to remove all the sulfide through precipitation. Sulfate was then measured according to the spectrofotometric method of Trüper & Schlegel (1964). Volatile fatty acids (VFA) were determined gaschromatographically after ethylether extraction of acidified samples. The gaschromatograph (Di200 GC, Delsi Instruments) was equipped with a flame ionization detector and a Delsi Nermag Enica 31 integrator. The FFAP capillary column (30 m by 0.53 mm; film thickness of 1.2 μm) had a temperature of 130 °C, while the temperature of the injection ports and detector was 195 °C. Nitrogen gas (N_2) was used as a carrier at a flow rate of 20 ml/min. The gas composition was analysed gaschromatographically with an Intersmat IGC 120MB GC connected to a Hewlett-Packard 3396A integrator. The gaschromatograph was equipped with a catharometer detector and a dual column arrangement, consisting of a Porapak (50–80 mesh) and a molecular sieve (60–80 mesh) column. The column temperature was 30 °C, and the carrier gas (helium) had a flow rate of 10 ml/min. Total suspended solids (TSS) and volatile suspended solids (VSS) were analyzed in correspondence with APHA (1992). Suspended solids in the effluent were determined by filtering over filter papers (pore size 8 μm) and drying at 105 °C during 3 hours. The calcium and iron content of the dried (105 °C during 24 hours) and ashed sludge (450 °C during 3 hours) was determined after acid extraction with 10 ml 14 N nitric acid during 15 minutes and subsequent filtering, after which the samples were diluted in double-demineralized water (Milli-Q). The analysis was done by atomic absorption spectrometry (Perkin Elmer 3110). The burning gas for the flame was a mixture of air and acetylene (4:1), and a mixture of air and argon was the flow gas in the furnace. The analysis was also performed on a sample of the tap water used for the preparation of the influent solution. The amount of carbonate precipitates of the sludge was estimated gravimetrically by substracting the weight of the ashed sludge after nitric acid digestion from the weight of the ashed sludge before digestion. The amount of phosphate precipitates of the sludge was determined spectrophotometrically (Gabriels et al. 1985) after acid extraction of the dried and ashed sludge with 10 ml 14 N nitric acid during 15 minutes.

SEM-photographs

Scanning electron micrographs were made after double fixation of the granular sludge with glutaraldehyde and osmiumtetroxide, dehydratation in a graded ethanol serie and critical point drying (Zellner et al. 1991).

Results

Reactor performance

Table 1 summarizes the overall reactor performance during the first 117 days of operation. Figures 1 and 2 show the loading and conversion rate curves for sulfate and acetate respectively, as well as the respective effluent concentrations. Sulfate reduction started quickly and the sulfate and COD loading rates gradually increased (Table 1: period 1 to 5). Acetate-COD was almost completely removed (> 90%) during the first three periods (days 1–22). The COD/S ratio was slightly increased to 2.2 on day 23 to prevent the electron donor from becoming limiting. The sulfate removal rate varied between 9 and 10 g SO_4^{2-}-S/l.d after only 60 days of operation (Table 1: period 6) at a loading rate of 10.4 g SO_4^{2-}-S/l.d. Sulfate reduction accounted for 80 to 90% of the total COD removal.

A further increase in the sulfate loading rate to 13 g SO_4^{2-}-S/l.d by raising the influent sulfate concentration from 800 to 1000 SO_4^{2-}-S/l did not result in an increased conversion during the following 45 days (Table 1: period 7).

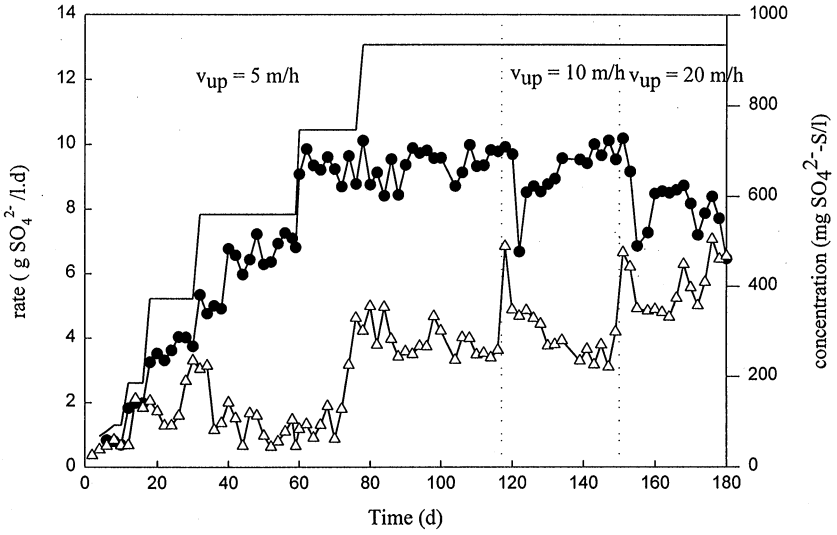

Figure 1. Evolution of the sulfate loading (–) and conversion (●) rate, and the residual sulfate concentration (△). Three periods can be identified as a function of the superficial upflow velocity.

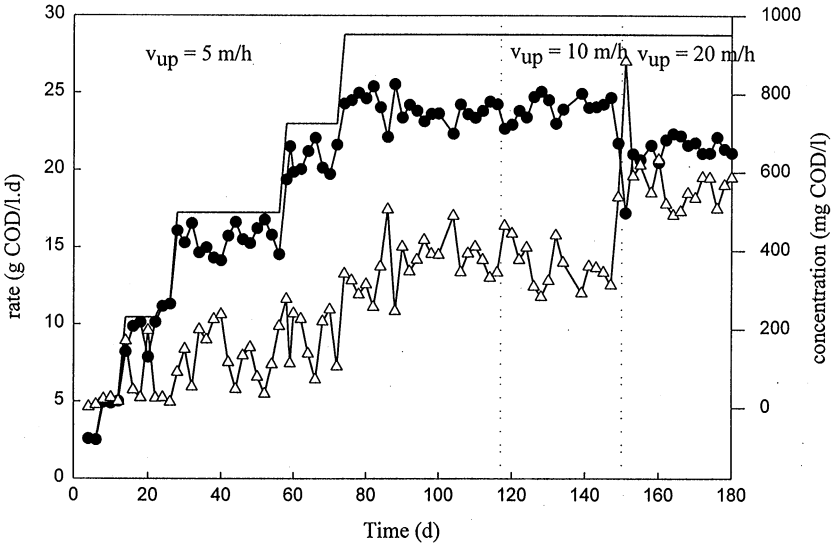

Figure 2. Evolution of the acetic acid loading (–) and conversion (●) rate, and the residual acetic acid concentration (Δ), expressed as COD. Three periods can be identified as a function of the superficial upflow velocity.

On day 117 the superficial upflow velocity was increased from 5 to 10 m/h by doubling the recirculation flow to approx. 470 l/d. Prior to that approximately one third of the sludge was removed from the bioreactor to avoid the expanded sludge bed filling the spherical settler unit and to prevent excessive loss of biomass from the reactor. Probably as a result of these disturbing interventions, the sulfate conversion efficiency dropped severely to less than 7 g SO_4^{2-}-S/l.d. The reactor performance slowly recovered and again reached reduction rates of 9 to 10 g SO_4^{2-}-S/l.d (70–75%) within 2 weeks. COD removal efficiencies were fairly constant during this period (80–85%). SRB thus accounted for 70–85% of the total COD uptake.

The upflow velocity was further increased on day 150 to 20 m/h by increasing the recycle flow to approx. 940 l/d. The sulfate removal rate and efficiency steadily decreased during the last 30 days of the experiment and levels as low as 6 to 8 g SO_4^{2-}-S/l.d (50–60%) were eventually reached. COD removal efficiencies only dropped slightly (to 70–80%), causing the COD removal through sulfate reduction to drop

Table 1. Overview of the EGSB reactor performace during the first 117 days of operation

Period	Time days	Influent sulfate conc. $MgSO_4^{2-}$–S/l	COD/S	Sulfate loading rate g SO_4^{2-}-S/l.d	Sulfate conversion rate g SO_4^{2-}-S/l.d	COD conversion rate g COD/l.d	Relative electron flow to SRB %
1	1–7	100	2	1.3	0.7–0.8 (60%)	2.5–2.6 (96–98%)	60
2	8–12	200	2	2.6	1.8–2.0 (70–76%)	4.9–5.0 (94–96%)	74–81
3	13–22	400	2	5.2	3.3–4.0 (62–77%)	8.2–10.1 (79–97%)	65–80
4	23–27	400	2.2	5.2	3.7–4.0 (72–77%)	11.1–11.3 (97–98%)	66–72
5	28–56	600	2.2	7.8	6.0–7.3 (76–93%)	14.1–16.8 (82–97%)	80–94
6	57–72	800	2.2	10.4	8.8–9.8 (84–94%)	19.4–22.0 (85–96%)	81–95
7	73–116	1000	2.2	13.1	8.4–10.1 (64–76%)	23.4–25.5 (81–89%)	70–85

to less than 70% (Figure 3), while biogas production increased (data not shown).

Sludge characterization and activity

A sludge balance was performed for the last 15 days of the experiment to evaluate the importance of sludge wash-out. Biomass changes in and wash-out from the reactor were measured during that period. The results shown in Table 2 suggest that a considerable amount (20% on VSS basis) of sludge was lost during this period, while the total amount of suspended solids slightly increased. The concentration of the non-granular fraction of the sludge (indicated by flocs in Table 2) doubled. The average concentration of suspended solids in the effluent was 80 $\pm$ 13 mg SS/l (n = 7). A sludge yield coefficient Y of 0.02 g VSS per g COD removed (= 2%) could be calculated with the data from Table 2 and the results of the wash-out monitoring. This value corresponds well with literature results for acetate utilizing SRB (Maillachervu & Parkin 1996). The overall specific conversion rates at the end of the continuous EGSB experiment were 1.0 $\pm$ 0.1 g C_2-COD/g VSS.d and 0.38 $\pm$ 0.06 g SO_4^{2-}-S/g VSS.d.

Table 3 shows the dry matter composition of the sludge samples. Iron and phosphate precipitates accounted for less than 1% by weight on SS basis. The calcium concentration of the granules and the flocs was 4.5 $\pm$ 0.4 and 0.11 $\pm$ 0.01 g Ca/g VSS respectively. Calcium deposits were mainly carbonates. The tap water used for the preparation of the influent solution contained 106 mg Ca/l.

SEM-photographs

The SEM-pictures taken at the end of the experiment revealed the heterogenous nature of the sludge granules and the relative diversity of the attached microbial population as observed and described in an earlier study (De Smul et al. 1997). Some granules however seemed to consist mainly of inorganic material (Figure 4-a), or were only very scarcely populated (Figure 4-b). Precipitates were omnipresent (Figure 4-c).

Discussion

The competition between SRB and MPB for common substrates, such as hydrogen and acetate, has been extensively studied, both in natural systems (marine and fresh water sediments) as in anaerobic reactors. It is accepted that SRB are able to outcompete MPB for hydrogen in all cases. The picture is far less clear however with respect to the anaerobic utilization of acetate (Oude Elferink et al. 1994). Although thermodynamic and kinetic considerations favor sulfate reduction over methanogenesis (Table 4), it has often been observed that MPB are able to effectively outcompete SRB for acetate in anaerobic reactors (Isa et al. 1986a and 1986b; Yoda et al. 1987; Qatibi et al. 1990; Polprasert & Haas 1995).

The present study aimed at efficiently operating a high rate completely sulfidogenic EGSB bioreactor with acetate as sole source of carbon and energy. A fairly stable sulfate conversion rate of 9 to 10 g SO_4^{2-}-S/l.d was observed after only 60 days of operation. Both COD and sulfate conversion were highly efficient (period 6 in Table 1). These results were

Table 2. Sludge content distribution in the EGSB reactor over a 15-day period at the end of the experiment: the average concentration and standard deviation (n = 2) of suspended and volatile suspended solids (SS respectively VSS) for the granular and non-granular fraction of the biomass

	g SS/l			g VSS/l		
	day 0	day 14	Δ	day 0	day 14	Δ
Granules	198 ± 4	202 ± 8	+ 4	23.1 ± 0.4	16.5 ± 0.3	− 6.6
Flocs	2.2 ± 0.3	4.8 ± 0.2	+ 2.6	1.4 ± 0.3	3.0 ± 0.3	+ 1.6
Total	200	207	+ 7	24	19	− 5

Table 3. Composition of the granular and non-granular fraction of the sludge dry matter at the end of the experiment: the relative amount of organic matter, phosphate, iron, calcium and carbonate precipitates (n = 2), expressed as% of SS

	VSS (% of SS)	P (% of SS)	Fe (% of SS)	Ca (% of SS)	$CaCO_3$ (% of SS)
Granules	7.2 ± 0.6	0.64 ± 0.05	0.15 ± 0.07	32 ± 1	78 ± 7
Flocs	62 ± 6	0.43 ± 0.05	0.2 ± 0.1	5.4 ± 0.3	13 ± 2

obtained by succesfully applying the operational conditions identified in an earlier study (De Smul et al. 1997).

Firstly the near-stochiometrical COD/S ratio (2.2) allowed complete COD removal through sulfate reduction (Gupta et al. 1994). Secondly, the pH value in the reactor (7.9 ± 0.1) prevented the undissociated hydrogen sulfide (H_2S; pK_a = 7.0) to reach inhibitory levels. Acetotrophic SRB are highly sensitive to H_2S intoxication (Maillarchervu & Parkin 1996). Acetate degrading SRB remained active and dominant throughout the entire long-term experiment because the differential sulfide-sensitivity in the reactor was alleviated by keeping the H_2S concentration always lower than 100 mg H_2S/l (Stucki et al. 1993).

Since acetotrophic SRB lack the ability to consume acetate fermentatively in the absence of sulfate, and typically grow slowly on this low energy substrate (Table 2), the origin and history of the inoculum are key-factors in interpreting the experimental results. Visser (1995) estimated that it takes a long time (several hundred days) after an exposure to sulfate before considerable numbers of acetotrophic SRB are present when the anaerobic sludge used originates from sulfate-free environments. This effect is emphasized in anaerobic reactors based on high sludge retention time, such as the UASB or EGSB (Visser 1995). The granular sludge used in this study acclimated for 2 months in a high rate nitrogen gas stripped ethanol fed sulfidogenic EGSB reactor, described by De Smul et al. (1997). The experimental history of the seed sludge explains the observed quick start-up of the sulfate-reducing reactor (Table 1).

The applied operational conditions, the sludge acclimation discussed above, and the intrinsic kinetic and thermodynamic paramaters of acetate utilization by SRB (Table 4), resulted in an efficient and stable high rate sulfate reduction process over a prolonged period of time. Unlike results of Bhattacharya et al. (1996) and Yoda et al. (1987), almost complete sulfidogenesis was observed throughout the experiment. Similar results were only obtained by Stucki et al. (1993) with acetic acid in packed bed filters, by van Houten (1996) with synthesis gas in anaerobic gas-lift reactors and by De Smul et al. (1997) in ethanol fed EGSB reactors. To our knowledge, this is the first report of such high sulfate removal rates and efficiencies for an EGSB reactor configuration with acetate as sole carbon and energy source.

Although thermodynamically favorable, with a calculated ΔG of approximately -46 kJ/r under the actual experimental conditions, a further increase of the reactor performance seemed impossible. It was hypothesized that mass transfer limitations caused the observed leveling off of the sulfate removal (Figure 1). The size of the granules, of the order of several hun-

Table 4. Overall conversion reactions, free energy changes (ΔG°', at pH = 7.0) and reported range for Monod affinity constants (K_s) and growth rates (μ_m) for acetotrophic SRB and MPB (Thauer et al. 1977; Alphenaar 1994; Visser 1995)

	Reaction	ΔG°'(kJ/r)	K_s (mM)	μ_m (day^{-1})
SRB	$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2\ HCO_3^-$	− 39.5	0.10–0.23	0.51–1.44
MPB	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	− 28.2	0.44–6.39	0.11–0.69

dred μm, and the residual bulk sulfate concentration of 200 to 300 mg SO_4^{2-}-S/l (Figure 1), indicate, according to Overmeire et al. (1994), that film diffusion of sulfate from the bulk liquid to the surface of the granules would be the main mass transfer limiting process and not the diffusion into the granules themself. Further reserach is however needed to elucidate the importance of the observed massive calcium carbonate precipitation (Table 3) for the intra-granular diffusional process.

An increased upflow velocity to 10 m/h did not affect the performance (Figures 1 and 2), although supposedly decreasing film diffusion limitations. A further increase to 20 m/h resulted in deterioration of the granular sludge, yielding bare mainly inorganic granules (Table 3; Figure 3-a and 3-b), caused an increase of the suspended sludge fraction (Table 2), and a considerable loss of biomass into the effluent. This biomass loss was accompanied by a considerable drop in the sulfate reduction rate and efficiency (Figure 1) while the change in COD removal was relatively less important (Figure 2). This indicates a shift from sulfidogenic towards more mixed (sulfidogenic/methanogenic) conditions, clearly shown in Figure 3. These observations are consistent with results from Omil et al. (1996) showing a selective wash-out of sulfate-reducing bacteria from UASB reactors at moderate upflow velocities. SRB have poor attachment properties and are not able to form strong granules (Alphenaar 1994), and are therefore more sensitive to perturbartions of the sludge bed, e.g. caused by a higher recirculation flow. Sludge retention thus becomes an important limiting factor for the operation of a high rate sulfidogenic bioreactor.

The granules elemental analysis revealed (i) the high ash content ($\approx$ 90%) (ii) consisting mainly of $CaCO_3$ precipitates (Table 3). Thaveesri et al. (1995) report values of 1.2 to 1.8 g Ca/g VSS in some VFA-fed granules with a high ash content of 82 to 88%. Uemura & Harada (1995) found calcium concentrations of 6.2 g Ca/g VSS in the core of thermophilic granules from a sucrose fed UASB reactor (ash content cores = 94.5%). Calcium carbonate precipitation was favored by the more alkaline conditions inside the granules owing to the consumption of acetic acid (De Beer et al. 1992). It was also observed that an increased amount of calcium in the influent accelerated the precipitation (Uemura & Harada 1995). The tap water used in this experiment contained 106 mg Ca/l and could therefore be identified as the calcium source, while carbonate is the end-product of anaerobic acetate degradation (Table 4) yielding 2 moles of bicarbonate per mole acetate removed. The effect of these precipitates, specially with respect to possible encapsulation of biomass, is unknown, but clearly needs further research.

Conclusion

The near stoichiometrical COD dosage and slightly alkaline conditions applied in this study allowed the quick start-up and the efficient conversion of high sulfate loading rates by acclimated suldfidogenic granular sludge in an acetate fed EGSB reactor. High conversion rates and efficiencies were maintained throughout the entire long term experiment. Acetotrophic sulfate reducers were enabled to predominate by avoiding selective hydrogen sulfide induced inhibition. Mesophilic sulfate reduction rates in EGSB reactors seemed however to be limited to 10–11 g SO_4^{2-}-S/l.d. Increasing the upflow velocity resulted in an excessive wash-out of biomass and granular deterioration, which negatively affected both the overall performance and the sulfidogenic characteristics of the bioreactor. Sludge composition analysis showed a low organic matter content and a high amount of calcium in the granules, caused mainly by calcium carbonate precipitates.

Further research should focus on sulfate removal in EGSB reactors fed with an economically attractive industrial waste stream. Furthermore, the possible influ-

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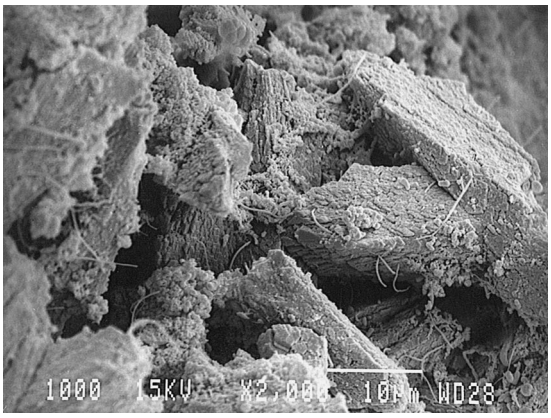

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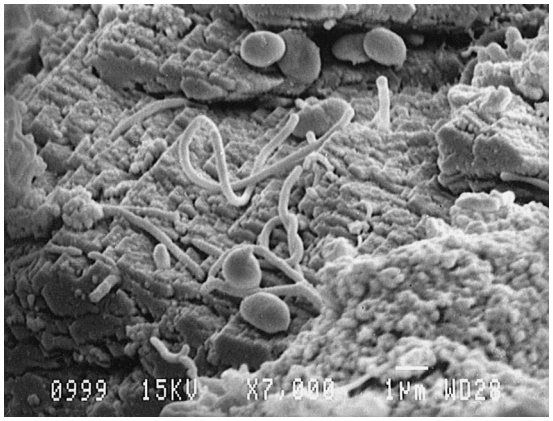

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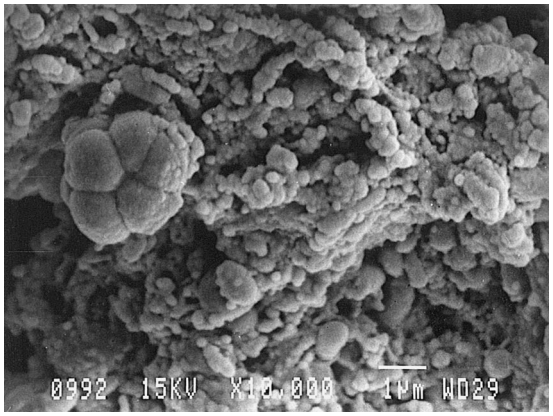

Figure 3. SEM-photographs of the granular sludge obtained from the EGSB reactor at the end of the continuous experiment, representing (a) a bare granule (lenght of bar = 10 μm), (b) the scarcely populated surface of some granules (lenght of bar = 1 μm) and (c) the ubiquitous precipitates (lenght of bar = 1 μm).

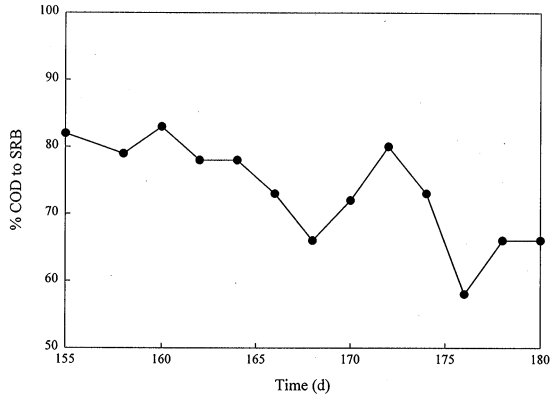

Figure 4. Relative electron flow to sulfate reducing bacteria during the last 25 days of operation.

ence of carbonate precipitation on reactor performance should be investigated more in greater detail.

Acknowledgments

Financial support was received from Biotim NV, Electrabel NV, Fabricom NV and Tractebel Energy Engineering.

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