Biodegradation **11:** 295–303, 2000.

Use of hydrophobic membranes to supply hydrogen to sulphate reducing bioreactors

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Accepted 29 August 2000

Key words: Biological sulphate reduction, hydrogen, membrane bioreactor, sulphide inhibition

Abstract

This paper reports on the application of hydrophobic membranes to supply the gaseous substrates hydrogen/carbon dioxide (H_2/CO_2) to a sulphate reducing bioreactor. For this, two flat 0.016 m^2 sheets of flouroplast microporous (0.45 μm) membranes were inserted in a 3.6 dm^3 bioreactor for the supply of H_2/CO_2 gas as small gas bubbles. The bioreactor was operated at 30 °C and pH 7.0 and was also equipped with an external ultra filtration module for biomass retention. At a sulphate loading rate (SLR) of 1.32 g SO_4^{2-} dm^{-3} day^{-1} and a hydraulic retention time (HRT) of 61 h, a sulphate reduction rate (SRR) of 0.90 g $SO_4^{2-}dm^{-3}$ day^{-1} was achieved. When the influent sulphate concentration was reduced from 3.36 to 0.75 g SO_4^{2-} dm^{-3} by lowering the HRT to 10.3 h (SLR of 1.75 g SO_4^{2-} dm^{-3} day^{-1}), the SRR dropped to 0.22 g SO_4^{2-} dm^{-3} day^{-1}. The lower sulphate reduction efficiency was most probably caused by a too short biomass-substrate contact time or by irreversible sulphide inhibition. Mass transfer limitation of H_2 and improper mixing of the reactor liquid were shown not to contribute to the low sulphate reduction efficiency.

Abbreviations: HAB – homoacetogenic bacteria; HRT – hydraulic retention time; MB – methanogenic bacteria; SLR – sulphate loading rate; SRB – sulphate reducing bacteria; SRR – sulphate reduction rate; UF – ultra filtration.

Introduction

Inorganic sulphate-rich wastewaters contain little or no organic contaminants. They are produced by the chemical and photographic industries (Lens et al. 2000), and also during scrubbing of SO_2 containing flue gasses (Janssen et al. 2000). Metallurgical (e.g., galvano- and electroplating) and mining activities are another source of inorganic sulphate rich wastewaters, also containing high heavy metal concentrations (Lens et al. 2000). Biological sulphate reduction can be used to treat these inorganic wastewaters in order to achieve, in addition to sulphate removal, metal removal and neutralisation. Sulphate can be removed as elemental sulphur, via sulphide as an intermediate product, provided that a proper electron donor and carbon source is supplied (Van Houten & Lettinga 1996). Sulphide and alkalinity are produced by bacterial sulphate reduction, in stoichiometric amounts equivalent to the amount of sulphate reduced, which enables an efficient treatment of metal rich and acid wastewaters, respectively.

The biological sulphate removal process has developed over the past 15 years to a point that it can compete successfully with other sulphate removal technologies for full-scale treatment of inorganic wastewaters. Early studies concentrated on the use of organic matter, e.g., sucrose, pulp mill effluent or molasses, as the electron donor for sulphate reduction (Maree & Strydom 1985; Maree & Hill

1989). Since then, many investigations have been carried out to optimise the sulphate reduction efficiency, by optimising the type of electron donor, operating conditions and reactor design (Hiligsmann et al. 1998; Hulshoff Pol et al. 1998).

Du Preez et al. (1992) were the first to demonstrate that producer gas (a mixture of H_2, CO_2 and CO) can be utilised as carbon and energy source for biological sulphate reduction. This process was further optimised by Van Houten et al. (1994) in a gas lift reactor using pumice particles as support material. In this reactor system, they achieved an SRR as high as 30 g SO_4^{2-} dm^{-3} day^{-1} with a mixture of H_2/CO_2 gas. The presence of small amounts of CO (1–5%), as is the case for synthesis gas, decreased the SRR because of CO toxicity (Van Houten et al. 1996). In these H_2 utilising reactors using immobilisation of cells for biomass retention, the mass transfer capacity for H_2 from the gas to the liquid phase (reactor liquid) determines the maximum sulphate conversion rate (Du Preez et al. 1992; Van Houten et al. 1994; Van Houten & Lettinga 1996).

The problem of H_2 gas/liquid mass transfer is very similar to that of oxygen transfer for the aeration of aerobic microbial cultures or sludges, where the high oxygen uptake rates of the aerobic biomass can by far exceed the oxygen supply (Hartbrich et al. 1996). One way to overcome this limiting factor is to supply O_2 via the concept of bubbleless aeration (Semmens 1991; Brindle & Stephenson 1996). This is achieved by placing a thin film of synthetic polymer between a gas and a liquid. Oxygen is transported through the membrane and goes directly into solution. Bubbleless aeration has been applied in aerobic wastewater treatment (Cote et al. 1988; Semmens 1991; Pankhania et al. 1994; Brindle & Stephenson 1996) and in biotechnological applications, e.g., the cultivation of yeast (Golubev & Fedorovich 1992). This type of supply of gaseous substrates has excellent mass transfer properties and k_La values of 500–1000 h^{-1} have been obtained (Fedorovich 1991).

In view of the excellent mass transfer properties, application of membrane supported supply of gaseous substrates could be a good alternative to supply H_2/CO_2 to sulphate reducing bioreactors. This paper reports on the application of H_2/CO_2 supply by using hydrophobic microporous membranes to a sulphate reducing bioreactor. The feasibility and limitations of this concept for the biological sulphate reduction process are described.

Materials and methods

Sulphate reducing bioreactor

A hard PVC plastic bioreactor (Figure 1) with a biologically active reactor volume of 3.6 dm^3 (liquid height 0.225 m, inner diameter 0.16 m) was used in the experiment. It was constructed to be resistant to increased gas pressures (up to 5 bar) inside the reactor. The reactor was continuously stirred (using a Heidolph RZR 1 motor) at 235 rpm to keep the biomass in suspension. The stir stave had a long, but narrow blade (Figure 1) to prevent it from damaging the membranes. The modules were mounted with the membrane side facing the stir stave.

The reactor was operated at 30 °C by recirculation of water of a thermostatic bath (Haake DC 3) at that temperature through the reactor mantle. The pH of the reactor liquid was controlled with a sulphide resistant Flushtrode® pH-electrode (Hamilton Flushtrode, Hilkomij bv, Rijswijk, The Netherlands) and a controller with two changeable set points to correct the pH by adding concentrated NaOH or HCl solutions. The pH was maintained at 7.0 ($\pm$0.2) during the whole experimental period.

The bioreactor was inoculated with a cell suspension (cell conglomorates of less than 100 μm), obtained by crushing anaerobic granular sludge with a blender for 5 minutes. The granular sludge was obtained from an UASB reactor treating paper mill wastewater at Industrie Water NV (Eerbeek, The Netherlands). The initial quantity of wet seed sludge was 318 g corresponding to 12 g VSS $dm^{-3}_{reactor}$.

Gas supply to the bioreactor

A mixture (80 : 20%) of hydrogen and carbon dioxide (H_2/CO_2) gas was used as the influent gas. Its gas flow was set with two mass flow controllers (Brooks thermal mass flow meter, type 5850TR, Brooks Instruments, Veenendaal, The Netherlands), connected to a read out/control unit (Brooks type 5876, Brooks Instruments, Veenendaal, The Netherlands). The effluent gas flow was monitored with a wet-type precision gas meter (type 1, Meterfabriek Schlumberger Industries, Germany).

Two membrane modules were used to supply the influent gas to the reactor (Figure 1). The modules were constructed of PVC plastics, because stainless steel would corrode by the sulphide present in the reactor. In each module (0.150 m long and 0.105 m

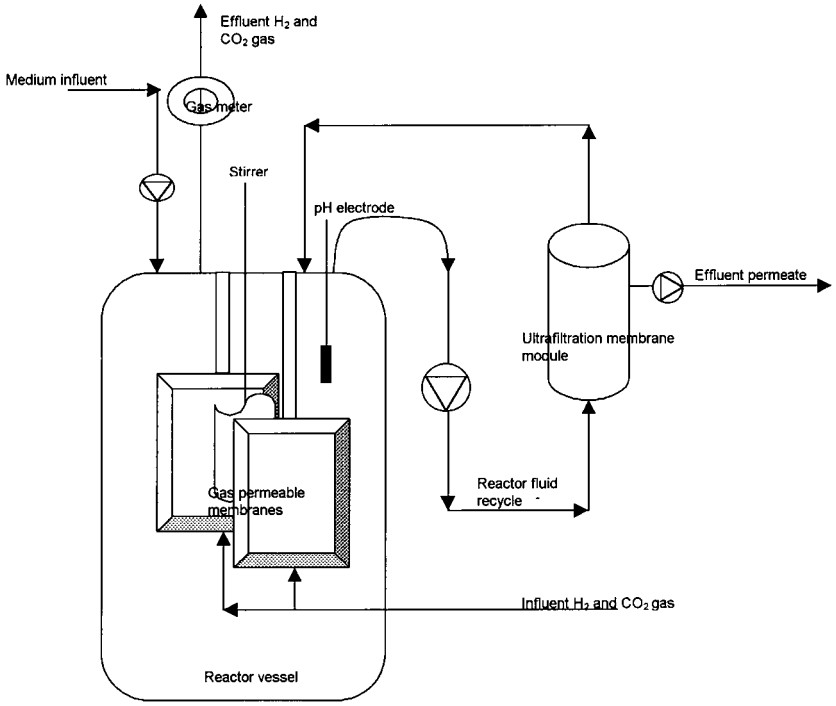

Figure 1. Schematic representation of the set-up of the membrane reactor for biological sulphate reduction.

wide), a flat sheet of a membrane was mounted. Unless otherwise stated, experiments were performed with hydrophobic flouroplastic membranes with a pore size of 0.45 μm (type MFFK-4; Polymersyntez, Vladimir, Russia). In some initial experiments, Nuclepore® Polyester membranes (Corning Separations Division, USA) were used as well. The latter type of membranes is used in molecular ecology to separate nucleic acids. The gas chamber under the membrane was 0.005 m deep. The membrane modules were designed with two cross bars at 1/3 and 2/3 of the length to prevent the membrane from bursting when pressure was exerted on it. Each module was investigated for leaks before being mounted in the reactor.

When the H_2/CO_2 mixture was forced through the surface of the membrane, pressure was exerted on the membranes. This pressure was measured in bars overpressure with a gas pressure controller. The gas flows applied never exceeded 0.14 bar overpressure, because of bursting of the membranes at higher overpressures.

Water circuit of the reactor

The bioreactor treated a synthetic wastewater (pH 7.0) containing (in g dm^{-3}): Na_2SO_4 (4.97), $Na_2HPO_4 \cdot 2H_2O$ (0.53), KH_2PO_4 (0.41); NH_4Cl (0.30), KCl (0.37), $MgCl_2 \cdot 6H_2O$ (0.10), $CaCl_2 \cdot 2H_2O$ (0.11) and $NaHCO_3$ (2.00). Micronutrients (2 ml/L) were added according to Stams et al. (1992).

The synthetic wastewater was pumped into the reactor with a minipulse 2 Gilson thin tubing pump. The reactor mixed liquor was continuously recycled at a flow rate of 115 cm^3 min^{-1} using a Watson-Marlow peristaltic pump (type 503 S, Watson Marlow, Falmouth, Cornwall, UK). In the liquid recirculation tube, an ultrafiltration (UF) membrane module (Ultrafilter type SPS 9005-8, Fresenius AG, Fresenius Institute, Taunusstein, Germany) was inserted for biomass retention (Figure 1). The UF module contained 0.7 m^2 surface area of tubular membranes over which a cross-flow velocity of 2.7×10^{-6} m sec^{-1} was achieved. Another minipulse 2 Gilson pump pumped the permeate from the UF module to the effluent collection vessel.

The UF module was cleaned once a month to remove accumulated biomass and to prevent membrane fouling. To clean the UF module, it was disconnected from the reactor and the in- and output tubes were submerged in a washing solution of hydrochloric acid (pH 4). The washing time was 2 to 3 hours. Thereafter, the UF module was rinsed with 5 litres water to remove remaining HCl traces.

Analytical methods

To determine the flow pattern in the reactor, a HRT distribution was determined by injecting a pulse of LiCl as the tracer (Omil et al. 1996). The Li^+ response curves were normalised and analysed using the 'tanks-in series' model of Levenspiel (1974) to calculate the experimental mean hydraulic residence time (HRT_{mean}), percentage dead zone (% DZ) and the theoretical number of ideal mixed reactors in series (N_{th}), according to the equations described by Grobicki & Stuckey (1992).

Sulphide was determined photometrically using a modified method of Trüper & Schlegel (1964). Sulphate was measured by a turbidimetric standard method (EPA-1985) or by high-pressure liquid chromatography (HPLC) as described in Omil et al. (1996). Volatile fatty acids (VFA) and gas phase composition (CO_2, H_2S, CH_4 and N_2) were determined using gas chromatography as described by Omil et al. (1996). Li^+ was determined by flame atomic absorbance/emission spectrometry as described by van Lier et al. (1996). All gas measurements are expressed at 0 °C and standard pressure (760 mm Hg).

Results

Selection of hydrophobic membranes

At the beginning of the experiment, the applicability of two types of hydrophobic membranes to supply H_2/CO_2 to the sulphate reducing bioreactor was investigated: flouroplastic and Nuclepore® Polyester membranes.

Nuclepore® membranes were mounted in the membrane modules and tested for three days in the reactor filled with tap water. This membrane was found unsuitable for the desired application because, despite its smaller pore size (0.2 μm), larger gas bubbles were produced compared to the flouroplastic membrane (pore size 0.45 μm). The gas flow, and thus also the over pressure needed to create bubbles on the surface of the Nuclepore® (PE) membrane was much higher compared to the flouroplastic membrane (Table 1). This resulted in swelling of the membrane and a complete loss of its elasticity. This was not observed with the flouroplastic membrane, which also contains a support layer with a much larger pore size to provide mechanical strength to this membrane type. Therefore, the flouroplastic membrane was used for the remainder of the experiments.

Table 1. Characteristics of the two types of membranes used in this study

Characteristics	Flouroplastic membrane	Nuclepore membrane
Material	Flouroplastic	Polyester
Pore size	0.45 μm	0.2-0.4 μm
Gas overpressure (bar)	0.01	0.15
Gas flow ($dm^3\ min^{-1}$)	11–28	>40
Bubble size	Small	Large

Start-up of the sulphate reducing bioreactor

At day 0, the influent SO_4^{2-} concentration was 3.36 g dm^{-3} and, after inoculation, the reactor was started in batch mode. A gas feed of 0.68 $dm^3\ h^{-1}$ was supplied, containing 99% H_2 and 1% CO_2. After 1 day, the reactor was operated at a HRT of 61 h. After 4 days, the gas feed composition was changed to 95% H_2 and 5% CO_2, but the total gas flow rate was kept constant at 0.68 $dm^3\ h^{-1}$. This start-up procedure was followed, as an immediate application of a 80 : 20% H_2/CO_2 gas mixture would cause reactor acidification (Du Preez et al. 1992).

During the start-up phase of continuous operation (the first 5 days), the SLR was 0.77 (±0.26) g SO_4^{2-} dm^{-3} day^{-1} and the SRR was 0.33 (±0.21) g SO_4^{2-} dm^{-3} day^{-1} (Table 2). The total liquid sulphide concentration was 69 (±82) mg S^{2-} dm^{-3} during the start-up phase.

Sulphate reduction under different operation conditions

During phase 1 of the continuous operation (Figure 2), the SLR was 1.32 g SO_4^{2-} dm^{-3} day^{-1} and the SRR was 0.90 (±0.12) g SO_4^{2-} dm^{-3} day^{-1} (Table 2), corresponding to a sulphate removal efficiency of 68 (±9)%. On day 6, the total sulphide concentration in the reactor had already increased to 374 mg dm^{-3}, following the SLR increase (Figure 2B). The maximum sulphide concentration in the reactor was 582 mg dm^{-3} during phase 1 (Figure 2B).

The SRR might have been incomplete in phase 1 because these high H_2S concentrations can be inhibitory for sulphate reducing bacteria. Therefore, the influent sulphate concentration was diluted approximately 5 times (to 0.75 g SO_4^{2-} dm^{-3}) on operational day 16. This was accompanied by a decrease of the HRT from 61 h to 10.3 h. The SLR

Table 2. Average values of the operation parameters during the continuous experiment.

Days	Influent flow ($cm^3\ h^{-1}$)	HRT (h)	SLR (g SO_4^{2-} $dm^{-3}\ day^{-1}$)	SRR (g SO_4^{2-} $dm^{-3}\ day^{-1}$)	Sulphide (mg dm^{-3})	Gas flow ($dm^3\ h^{-1}$)	Gas consumption ($dm^3\ h^{-1}$)	pH
Start-up[a]								
Days 1-5	35 ± 12	–	0.77 ± 0.26	0.33 ± 0.21	69 ± 82	0.68	0.23 ± 0.13	7.00 ± 0.00
Phase 1[a]								
Days 6-16	59 ± 0	61.0	1.32 ± 0.00	0.90 ± 0.12	412 ± 99	0.68	0.38 ± 0.08	6.98 ± 0.17
Phase 2[b]								
Days 17-25	350 ± 0	10.3	1.75 ± 0.00	0.41 ± 0.16	97 ± 50	0.68	0.55 ± 0.06	7.01 ± 0.16
Phase 3[b]								
Days 26-34	350 ± 0	10.3	1.75 ± 0.00	0.38 ± 0.12	58 ± 61	1.07	0.38 ± 0.12	6.86 ± 0.19

[a] Influent sulphate concentration – 3.36 g dm^{-3}.
[b] Influent sulphate concentration – 0.75 g dm^{-3}.

was thus increased from 1.32 g SO_4^{2-} dm^{-3} day^{-1} to 1.75 g SO_4^{2-} $dm^{-}3$ day^{-1}. Although the sulphide concentration dropped considerably (Figure 2B), the SRR remained low and amounted to 0.41 (±0.16) g SO_4^{2-} dm^{-3} day^{-1} (Table 2), corresponding to a sulphate removal efficiency of 23 (±16)%.

Another possible reason for the low SRR might be H_2 limitation. To overcome this, the gas flow was increased from 0.68 $dm^3\ h^{-1}$ to 1.07 dm^3h^{-1} during days 26–34 (Figure 2, phase 3). However, the SRR did not improve and was 0.38 (±0.12) g SO_4^{2-} dm^{-3} day^{-1}, corresponding to a sulphate removal efficiency of 22 (±7)% (Table 2).

Hydrodynamic characteristics of the membrane bioreactor

The HRT distribution of the reactor was determined during a run of the reactor, operating with the same sludge under the same operational conditions, but at a HRT of 5.6 h (data not shown). Table 3 shows that the experimentally determined HRT_{exp}(5.49 ± 1.71 h) did not differ very much from the theoretical HRT (HRT_{th} = 5.63 h). The percentage dead zone in the sulphate reducing bioreactor was 6.33% and its number of theoretical mixers was 0.58.

Table 3. Hydrodynamic characteristics of the bioreactor

Parameter	Unit	Determined value
HRT_{exp}	h	5.49
σ^2	–	1.71
HRT_{th}	h	5.37
Dead zone	%	6.33
Li^+-recovery	%	66
Number of mixers	–	0.58

Discussion

Use of hydrophobic membranes in sulphate reducing bioreactors

This paper shows that microporous hydrophobic membranes can be applied as a gas mass transfer membrane for the supply of the gaseous substrates H_2/CO_2 to a sulphate reducing bioreactor. This study further showed that the sulphate reducing efficiency in this type of bioreactor depends on several factors. The role of the principal factors, including mixing, contact time, sulphide inhibition and mass transfer is discussed below.

1. Hydrodynamics

The possibility of insufficient mixing and the presence of dead zones in the reactor were investigated by determining the HRT distribution. The latter indicated that there was practically a complete mixing in the reactor, as indicated by the N_{th}. Thus, bad mixing of the

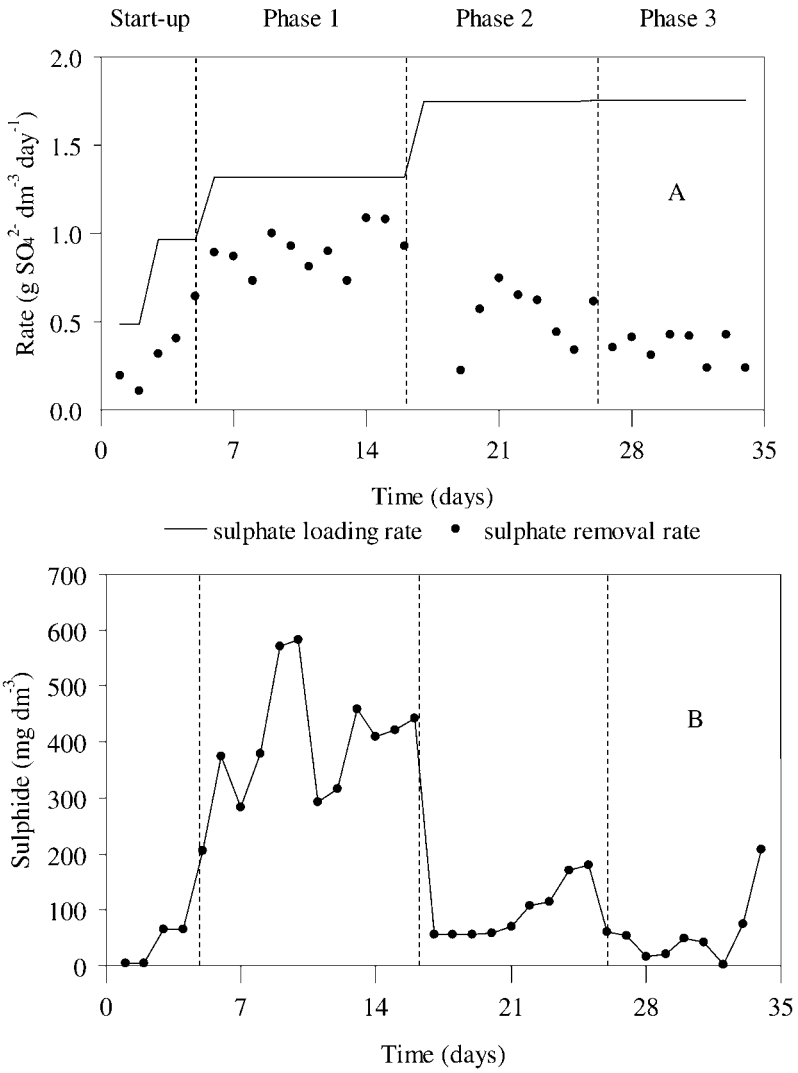

Figure 2. Performance of the hydrogenotrophic sulphate reducing bioreactor. (A) Sulphate loading and removal rates and (B) H_2S concentratons in the reactor mixed liquor.

soluble substrate SO_4^{2-} and thus bad biomass/SO_4^{2-} contact is rather unlikely. The recovery of the tracer was, however, rather low (66%), which might be due to sorption of the positively charged lithium ion to negatively charged biomass particles. Washout of the sorbed lithium may take some more time, i.e., several HRTs.

The sulphate reduction efficiency decreased significantly upon decreasing the HRT from 60 h (phase 1) to 10 h (phase 2). In the remaining phases, the HRT in the bioreactor was about 10 hours (Table 2), which is still the double of the HRT applied in high rate sulphate reducing UASB reactors (Lettinga 1995; Hulshoff Pol et al. 1998). However, the biomass concentration (12 g dm^{-3}) was much lower compared to UASB reactors (>40 g dm^{-3}). Thus, although wash out of biomass as such was not a problem in the experimental set-up (incorporation of an UF module), the applied HRT might have been too short to achieve a complete reduction of the supplied sulphate by the biomass present in the reactor.

2. Sulphide inhibition

The maximum value of total sulphide in the membrane bioreactor was 582 mg H_2S dm^{-3} (Figure 2B). Taking into account that the relative distribution of H_2S and HS^- at pH 7.0 is about 1 : 1 (pKa of H_2S is 7.0 at 25 °C), the maximal concentration of free H_2S was

below 300 mg dm^{-3}. Such a H_2S concentration is rather low to be inhibitory, e.g., in a hydrogenotrophic gas lift reactor, sulphide inhibition occurred only at free H_2S concentrations exceeding 450 mg H_2S dm^{-3} (Van Houten et al. 1994). By contrast, a pure culture of *Desulfotomaculum acetoxidans* was already inhibited at 85 mg dm^{-3} H_2S (O'Flaherty et al. 1998). In general, cell suspensions, as used in this study, are much more susceptible to H_2S toxicity compared to granular sludge (O'Flaherty et al. 1998; Lens et al. 2000).

In high rate sulphate reducing bioreactors, where H_2S concentrations of up to 1.5 g dm^{-3} can be easily obtained (Lens et al. 2000), removal of the reaction product sulphide is a prerequisite. The gas supply method applied in this study does not provide H_2S stripping, as the gas bubbles are not large enough to reach the surface. The introduction of extractive H_2S membranes (De Smul & Verstraete 1999) into the bioreactor mixed liquor might be an elegant and effective H_2S removal method, that allows a direct recovery of elemental sulphur if a Fe^{3+} solution is used as the extraction solution. Alternatively, an extra gas stream (e.g., N_2) can be introduced into the reactor from which H_2S is scrubbed (e.g., by bubbling through a $FeCl_3$ solution) during its recirculation.

3. Mass transfer limitation of hydrogen

The SRR was not affected by the H_2/CO_2 gas flow into the membrane modules, which varied between 0.68 and 1.07 dm^3 h^{-1} (Table 2; Figure 2). Even in a run with a H_2/CO_2 gas flow of 1.69 dm^3 h^{-1} (corresponding to 0.14 bar of overpressure) with the same sludge, there was no increase in the SRR (data not shown). These data suggest that mass transfer limitation of H_2/CO_2 was not the reason for the low SRR. Compared to other H_2/CO_2 fed sulphate reducing bioreactor systems, the applied gas flow is nevertheless rather low. In a gas lift reactor (Van Houten et al. 1994), the influent gas flow rate was 2.55 dm^3 h^{-1} and the gas recycle flow rate was 53–547 dm^3 h^{-1}. It should, however, be noted that the latter reactor operated at a much higher SLR - 30 g SO_4^{2-} dm^{-3} day^{-1} (Van Houten et al. 1994).

In this study, H_2/CO_2 was supplied via a microporous membrane. In these microporous membranes, the H_2/CO_2 mixture is transported through the pore system, rather than diffusion through the polymer, as is the case in dense permeable polymer membranes (Cote et al. 1988). At the gas pressures applied in this study, H_2/CO_2 gas bubbles were formed on the polymer surface. This has also been reported for membrane mediated oxygen supply (Cote et al. 1988), where the surface tension of the membranes was found to keep the gas bubbles attached to the membrane. Because a hydrophobic membrane was used in this study, bubbles were formed at the water side of the membranes. Thus, the pores are filled with the gas mixture, which allows fast gas transport mechanisms through the pores, e.g., gas-gas diffusion or Knudsen flow (Yasuda & Lamaze 1972). This is an important advantage over hydrophilic membranes, as bubbles are formed at the gas side of these membranes, so that H_2 first has to diffuse through the water filled pores via molecular diffusion before it can reach the reactor liquid.

Use of the UF module for biomass retention

The UF module was effective for the complete retention of biomass, but clogged after one month of operation at a biomass concentration of 12 g dm^{-3}. Clogging might be due to adsorption of organic matter, biofilm formation or the formation of inorganic precipitates (Choo & Lee 1996; Elmaleh & Abdemounni 1998). Besides biofilm formation, also sulphide precipitates are an important contributor to fouling in sulphate reducing bioreactors (Mizuno et al. 1998). Fouling could be overcome by increasing the cross flow velocity over the UF membranes, as the applied cross flow velocity over the UF membrane was very low (2.7×10^{-6} m s^{-1}). In literature, much higher cross flow velocities (2-5 m s^{-1}) have been applied (Muller et al. 1995). However, in that case, the cell structure of the biomass may be damaged by the mechanical parts of the UF module and the pump, as reported by Gyoot & Verstraete (1997).

The biomass concentration (around 12 g VSS dm^{-3}) did not vary much through the experiment (data not shown). In literature, a high biomass concentration in bubbleless aeration systems is reported to lower the mass transfer rate. A reason for this effect is the growing bubble size with increasing viscosity at increasing biomass concentrations (Lübbecke et al. 1995). Therefore, the biomass retention should not increase above a critical level (20 g dm^{-3}) to keep an optimal mass transfer (Lübbecke et al. 1995). The biomass concentration in the present study was well below this limit set by Lübbecke et al. (1995).

Sludge characteristics

The following hydrogenotrophic microbial populations present in the inoculum can also proliferate in

the reactor sludge: sulphate reducing bacteria (SRB), homoacetogenic bacteria (HAB) and methanogenic bacteria (MB). In the sludge that developed in the bioreactor, H_2 was used for sulphate reduction by SRB (Figure 2) and acetate production by HAB. The effluent acetate concentration of the bioreactor was less than 50 mg dm^{-3} (data not shown). In batch activity tests using reactor sludge, less than 5% of the H_2 was utilised by HAB (Greben 1999). This suggests that homoacetogens did not consume much H_2, as activity tests showed that acetoclastic sulfate reducing and methanogenic activity was absent (data not shown). The role of the HAB might still be very important in this type of bioreactors, as some H_2 utilising SRB use acetate as the carbon source instead of HCO_3^- (Van Houten et al. 1994). In that case, the activity of heterotrophic H_2 utilising SRB depends on the activity of HAB.

No methanogenesis was observed in the bioreactor (data not shown). Also in batch activity tests using reactor sludge (Greben 1999), hydrogenotrophic methanogenic activity was absent. This is somewhat surprising, as MB activity is known to be very difficult to suppress in sulfate reducing gas lift (Van Houten et al. 1994, 1996) or granular sludge (Omil et al. 1998; Lens et al. 2000) reactors. More research is needed to determine if the applied suspended cell based bioreactor concept is indeed an effective way to develop a fully sulphate reducing sludge.

Practical aspects of membrane supply of gaseous substrates

In bioreactors, most membranes used for oxygen transfer operate with a biofilm attached to it (Brindle & Stephenson 1996), and some bacteria even grow in the pores of the membrane (Rothemund et al. 1994). Also in this study, a small biofilm (<100 μm) developed on the hydrophobic membranes. Because the reactor treated inorganic wastewater, the thickness of the biofilm was rather small, in contrast to membranes exposed to high strength organic wastewaters, where biofilms of several mm can develop (Rothemund et al. 1994; Brindle & Stephenson 1996). However, to ensure a long-term operation, cleaning procedures will be required, as have already been developed for hollow fibre membranes (Pankhania et al. 1994).

Membrane supply of H_2/CO_2 offers several operational benefits. Because the gas and the liquid are physically separated, the gas supply and mixing functions are uncoupled, which allows a better control of the H_2 supply. Moreover, the H_2 transfer surface area is constant, so that the process is not sensitive to factors that affect the size and residence time of the H_2 bubbles as in conventional gas lift systems. In addition, membrane supply of H_2/CO_2 has potential for those cases where conventional H_2 supply gives unsatisfactory results, such as foam formation or stripping of volatile organic compounds. The latter is, however, also an operational drawback of sulphate reducing systems, because of the lack of H_2S stripping (see above). Membrane supported H_2/CO_2 supply has also obvious economical drawbacks when compared to conventional gas lift systems. There is a capital cost associated with the membranes and their useful lifetime is unknown. Furthermore, the membrane represents an added resistance to H_2 transfer, which translates into an energy cost.

Acknowlegement

The financial support of The Netherlands Organisation for Scientific Research (grant N299825) is greatly appreciated.

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