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Understanding the limits of H<sub>2</sub>S degrading biotrickling filters using a differential biotrickling filter

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# Abstract

The removal of  $H_2S$  in high performance biotrickling filters was investigated using a differential biotrickling filter. The differential biotrickling filter was designed to reach high gas velocities through a minature packed bed, in this case a single 4-cm open-pore polyurethane foam cube. External mass transfer was limiting below air velocities of  $3000-4000 \, \text{m} \, \text{h}^{-1}$ , with possible other parameters such as biological kinetics or diffusion-controlled performance above  $4000 \, \text{m} \, \text{h}^{-1}$ . The effect of the liquid trickling rate on  $H_2S$  elimination was found to be nil at low gas velocity, and significant at high gas velocity, consistent with speculations on the wetting of the packing and the rate-limiting step at the conditions of the experiments. The effect of additions of various species of sulfur on  $H_2S$  treatment was investigated. Sulfide negatively affected  $H_2S$  removal, while sulfate and sulfite had no effect. Interestingly, traces of thiosulfate resulted in improved  $H_2S$  removal rates. Cell activity assessed by oxygen-uptake rate determinations was the greatest at near neutral pH. Finally, biokinetic parameters for  $H_2S$  elimination obtained in the differential biotrickling filter and in a batch suspended culture were compared. The rates in the differential biotrickling filter were much higher, indicating that the batch reactor was subject to mass transfer limitation, and illustrating that the biokinetic parameters determined in shake flask systems may not necessarily apply in biotrickling filters. Overall, the study highlights that a differential biotrickling filter is a useful tool for investigating the performance and limits of  $H_2S$  biotrickling filtration, and that detailed studies help in understanding the mechanisms of pollutant removal in biotrickling filters.

Keywords: Biotrickling filter; H2S degrading; Biokinetic parameters

#### 1. Introduction

Emission of objectionable odors is a major problem for wastewater treatment and other processing facilities. Biological treatment is an established alternative to conventional odor control methods [1,2], but until recently biotreatment always required significantly larger reactor volumes than chemical scrubbers. In 2001, five full-scale chemical scrubbers were converted to biotrickling filters at the Orange County Sanitation District (OCSD) and have since been operated at gas contact times ranging from 1.6 to 4 s, which are similar to contact times for chemical scrubbers [3]. Even at very short contact times, H<sub>2</sub>S removal was in excess of 97% for

inlet H<sub>2</sub>S concentrations as high as 30-50 ppm<sub>v</sub>. The corre-

sponding volumetric elimination rates of H<sub>2</sub>S are 95-105 g  $H_2S m^{-3} h^{-1}$ . Compared with other biofilters or biotrickling filters treating concentrations of H<sub>2</sub>S in the range of 50 ppm<sub>v</sub> or less, the elimination rate is large [1,4]. Possible explanations for the unusually high performance observed at OCSD are the high pollutant mass transfer rate due to the large surface area of the packing, an extremely high gas linear velocity  $(1.8 \,\mathrm{m\,s^{-1}}\,\mathrm{or}\,6500\,\mathrm{m}\,\mathrm{h}^{-1})$  and optimum operating conditions (nutrients, pH, CO<sub>2</sub>). The unconventional conditions of the biotrickling filters at OCSD suggest that study of the limits of H<sub>2</sub>S-degrading biotrickling filters can lead to a better understanding of the process, and to optimization of their performance. In particular, mass transfer and H<sub>2</sub>S biodegradation kinetics in high performance biotrickling filters require further definition. Hence, the present study focused on the effects of selected parameters on the performance of H<sub>2</sub>S-degrading

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biotrickling filters. A differential biotrickling filter described earlier [4] was used for these experiments.

During biotreatment, H2S is oxidized by bacteria to SO<sub>4</sub><sup>2-</sup>. H<sub>2</sub>S or its ionic forms HS<sup>-</sup> or S<sup>2-</sup> are used as energy source by litho-autotrophic bacteria, which require carbon dioxide or dissolved carbonate as a carbon source. There are several possible intermediate sulfur species such as  $S^0$ ,  $S_2O_3^{2-}$  and  $SO_3^{2-}$  that may be produced during the oxidation process [5]. Their production depends on the H<sub>2</sub>S loading, pH, bacteria, oxygen concentration and temperature [5–8], however, little is known about the biokinetic factors and possible inhibitions that govern the conversion of H<sub>2</sub>S to its end-product. A better definition of these relationships could help in understanding the limits of the process. Also, in industry, conditions may result in a sudden excess amount of one or more of the intermediate sulfur species which is expected to affect treatment performance, but again little is known about the response of biotrickling filters to such exposure. The impact of the various sulfur species is expected to vary depending on the rate-limiting step of the process, therefore, studies on the effect of sulfur species on biotreatment should be closely linked with mass transfer studies. Thus, the objectives of this study were (1) to determine the effect of gas velocity on the performance of a H<sub>2</sub>S-degrading biotrickling filter using a differential biotrickling filter; (2) to determine the effect of operational parameters and a sudden increase of selected sulfur species on the performance of a H<sub>2</sub>S biotrickling filter at low and high gas velocities; (3) to determine biokinetic parameters in a biotrickling filter and compare them to those obtained in a batch stirred-tank bioreactor.

# 2. Materials and methods

# 2.1. Differential biotrickling filter equipment and operation

A small differential biotrickling filter was used in this study. It was filled with a single cube  $(4 \text{ cm} \times 4 \text{ cm} \times 4 \text{ cm})$  of open-pore polyurethane foam packing (EDT, Eckental, Germany) identical to the packing used in the field study at the Orange County Sanitation District. The foam cube placed in the differential biotrickling filter was taken from a conventional biotrickling filter (see below) operated in a laboratory with H<sub>2</sub>S as the sole pollutant, hence, the foam cube had an already established active biofilm of H2S-oxidizing bacteria, and little or no biomass growth occurred during the experiments in the differential biotrickling filter. Prior to the experiment, the foam cube was placed in 150 mL of mineral medium [9] for 20 min, which removed some loose biomass not firmly attached to the foam cube. The procedure reduced the uncertainties in the amount of protein-biomass attached to the packing during the experiment. The pH of the mineral medium for washing the cube was adjusted to the same pH as the trickling water in the source biotrickling filter by titrating

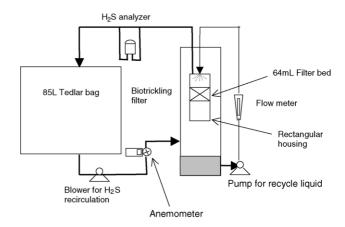


Fig. 1. Schematic of the experimental setup (not to scale).

with 2 M HCl. The conditions in the differential biotrickling filter, e.g., composition of the trickling liquid were matched as closely as possible to those in the source biotrickling filter to minimize the possibility of short-term acclimation effects in the differential reactor. The single foam-cube bed was housed in a larger (10 cm i.d.) clear PVC pipe (Fig. 1) [4]. The biotrickling filter system was designed to run as a batch system to ease determination of the biokinetic parameters. Batch operation also allowed large gas flow rates so that gas film mass transfer resistance could be reduced or possibly neglected. The H<sub>2</sub>S-degrading biotrickling filter was operated in a counter-current mode, i.e., similar to most H<sub>2</sub>Sdegrading biotrickling filters, with the gas flowing upward and recycled mineral medium flowing downward. The air flow was circulated in a closed loop from an 85 L Tedlar bag to the differential biotrickling filter by a 0.2 HP blower (Ametek, Paoli, PA) up to a maximum linear velocity of 3 m s<sup>-1</sup>. The highest air flow resulted in an empty bed retention time (EBRT) of 0.01 s in the foam cube. The recycle liquid was uniformly sprayed on the top of the bed through a nozzle. The recycle liquid consisted of reclaimed water (chlorinated secondary effluent from OCSD) that was sprayed over the filter bed using a peristaltic pump at a rate of  $2.4 \,\mathrm{Lh^{-1}}$  and a WL 1/4 BETE spray nozzle (BETE, Greenfield, MA). Free and residual chlorine in the reclaimed water was negligible and did not affect the experiments. The pressure required for the spray nozzle was less than 0.7 bar. The pH of the recycle liquid depended on the experiment. During a single test, the pH of the recycle liquid never decreased by more than 0.2 pH units. Each experiment took 1–6 h depending on the type of experiment. In most cases, the foam cube was removed from the system after one experiment so that its biomass content could be determined.

At the beginning of each experiment, pure  $H_2S$  (Matheson, Newark, CA) was injected into the differential biotrickling filter system using a 20 mL syringe. In most cases, the experiment consisted of monitoring the  $H_2S$  decrease over time under selected conditions, in particular with varying gas or liquid flow rate. In a differential biotrickling filter, at a given time, conditions do not change greatly from the inlet

to outlet ports of the reactor. Therefore, the observed kinetics correspond to the kinetics of the entire bioreactor at the given time under the given conditions. Because of the experimental conditions, the differential biotrickling filter was always at a pseudo-steady state, and the rate of H<sub>2</sub>S decrease in the system served to calculate the H<sub>2</sub>S elimination capacity (EC) of the biotrickling filter. The short duration of each experiment implied that little biomass growth occurred. Duplicate experiments were conducted and, when different foam cubes were used, the degradation rates were normalized by the amount of biomass to minimize the effect of the variability of immobilized biomass density. In selected experiments, some chemicals were injected in the trickling liquid to determine whether the chemicals had an impact on H<sub>2</sub>S removal. To investigate the effects of sulfite and sulfate, Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> were used, respectively, for injection. The following amounts of solution were added to mineral medium to make up the trickling liquid: 0.12, 0.36,  $1.0 \,\mathrm{mg} \,\mathrm{SO_3}^{2-}$  solution; 650, 1300, 2600 mg SO<sub>4</sub><sup>2-</sup> solution; 0.4, 1.4, 4.3 mg  $S_2O_3^{2-}$  solution. The amounts of sulfur species in the trickling liquid were 0.05-0.2 mg for  $SO_3^{2-}$ , 1300 mg for  $SO_4^{2-}$ and 1.4 mg S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. The addition of small quantities of the sulfur-containing solutions did not affect the pH of the trickling liquid.

The source of biologically active foam cubes used in the differential biotrickling filter was a 20 L H<sub>2</sub>S-degrading biotrickling filter operated as previously described [10]. The normal operating pH of the biotrickling filter was 1.8–2.5, although it was also operated at pH 5 or pH 6.5 for the experiment on the effect of pH. In this case, the pH of the biotrickling filter was increased and maintained at the desired value by supplying an excess of mineral medium. Once the desired pH was obtained, the operating conditions were kept constant for at least one week so that the microbial community could acclimate. Foam cubes were then used for the pH-effect experiments in the differential biotrickling filter.

A  $3.8\,L$  gas-tight stirred-tank reactor was used for the determination of some biokinetic parameters. An aliquot of  $350\,\text{mL}$  of mineral medium with the same pH as the cell suspension was placed in the reactor. The mineral medium was stirred at constant speed of  $\sim\!200\,\text{rpm}$  by a magnetic stirrer. Gaseous  $H_2S$  was then injected through a septum, and the concentration was measured by a  $H_2S$  data-logger. A foam cube taken from the source biotrickling filter was pounded in  $100\,\text{mL}$  mineral medium to extract the biomass. The cell suspension was centrifuged at  $3000\times g$  for  $15\,\text{min}$ . The pellet was re-suspended in  $10\,\text{mL}$  mineral medium. The cell suspension was injected into the stirred-tank reactor after gas-liquid equilibrium of  $H_2S$  was reached, and the removal of  $H_2S$  concentration was monitored over time.

### 2.2. Analytical methods

The concentration of  $H_2S$  was determined with a continuous analyzer/data-logger (App-Tek Odalog, distributed by Detection Instruments, Phoenix, AZ). The  $H_2S$  gas ana-

lyzer was placed outside of the biotrickling filter. The H<sub>2</sub>S-containing air was supplied to the analyzer by a peristaltic pump (Cole-Parmer, Masterflex, Vernon Hills, IL) at a flow rate of 250 mL min<sup>-1</sup> through tubing (0.64 cm i.d.) and returned back to the biotrickling filter system. The liquid recycle flow was measured with an on-line rotameter (Dwyer, Michigan City, IN), while the air flow rate was measured using an anemometer (HHF300A, Omega, Stamford, CT).

The amount of protein on each foam cube was determined after each experiment. The foam cube was removed from the reactor, placed in 50 mL of 1N NaOH and pounded for several minutes [11]. The solution with the foam cube was then kept in a boiling water bath for 5 min to further extract biomass from the foam cube. It was then cooled down in a cold water bath. The solution was centrifuged at  $2000 \times g$  for 2 min to remove foam debris, and 0.1 mL supernatant used for protein analysis. The sample was mixed with the reagents from a BCA protein assay kit (Pierce, Rockford, IL) and incubated in water at 60 °C for 30 min to allow for color development [12]. Absorbance was measured at 562 nm using a spectrophotometer (BioRad, Smartspec 3000, Hercules, CA). The average protein content of one foam cube was 17.4 mg (standard deviation 6.8 mg, N = 18), while the standard deviation of replicate protein determinations for a single foam cube was usually less than 5%. Biomass dry weight was assumed to contain 50% protein by mass.

The activity of mixed cultures at various pH was determined by measuring oxygen-uptake rate (OUR) [10]. The mixed cultures were acclimated at various pH in the 20 L H<sub>2</sub>S-degrading source biotrickling filter before the OUR experiments (see above). To harvest the mixed cultures from the packing, foam cubes were pounded in 50 mL mineral medium for several minutes. The solution was centrifuged at  $3000 \times g$ for 15 min. The pellet containing the sulfide-degrading bacteria was resuspended in 5 mL mineral medium. Deionized water was placed in a custom-made thermostated glass vessel fitted with an oxygen electrode (YSI, Yellow Springs, OH) and saturated with air at 25 °C. After reaching saturation, 2.5 mL of mixed cultures acclimated at different pH (see above) were placed in the vessel. Endogenous respiration was first monitored, after which 0.2 mL of a 1.5 mg Na<sub>2</sub>S mL<sup>-1</sup> solution in mineral medium was injected in the vessel to determine sulfide-induced OUR. The endogenous respiration was subtracted from the total OUR in order to obtain the sulfide induced OUR. The pH was measured using an Accumet pH meter (Accumet model 15, Fisher Scientific, Pittsburgh,

For denaturing gradient gel electrophoresis (DGGE) analysis, bacterial cells were harvested by centrifugation  $(4000 \times g)$  and the DNA extracted with a Bio101 kit (Bio-Rad). DNA concentration was determined with a Smart-Spec3000 spectrophotometer (BioRad), and kept frozen at  $-20\,^{\circ}$ C until required. The genomic DNA was PCR-amplified using the primers PRBA338F and PRUN518 [13] that amplify the V3 region of the 16S ribosomal DNA. Composition of PCR mixtures used in all reactions was 2.5  $\mu$ L

Tris (0.5 M, pH 8.3), 2.5 μL MgCl<sub>2</sub> (25 mM), 1.25 μL BSA (10mg/ml), 1.25 µL dNTPs (5 mM ea), 1 µL of each primer  $(5 \text{ pmol/}\mu\text{L})$ ,  $0.25 \text{ }\mu\text{L}$  Taq polymerase  $(5 \text{ units/}\mu\text{L})$ ,  $1 \text{ }\mu\text{L}$ template DNA in sterile water, and sterile water was added to a final volume of 25 µL. The DNA was amplified in a PTC-200 Peltier Thermal Cycler (MJ Research Inc., MA, USA) with the following program: 95 °C for 2 min, followed by 30 cycles of 92 °C for 1 min, 55 °C for 30 s and 72 °C for 1 min, and a single final extension step consisting of 72 °C for 6 min. The DGGE analyses were performed with 8% (w/v) acrylamide gels in a perpendicular gradient from 20 to 70% denaturant (7 M urea plus 40% (v/v) formamide), the gels were electrophoresed for 3.5 h at 60 °C and 200 V in a DCode universal mutation detection system (BioRad) [14,15]. The gels were stained with ethidium bromide and analyzed in a Quantity One Photodocumentation System (BioRad).

## 3. Results and discussion

# 3.1. Effect of gas velocity

Single foam cubes were taken from the source biotrick-ling filter when operated either at pH 2 or pH 5 and placed in the differential biotrickling filter, and within a short time, gas velocity was varied to determine its effect on  $H_2S$  elimination capacity. By using the same foam cube to test the entire range of gas velocities, the variability due to differences in biomass content of different foam cubes experienced earlier [4] could be avoided. Replicate experiments were conducted and results in Fig. 2 were normalized by biomass content to compare the removals at two different pH levels. The  $H_2S$  elimination capacities (0.2 to 0.9 g  $g_{dw}^{-1}$  h<sup>-1</sup> corresponding to about 35 to 125 g m<sup>-3</sup> h<sup>-1</sup>) reported in Fig. 2 were lower than in previous experiments conducted in this lab and, for the experiment at pH 2, lower than observed in the field

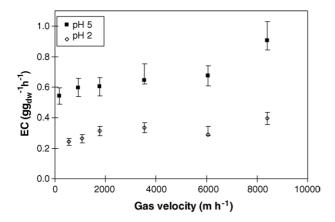


Fig. 2. Effect of gas velocity and pH on  $H_2S$  elimination capacity (EC) in a differential biotrickling filter at a liquid trickling velocity of  $1.5\,m\,h^{-1}$ . Initial  $H_2S$  concentrations were between 50 and 65 ppm $_v$ . The error bars represent the experimental error determined from replicates experiments, and uncertainties in concentration, system and bed volumes and biomass measurements.

[4,16]. The lower EC was probably due to a lower density of biomass in the foam cube selected for these experiments, and has no further consequences as far as discussing the trend of Fig. 2. With the exception of the point at  $8000 \,\mathrm{m}\,\mathrm{h}^{-1}$  collected under flooding conditions, the results show that H<sub>2</sub>S elimination capacity appears to be a weak function of gas velocity until it reached about  $4000 \,\mathrm{m}\,\mathrm{h}^{-1}$ . The interpretation of a dependence on gas velocity is that the biotrickling filter that was tested had some external mass transfer limitation at lower gas velocities. The finding suggests that the performance of H<sub>2</sub>S-degrading biotrickling filters operated at low gas velocity can be improved by increasing external mass transfer. Increasing the gas velocity to increase  $k_G$ , the gas film mass transfer coefficient, or increasing the specific surface area of the packing can improve external mass transfer. The H<sub>2</sub>S elimination capacity did not exhibit a significant change between gas velocities of 4000 and 6000 m h<sup>-1</sup>. At these conditions, H2S removal must have been controlled either by the biodegradation kinetics, transport in the liquid or by diffusion in the biofilm. Without further detailed experiments, it is difficult to identify which of those processes was limiting. As previously mentioned, the system experienced flooding when the gas velocity exceeded  $8000 \,\mathrm{m}\,\mathrm{h}^{-1}$ , and the elimination capacity was very unstable and subject to large variations both within an experiment with a single foam cube, or between experiments with different foam cubes. Overall, the results of Fig. 2 show a similar, though less pronounced trend than that presented and discussed in an earlier study by the authors [17]. The reasons for the differences between the studies are not clear, but they highlight the complex nature of H<sub>2</sub>S removal in high performance biotrickling filters. Data at pH 5 are also reported on Fig. 2, and exhibit significantly higher H<sub>2</sub>S elimination capacities, which is contrary to what is observed in the field biotrickling filters at OCSD. Abiotic control experiments at pH 2 and 5 (not shown) resulted in only about a 20% higher absorption rate at pH 5 than at low pH. The slightly greater absorption is consistent with the acid-base equilibria of sulfides, which predict that below pH 6, dissolved sulfide is essentially present as H<sub>2</sub>S and not HS<sup>-</sup> or S<sup>2-</sup> [18]. The increased performance at pH 5 may be the result of greater activity of the mixed culture developed at pH 5 and is discussed later in the paper.

#### 3.2. Effect of trickling liquid velocity

In Fig. 3, the effect of the liquid trickling velocity at two different gas velocities is presented. The trickling velocity did not affect the rate of H<sub>2</sub>S removal at 4000 m h<sup>-1</sup>, which is about the upper limit of air velocity at which external mass transfer limitations were thought to occur, but H<sub>2</sub>S elimination capacity was proportional to the liquid trickling rate at high gas velocity, i.e., in the absence of external mass transfer limitation. Simple physical absorption of H<sub>2</sub>S into the increased liquid flow could not explain the observed increase in removal. Further discussion of the observation is warranted. A biotrickling filter is composed of three phases: gas, liquid

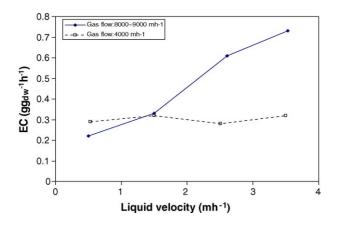


Fig. 3. Effect of trickling liquid (pH 1.7–2.4) on H<sub>2</sub>S elimination capacity in the differential biotrickling filter. The experiments were performed with several foam cubes and EC on the *Y*-axis was normalized by the biomass dry weight to allow for direct comparison.

and biofilm. The biofilm can be wetted by the trickling liquid, or non-wetted, i.e., in direct contact with the gas undergoing treatment. As discussed and modeled in a previous paper [4], H<sub>2</sub>S gas can be transferred first to the trickling liquid and then to the wetted biofilm, or it can be transferred directly to nonwetted biofilm. Therefore wetting, and liquid mass transfer parameters, may be key factors in defining H<sub>2</sub>S elimination capacity. Onda et al. [19] determined that wetting is solely related to the liquid velocity, thus Fig. 3 can be viewed as being the effect of various degrees of biofilm wetting. Even so, one can question whether gas velocity should not play a role in wetting, especially at high gas velocity and in packings with narrow openings, as we found that high gas velocity affects liquid hold-up and thus it probably affects the liquid flow pattern. Nevertheless, a possible explanation for the results of Fig. 3 is as follows. At low gas velocity, external mass transfer was the main limiting factor, therefore, elimination capacity was not affected by changes in liquid flow rate. At high gas velocity, the external mass transfer resistance becomes negligible, but transfer from the liquid to the biofilm becomes limiting. Possible reasons for limitation by the trickling liq-

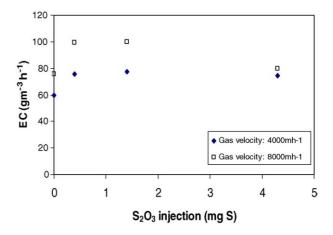


Fig. 4. Effect of sulfur species on  $H_2S$  elimination capacity in a differential biotrickling filter at gas velocities of 4000 and 8000 m h<sup>-1</sup>. Thiosulfate added: 0.4, 1.4, 4.3 mg (corresponding concentration: 0.7–7 mg S L<sup>-1</sup>); pH was 1.9–2.1.

uid are liquid channeling, non-uniform spraying of the foam cube, partial wetting and stagnant water due to the structure of the foam cube. Because those are probably alleviated by increasing the trickling velocity, increasing the trickling velocity resulted in an increase in  $H_2S$  elimination capacity. Verification of the above explanation by means other than the determination of  $H_2S$  elimination is warranted.

# 3.3. Effect of intermediate sulfur species

The effect of adding various sulfur species to the trickling liquid was investigated. The addition of dissolved sodium sulfide (1–3.5 mg S  $L^{-1}$ , results not shown) resulted in a delay in  $H_2S$  gas degradation at pH 1.9–2.1. Sulfide is the deprotonated form of dissolved  $H_2S$ , but rapidly would equilibrate with whatever form of S is utilized by the microbial population; hence, addition of sodium sulfide competed with  $H_2S$  gas for biodegradation. Surprisingly, addition of traces of thiosulfate (0.7–7 mg S  $L^{-1}$  adjusted to a pH of 1.9–2.1) resulted in a 5–30% enhancement

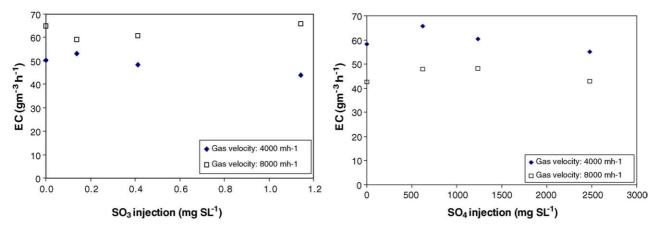


Fig. 5. Effect of sulfur species on  $H_2S$  elimination capacity in a differential biotrickling filter at gas velocities of 4000 and 8000 m h<sup>-1</sup>. (Left) Sulfite added was 0.12, 0.36 and 1 mg (concentrations 0.14–1.14 mg  $SL^{-1}$ ); (right) sulfate added 650, 1300 and 2600 mg (614–2450 mg  $SL^{-1}$ ); pH was 1.9–2.1.

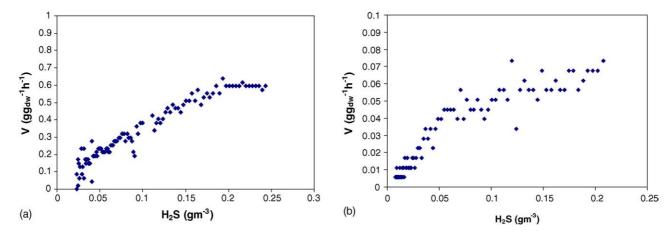


Fig. 6. Michaelis-Menten type plots for: (a) differential biotrickling filter at high gas velocity ( $V_{\rm max} = 0.61~{\rm g~g_{dw}}^{-1}~h^{-1}$ ;  $K_{\rm s} = 0.068~{\rm g~m}^{-3}$ ) and (b) batch bioreactor with liquid culture and H<sub>2</sub>S head-space monitoring ( $V_{\rm max} = 0.066~{\rm g~g_{dw}}^{-1}~h^{-1}$ ;  $K_{\rm s} = 0.044~{\rm g~m}^{-3}$ ), pH: 1.8–2.0.

of  $H_2S$  removal rate (Fig. 4). Previous experiments in conventional biotrickling filters by others in our lab (Strauss and Deshusses, 2003, unpublished) found that pulses of thiosulfate (300–350 mg  $SL^{-1}$ ) had a significant inhibitory effect on  $H_2S$  removal rather than improved removal. However, the latter experiments were conducted at much higher concentrations, which is most probably why some biokinetic competition occurred. The results of trace thiosulfate addition are intriguing as they indicate the possibility that the performance of  $H_2S$ -degrading biotrickling filters could be improved by adding trace amounts of thiosulfate.

The results of the addition of sulfite and sulfate are shown in Fig. 5. The amount of sulfite and sulfate injected was five times the concentration measured during normal operation. Sulfite traces had no effect on the process (Fig. 5left). Similarly, sulfate injections up to 2450 mg S L $^{-1}$  had no significant effect on the removal of  $\rm H_2S$  (Fig. 5right). The latter is consistent with the findings by Yang and Allen [20] who saw no inhibitory effect of sulfate in a biofilter up to pore water concentration of sulfate up to 15,000 mg S L $^{-1}$ . The finding suggests that the process is not sensitive to the accumulation of sulfate, the end-product of  $\rm H_2S$  biodegradation. Insensitivity to sulfate accumulation is useful knowledge for practical applications since in the field, a relatively large range of sulfate concentrations exists.

### 3.4. Biokinetic parameter analysis

As discussed for Fig. 2, at gas velocities between 4000 and  $6000 \, \text{m} \, \text{h}^{-1}$ , external mass transfer was thought not to be significantly limiting, hence the decrease of  $H_2S$  over time in the differential biotrickling filter could be used to determine the rate of  $H_2S$  biodegradation versus the gaseous concentration of  $H_2S$ , thereby obtaining a Michaelis–Menten type plot. The results are shown in Fig. 6a and reveal that the rate of  $H_2S$  elimination was constant above about  $0.2 \, \text{g} \, \text{m}^{-3} \, H_2S$ , i.e., 150 ppm, while it decreased linearly with concentration below that level, with little transition between the two

regions. A comparison was made with the elimination of H<sub>2</sub>S in a stirred-tank reactor by suspended bacteria extracted from a foam cube that was degrading H2S. The rationale for the comparison was to avoid any liquid-phase diffusional resistance, as the liquid batch culture was well-stirred and bacteria were finely dispersed. H<sub>2</sub>S removal rates in the liquid batch culture were about 10 times lower than in the biotrickling filter, and rates appeared to follow two different linear regimes depending on H2S concentration with a transition at about 0.07 g m<sup>-3</sup>. A probable explanation for the lower rates is the difference in the gas film mass transfer coefficient between the two systems and in gas-liquid interfacial areas (0.038 m<sup>2</sup> for the foam cube and 0.013 m<sup>2</sup> for the liquid reactor) that may have limited H<sub>2</sub>S transfer from the head-space of the stirred liquid reactor. The complex behavior, and the discrepancies observed between the biokinetic parameters determined with the two bioreactor systems suggest that further research is needed in order to determine the intrinsic biokinetic parameters in the absence of mass transfer or diffusion limitations. This will help model the process and optimize the rate of  $H_2S$  removal.

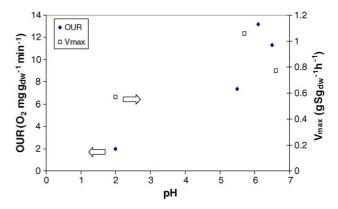


Fig. 7. Effect of pH on the oxygen uptake rate (OUR) and maximum reaction rate ( $V_{\rm max}$ ).  $V_{\rm max}$  was measured in the differential biotrickling filter at  $8000\,{\rm m\,h^{-1}}$  gas velocity.

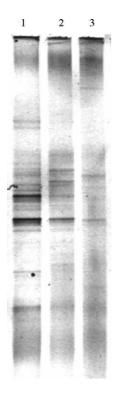


Fig. 8. Denaturing gradient gel electrophoresis (DGGE) analysis. Lane 1: pH 2, lane 2: pH 5, lane 3: pH 6.3.

As discussed earlier, pH is an important parameter, as it impacts on both the process microbiology and the acid-base equilibrium of H<sub>2</sub>S. The biotrickling filtration results of Fig. 2 exhibited a marked difference in the removal of H<sub>2</sub>S at different pH. Hence, biokinetic analyses were performed to determine how sulfide biodegradation activity within the batch-reactor varied with the pH at which the culture filter was acclimated, and the activity of the culture measured by OUR was compared to the performance of the differential biotrickling filter at various pH (Fig. 7). The biodegradation activity (determined by sulfide-induced OUR) increased about five-fold with increasing pH from 2 to near neutral, indicating that mixed cultures grown at near neutral pH were intrinsically more effective. Further examination of the mixed cultures composition using DGGE (Fig. 8) revealed that DNA band patterns had some similarities, but were significantly different. Spatial differences observed by others [21] could be excluded, as all foam cubes were collected from the inlet port of the 20L source biotrickling filter operated at various pH values. Therefore, the differences in the microbial communities depicted in Fig. 8 were caused by differentiated cell growth at the various pH values. Further detailed analysis of the microbial communities that evolved at the different pH would be necessary to determine whether the bands that exhibited changes in Fig. 8 were those of H<sub>2</sub>S degrading organisms, or those of secondary degraders. However, the results of Fig. 8 are consistent with the fact that different sulfide oxidizing bacteria have different optimum pH for growth [22], and that some shifts in at least those populations are expected. Altogether, the results of Figs. 7 and 8 support the explanation that different bacterial populations were responsible for the better performance of the differential biotrickling filter operated at near neutral pH. As mentioned earlier, results from field studies [23] have demonstrated that operation at low pH resulted in significantly better H<sub>2</sub>S removal performance. This inconsistency suggests that further research is needed to reconcile lab-scale and field results.

### 4. Conclusions

There are still a large number of unknowns in the biotreatment of  $H_2S$  and odors in high performance biotrickling filters. Detailed applied studies of the type presented and discussed here allow a better understanding of the transport and the biodegradation of pollutants in biotrickling filters, as well as to identify means to possibly optimize performance. For example, the finding that external mass transfer may play an important role has not been widely reported. It warrants further investigation into pollutant mass transfer in biotrickling filters, as the extent of mass transfer limitation may ultimately motivate drastic changes in the design of biotrickling filters.

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