Development and Experimental Validation of a Conceptual Model for Biotrickling Filtration of H_2S

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A dynamic model that describes the behavior of high-performance hydrogen sulfide (H_2S)-degrading biotrickling filters for odor control was developed. The model attempts to accurately describe pollutant mass transfer in the biotrickling filter, i.e., external mass transfer resistances, and both direct gas-biofilm and gas-liquid-biofilm mass transfer were considered. In order to calibrate the model, an innovative differential biotrickling filter was constructed in which the effect of air velocity on the removal of H_2S could be studied. Model outputs were compared with experimental data to determine the sensitivity of the system to selected parameters. At low H_2S concentration, diffusion of H_2S within the biofilm, and biofilm thickness were the major governing factors among nine considered model parameters. At higher H_2S concentrations and lower air flow rates, external mass transfer played a very important role. This new finding, confirmed experimentally, has important implications, as it proves that the performance limit of H_2S degrading biotrickling filters has not yet been reached.

INTRODUCTION

Odor emissions are a major concern for wastewater treatment plants and many processing facilities located close to residential areas. A number of different techniques are now available for odor control, and, of these, biological treatment appears to be one of the most cost-effective [1, 2]. But, until recently, its use in urban areas was limited because of a perception that biotreatment required significantly larger reactor volumes than chemical scrubbers due to the longer gas contact time needed for effective treatment. After research and proof of concept in the laboratory, our research group converted an existing full-scale chemical scrubber to a biological trickling filter at the Orange County Sanitation District (OCSD), and showed that effective treatment of hydrogen sulfide (H_2S) in the converted scrubber was possible, even at gas contact times as low as 1.6 seconds [3, 4]. Continuous operation of the biotrickling filter for more than 18 months showed stable performance and robust behavior for H_2S treatment, with pollutant removal performance similar to that achieved using a chemical scrubber. Removal rates for H_2S in the field biotrickling filter was in excess of 98% for inlet concentrations as high as 30 to 50 ppm_v. This corresponds to volumetric elimination rates of H_2S of 95 to 105 g H_2S m^{-3} h^{-1}.

Such performance is exceptionally high compared with other biofilters or biotrickling filters removing low concentration of H_2S, even at higher gas contact times [5-7]. This observation raises the question of why such high performance was observed when extrapolation from laboratory experiments predicted only partial H_2S removal [4]. The best available explanation is a combination of high pollutant mass transfer rate due to a high surface area packing and extremely high gas linear velocity (1.8 m s^{-1} or 6,500 m h^{-1}), and optimum operating conditions (nutrient, pH, CO_2, no air short-circuiting). However, detailed investigations were warranted to confirm these speculations, and possibly build upon the findings to further improve H_2S treatment and odor control in other biotrickling filters. The approach considered both experiments using a small differential biotrickling filter to study the details of mass transfer and H_2S biodegradation kinetics, and detailed mathematical process modeling. Both the development of the mathematical model and its experimental verification are presented and discussed in this paper.

Several mathematical models have been developed for the removal of volatile organic compounds (VOCs) in biotrickling filters [8-12], but fewer of these deal specifically with the treatment of H_2S in biofilters, or in biotrickling filters [13-18]. This is unfortunate as VOC biotrickling filtration models do not necessarily apply to H_2S, as treatment of H_2S and of other reduced compounds may often be mass transfer limited [15], while

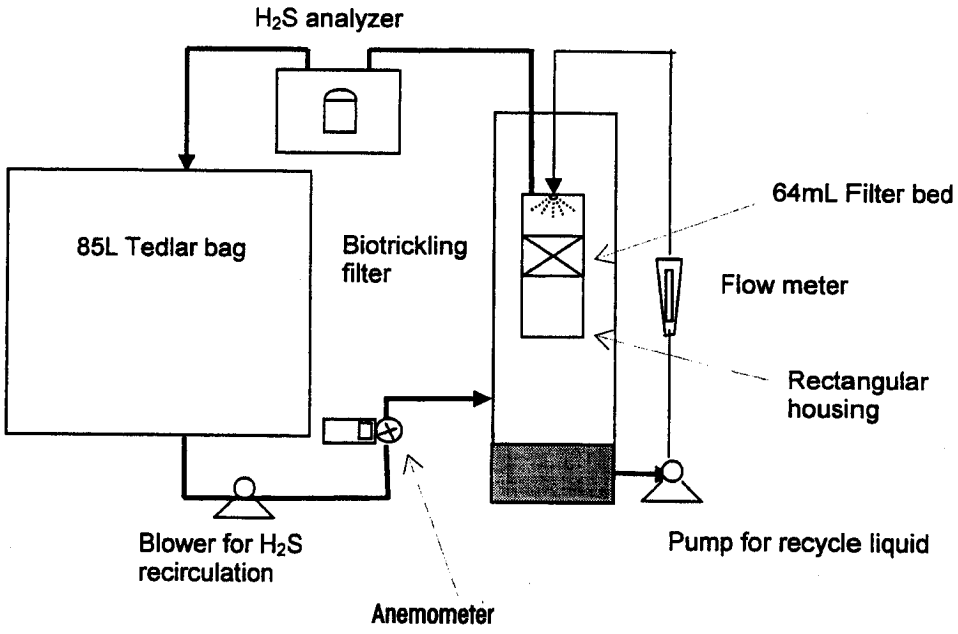

Figure 1. Schematic of the experimental setup (not drawn to scale).

VOC treatment is often kinetically limited [19]. Also, H_2S-degrading biotrickling filters often have very thin biofilms, while those for VOCs usually have thick biofilms, a probable consequence of the difference in the process biology.

A review of existing biotrickling filter models shows that, among the three phases present in a biotrickling filter, the free liquid phase is often neglected because it is assumed to have no mass transfer resistance [8]. The rationale for such an omission is often empirical rather than experimentally-proven, and is based on the fact that the liquid trickling rate is slow, and, hence, the liquid film is assumed to be thin. Interestingly, when a two-phase model [8] was expanded to include trickling liquid, experimental data and model simulations [9, 10] showed that the mass transfer resistance of the trickling liquid was significant, suggesting that this phase should be taken into account. Indeed, the studies on VOC control by Zhu, *et al.* [10] and Baltzis, *et al.* [11] show that performance of biotrickling filters can be quite dependent on the rate of liquid trickling.

On the other hand, Barton, *et al.* [12] found that their model—though developed for VOC biodegradation in biotrickling filters—was most sensitive to parameters that affect the biological kinetics, such as biomass concentration and temperature. More recently, Li, *et al.* [13] and Martin, *et al.* [17] presented and discussed a mathematical model of an H_2S-degrading biotrickling filter that assumed the compound was either transferred directly from the gas, or to the trickling liquid prior to being transferred to the biofilm. But, the model did not allow for the two transfer paths to occur simultaneously. Both papers discuss the details of the model sensitivity and application for reactor design. Their findings were similar to those of Barton, *et al.* [12]: namely, that biokinetic parameters played a major role in their model and experiments, and that external mass transfer resistance had little effect.

However, as mentioned above, the extremely high performance of the biotrickling filter operated at OCSD suggested that some external mass transfer effect, neglected until now, required further examination. In particular, improvements over existing models should consider: a) the possibility of a gas-film mass transfer limitation, b) the existence of wetted and non-wetted biofilms and the resulting differences of pollutant mass transfer rates, and c) the fact that high performance packings for biotrickling filtration have a very high interfacial area, and that H_2S-degrading bacteria do not form thick biofilms. A model that includes such improvements, and its experimental verification, are presented and discussed in this paper.

MATERIALS AND METHODS

Differential Biotrickling Filter Equipment

A small differential biotrickling filter, filled with a single cube (4 x 4 x 4 cm) of open pore polyurethane foam packing (M+W Zander, Germany) was used in this study. The foam cube placed in the differential biotrickling filters was taken either from the field reactor operated at OCSD [3, 4], or from a stock lab-scale biotrickling filter operated in the laboratory with H_2S as the sole pollutant. Hence, the foam cube had an active biofilm of H_2S-oxidizing bacteria. The actual bed was housed in a larger (10 cm ID) clear PVC pipe (See Figure 1).

The biotrickling filter system was designed to run as a batch to ease determination of the biokinetic parameters, and allowed operation at extra-high gas flow rates, so that gas film mass transfer resistance could be reduced to negligible levels. The H_2S-

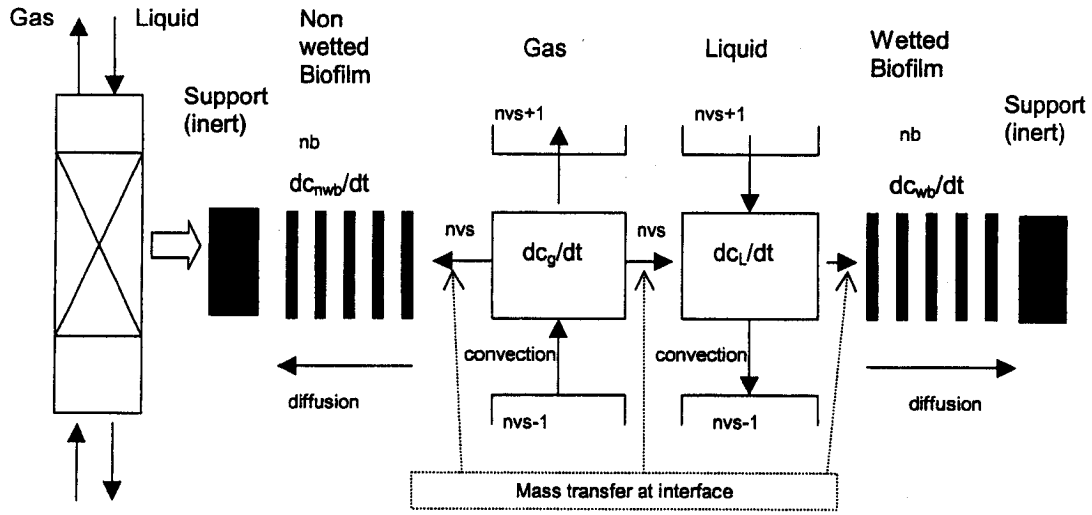

Figure 2. Schematic of the model structure with wetted and non-wetted biofilms.

degrading biotrickling filter was operated in a counter-current mode, with gas flowing upward and recycled mineral medium flowing downward. The air flow was circulated from the 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 8.5 m s^{-1}, which is at least 5-10 times higher than any previous biotrickling filter application reported by others. The highest air flow resulted in an empty bed retention time (EBRT) of 0.005 s in the foam cube.

The recycle liquid, which consisted of reclaimed water (chlorinated secondary effluent from OCSD), was uniformly sprayed on top of the filter bed, using a peristaltic pump at a rate of 1.9 L h^{-1} and a WL 1/4 BETE spray nozzle (BETE, Greenfield, MA). The pressure required for the spray nozzle was less than 0.7 bar. Prior to all experiments, the pH of the recycle liquid was adjusted to 1.7-1.8 (i.e., values similar to the field biotrickling filter) using hydrochloric acid. During the experiments, the pH of the recycle liquid never decreased by more than 0.2 pH units.

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 flow rate. All decreases in H_2S concentration were attributed to biodegradation. This is a reasonable assumption as abiotic controls were conducted to verify the integrity of the differential biotrickling filter system, and all experiments were conducted at a pH of 1.7-1.8. At this pH, and for a gas/liquid volume ratio of 230, 98.9% of the H_2S is in the gas phase.

In parallel to the differential setup, a 20-L H_2S-degrading biotrickling filter packed with identical foam cubes was operated as before [6] in the laboratory to serve as a stock for biologically active foam cubes to be used in the differential biotrickling filter. Selected experiments involved foam cubes taken directly from the biotrickling filter operated at OCSD [3].

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 data logger was placed in the water knock-out bottle at the outlet of the biotrickling filter. 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 pH of the recycle liquid was determined off-line using an Accumet pH meter (Fisher, Pittsburgh, PA). The amount of biomass on each foam cube was determined after each experiment. The foam cube was taken from the biotrickling filter, thoroughly washed, and squeezed in two subsequent 100 mL volumes of deionized water. The two suspensions were pooled and filtered through a 0.45 μm pore filter. The filter was dried 24 hours at 60° C and the amount of dry biomass determined by weighing.

MODEL DEVELOPMENT

Model Concept

The model proposed here attempts to make an exact representation of the processes occurring in the biotrickling filter. It considers three phases in the reactor: gas, liquid, and biofilm, with gas and liquid flowing counter-currently (See Figure 2). The pollutant (H_2S) is removed by the process culture immobilized on the packing of the biotrickling filter. For H_2S present in the gas phase to be degraded, it has to be transferred to the biofilm. However, the biofilm on the packing material is not completely wetted by the trickling liquid. Therefore, some of the pollutant will transfer directly from the gas

phase to the biofilm without passing through the liquid, while some will be transferred to the liquid first, and then to the biofilm. In the biofilm, diffusion and biodegradation occurs.

Model Assumptions

The model depicted schematically in Figure 2 embodies the following assumptions:

1. The packing material is completely covered by the biofilm, which has a uniform thickness.
2. The biofilm is not fully wetted by the liquid, so both wetted and non-wetted biofilm are included. This is consistent with visual observation of non-wetted packing during biotrickling filter operation, and with the application of correlations such as the one developed by Onda, *et al.* [20] that indicates a significant fraction of the packing is not wetted.
3. Wetted biofilm remains wetted and non-wetted biofilm remains non-wetted, i.e., dynamic changes in wetting are not considered.
4. Adsorption of pollutant onto the support is neglected.
5. For finite differentiation, each subdivision shown in Figure 2 is ideally mixed.
6. The flow in the axial direction is by plug flow. There is no radial velocity gradient or axial dispersion. This can be justified by the high gas velocity in the biotrickling filter systems considered, and that Peclet numbers in biotrickling filters are usually large (> 10), indicating a near plug-flow behavior.
7. The mass flux at the gas-liquid, gas-biofilm, and liquid-biofilm interfaces can be expressed by mass transfer coefficients (k_{g1}, k_{g2}, k_L).
8. The mass transfer coefficients from gas to liquid (k_{g1}), and from gas to non-wetted biofilm (k_{g2}), have the same value.
9. Consistent with the film theory, gas-liquid, liquid-biofilm, and gas-biofilm interfaces are at equilibrium.
10. The diffusion in the biofilm is described by Fick's law.
11. The biodegradation kinetics in the biofilm are described by a Michaelis-Menten relationship, with H_2S the only rate-limiting substrate. The H_2S is used as an energy source, and it is assumed that the carbon source (CO_2) is not rate-limiting. Further, the use of Michaelis-Menten kinetics, rather than Monod kinetics, is justified by the essentially no-growth situation of the process culture biotrickling filter. The biokinetic constants are the same for wetted and non-wetted biofilms.
12. There is no reaction in the liquid phase. This can be justified since only a negligible amount of biomass is present in the recycle liquid.
13. The effect of pH is neglected. This can be easily changed, but is a reasonable assumption since all experiments were conducted at the same pH. Consequently the acid/base reaction of H_2S is neglected, and sulfur species are lumped as H_2S in the kinetic relationships.
14. For modeling of the experimental setup of Figure 1, the air reservoir (Tedlar bag) is considered to be ideally mixed.

Model Equations

The model equations were derived from these assumptions and the model structure. The main mass balances in each phase are described by the following equations, where j refers to the vertical segment along the height of the biotrickling filter, numbered from the bottom of the reactor, and i refers to the segment depth in the biofilm numbered from the interface. See Figure 2 for a schematic of the concept, and Table 1 and the Nomenclature section for a list of symbols and parameters.

Gas phase:

$$V_g \frac{dC_g[j]}{dt} = F_g\left(C_g[j-1] - C_g[j]\right) - k_{g1}A_w\left(C_g[j] - C_{gi1}[j]\right) - k_{g2}A_{nw}\left(C_g[j] - C_{gi2}[j]\right) \quad (1)$$

Liquid phase:

$$V_L \frac{dC_L[j]}{dt} = F_L\left(C_L[j+1] - C_L[j]\right) + k_{g1}A_w\left(C_g[j] - C_{gi1}[j]\right) - k_L A_w\left(C_L[j] - C_{Li2}[j]\right) \quad (2)$$

The mass balance for most wetted biofilm segments is expressed by Equation 3, except for the first and the last layers, which bear boundary constraints. The equation for the first biofilm layer near the interface takes the form of Equation 4, while that of the last layer before the substratum is represented by Equation 5. In a similar manner, pollutant mass balances for the non-wetted biofilm segments are described by Equations 6-8. Note the different boundary at the liquid-biofilm and gas-biofilm interfaces (Equation 7 vs. Equation 5).

Wetted biofilm phase:

$$\frac{dC_{wb}[i,j]}{dt} = \frac{D}{(FT)^2}\begin{pmatrix} C_{wb}[i-1,j] - \\ 2C_{wb}[i,j] + \\ C_{wb}[i+1,j] \end{pmatrix} - R_{wb}[i,j] \quad (3)$$

$$\frac{dC_{wb}[1,j]}{dt} = \frac{D}{(FT)^2}\begin{pmatrix} C_L[j] - 2C_{wb}[1,j] + \\ C_{wb}[2,j] \end{pmatrix} - R_{wb}[1,j] \quad (4)$$

$$\frac{dC_{wb}[N,j]}{dt} = \frac{D}{(FT)^2}\begin{pmatrix} C_{wb}[N-1,j] - \\ C_{wb}[N,j] \end{pmatrix} - R_{wb}[N,j] \quad (5)$$

Table 1. Summary of main parameter values for model simulations.

Symbol	Parameter	Numerical Value	Method for Determination/Reference
k_g	Gas-liquid mass transfer coefficient	1,215* (m h^{-1})	Onda correlation [20]
k_L	Liquid-biofilm mass transfer coefficient	109* (m h^{-1})	Onda correlation [20]
FT	Biofilm thickness	23 μm	Calculation based on biomass and packing area
R_m	Maximum reaction rate	58,400 (g m^{-3} h^{-1})	Experimental fitting of H_2S decrease at high concentration (see text)
K_s	Michaelis-Menten constant	0.0279 (g m^{-3})	Experimental fitting of H_2S decrease at low concentration (see text)
H	Henry's constant of H_2S	0.387 (-)	*Perry's Handbook* [21]
D	H_2S diffusion coefficient	5.796e-6 (m^2 h^{-1})	*Perry's Handbook* [21]
a	Specific interfacial area	600 m^2 m^{-3}	Packing manufacturer [22]
V_L	Dynamic holdup	0.00001 x liquid flow (m^3 h^{-1}) + 0.0000008 (m^3 per cube of foam)**	Experimental determination with clean foam
nb	Number of segments in biofilm	10	Determined by study of sensitivity to nb
nvs	Number of vertical segments in the biotrickling filter	10	Determined by study of sensitivity to nvs

* Listed are the mass transfer coefficients at gas flow rate of 9,400 m^3 m^{-2} h^{-1}, and a trickling rate of 11.8 m^3 m^{-2} h^{-1}, but the model considers changes of k_g and k_L with the air and liquid flow, respectively.
** Valid for one foam cube only, not for extrapolation.

Non-wetted biofilm segments:

$$\frac{dC_{nwb}[i,j]}{dt} = \frac{D}{(FT)^2}\begin{pmatrix} C_{nwb}[i-1,j]- \\ 2C_{nwb}[i,j]+C_{nwb}[i+1,j] \end{pmatrix} - R_{nwb}[i,j] \quad (6)$$

$$\frac{dC_{nwb}[1,j]}{dt} = \frac{D}{(FT)^2}\left(\frac{C_g[j]}{H} - 2C_{nwb}[1,j]+ C_{nwb}[2,j]\right) - R_{nwb}[1,j] \quad (7)$$

$$\frac{dC_{nwb}[N,j]}{dt} = \frac{D}{(FT)^2}\begin{pmatrix} C_{nwb}[N-1,j]- \\ C_{nwb}[N,j] \end{pmatrix} - R_{nwb}[N,j] \quad (8)$$

Reaction rates:
For wetted biofilm:

$$R_{wb}[i,j] = \frac{R_{max}C_{wb}[i,j]}{K_s + C_{wb}[i,j]} \quad (9)$$

For non-wetted biofilm

$$R_{nwb}[i,j] = \frac{R_{max}C_{nwb}[i,j]}{K_s + C_{nwb}[i,j]} \quad (10)$$

RESULTS AND DISCUSSION

Determination of Model Parameters

Model parameters fall in the following categories: physico-chemical properties, and systems specific (dimensions), biokinetic, and mass transfer parameters. Those belonging to the last two categories are the most difficult to obtain. When possible, independent experiments were conducted or correlations were used to obtain a given parameter to minimize the degree of data fitting. Table 1 lists the values of the main parameters, and how they were obtained. Comments on selected parameters are found below.

Ideally, gas and liquid film mass transfer coefficients, and wetted/non-wetted area would have been determined experimentally for the packing and conditions of the biotrickling filtration experiments, however this is not a trivial exercise. Therefore, Onda, Sherwood, and Shulman correlations, which are commonly used in chemical scrubbers, were evaluated [20, 23, 24]. Onda's correlations appear to have the widest

applicability for different packing materials and conditions [25], and were selected for the determination of mass transfer coefficients and wetted area in the present biotrickling filter model. Others [11, 26] have used Onda correlation in biotrickling filters, but the applicability of this correlation to the open pore PU foam packing remains to be verified. Onda's correlations for liquid and gas film mass transfer coefficients are given in Equations 11 and 12, whereas the wetted fraction is calculated using Equation 13. It is important to realize that the wetting ratio changes as the liquid trickling rate is changed, thereby changing the path of pollutant mass transfer.

$$k_L = 0.0051\left(\frac{L}{A_w\mu_L}\right)^{2/3}\left(\frac{\mu_L}{\rho_L D}\right)^{-0.5}\left(aD_p\right)^{0.4}\left(\frac{\rho_L}{\mu_L g_c}\right)^{-1/3} \quad (11)$$

$$k_g = 5.23\left(\frac{G}{a\mu_g}\right)^{0.7}\left(\frac{\mu_g}{\rho_g D_g}\right)^{1/3}\left(aD_p\right)^{-2} aD_g \quad (12)$$

$$\text{Wetting ratio} = \frac{A_w}{A} = 1-\exp\left\{-1.45\left(\sigma_p/\sigma\right)^{0.75}(\text{Re})^{0.1}(Fr)^{-0.05}(We)^{0.2}\right\} \quad (13)$$

Another area that requires further evaluation is the degree of packing coverage with biofilm. As listed in Table 1, gravimetric determination of biofilm volume, divided by the packing interfacial area resulted in a relatively thin biofilm (23 μm). This appears not to be uncommon for H_2S degrading biotrickling filters [16], but certainly requires further independent verification.

Biokinetic parameters were determined experimentally in the differential biotrickling filter using a combination of model fitting and simple algebraic calculations. For example, experimental data for H_2S removal at the highest gas flow rate were used to determine the maximum degradation rate, since one could, in a first approximation, assume that little or no gas film mass transport limitation occurred under these conditions. This is shown in Figure 3, where a quasi-linear decrease of H_2S concentration is reported in the first 30 minutes of the experiment. Hence, the first part of the experiment was used to determine R_m (See highest observed rate in Figure 3 inset).

After the first 30 minutes, the decrease in H_2S concentration was no longer constant and the apparent removal rate decreased. Thus, an effort was made to use the latter part of the experiment to determine K_s by simply taking the concentration in equilibrium with the gaseous concentration at which half the maximum rate was observed. This proved to be incorrect, as the biotrickling filter model showed that the process was diffusion limited at low concentrations, i.e., it predicted only little penetration of H_2S in the biofilm. Hence, K_s was determined by fitting the model to one experiment, instead of using simple plots of observed removal rate.

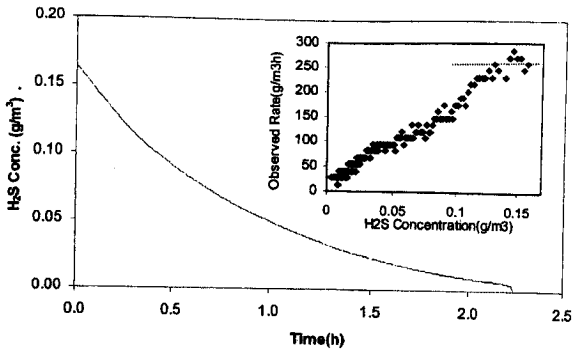

Figure 3. H_2S concentration in the differential biotrickling filter as a function of time for one of the experiments at a linear gas velocity of 9,400 m h^{-1}. Because of the large number of data points, data are shown as a line. For conversion 0.1 g m^{-3} H_2S corresponds to 73 ppm_v.

Comparison of Experimental Data and Model Simulations

Comparison of model simulations and experimental data is shown in Figure 4. The model fitted the experiment well at high H_2S concentration, but when used to predict another experiment conducted at a lower concentration, it overestimated the H_2S concentration. Since this was difficult to explain, nine model parameters were considered for detailed sensitivity analysis of H_2S removal at low concentrations. These were: gas and liquid flow rates, wetting ratio of packing material, biofilm thickness, maximum reaction rate (R_m), half-saturation reaction rate constant (K_s), mass transfer coefficient for gas and liquid, and diffusion coefficient. Interestingly, except for the diffusion coefficient, the selected model parameters had only limited effect on the simulated performance of the biotrickling filter at low concentrations. This suggests that the process, as described by the model, was limited by diffusion of H_2S in the biofilm. Indeed, examination of H_2S concentration profiles in the biofilm (not shown) revealed that H_2S did not fully penetrate the biofilm at low concentration.

The sensitivity of the model to H_2S diffusivity is illustrated in Figure 4, which shows results for the low concentration case with a 69% higher value for the diffusion coefficient. A much better fit of the experimental data was obtained. At this time, without detailed information on actual H_2S biofilm concentrations, it is difficult to explain why the model would underestimate H_2S removal at low concentrations. Our experience with other biofiltration models is that they often overestimate performance at low concentration, and investigators often compensate for such a discrepancy by increasing the half saturation rate constant. The observations reported in Figure 4 could indicate that there is either a limitation at higher concentration that was not taken into account, or that one or more parameters has been incorrectly determined.

Sensitivity Analysis

A sensitivity analysis of key model parameters was performed to find out the dependency of system performance on model parameters. The effect of four

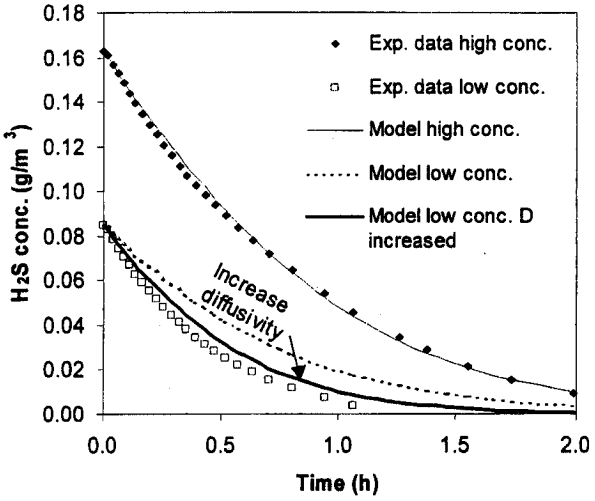

Figure 4. Comparison of two sets of experimental data (symbols) and model simulations (lines and dashes). The air velocity in the differential biotrickling filter was 9,400 m h^{-1}.

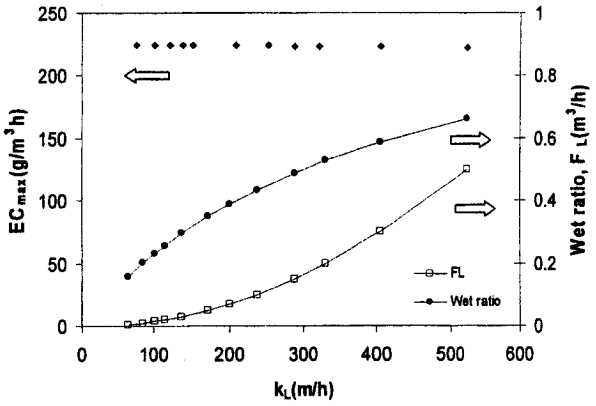

Figure 5. Effect of mass transfer coefficient for liquid (k_L) on elimination capacity (EC) and wetting ratio at high gas linear velocity (9,400 m h^{-1}). k_L was changed by varying the liquid trickling rate (F_L).

model parameters was investigated by running the model to simulate typical experiments, such as the one shown in Figure 3. From the model output of H_2S concentration vs. time, the maximum slope, observed at the beginning of the simulated experiment, determines the maximum elimination capacity (EC_{max}). The initial concentration of H_2S for the model sensitivity studies was 0.16 g m^{-3}, which corresponds to 116 ppm_v. The effect of the following parameters was investigated: liquid film mass transfer coefficient k_L, diffusivity of H_2S, and the biokinetic parameters R_m, and K_s. All the other model parameter values were kept constant as listed in Table 1. The results are presented in Figures 5-8.

The sensitivity of the modeled H_2S elimination capacity to the liquid film mass transfer coefficient k_L is reported in Figure 5. The results show that, under the conditions studied, the maximum achievable elimination capacity is not affected by the trickling rate. This is in spite of the fact that, while changing k_L, the calculated wetting ratio of the biofilm increases from 0.15 to 0.56, which shifts the pollutant mass transfer path from gas-biofilm at low trickling rates, to gas-liquid-biofilm at high trickling rates. The absence of the effect of trickling rate was experimentally observed under selected conditions (data not shown) and suggests that, under the conditions of Figure 5, the liquid offers only a very low mass transfer resistance compared to other possible rate limiting processes. Indeed, the model indicates that, under these conditions, the system is limited both by diffusion in the biofilm, and by the biological degradation kinetics.

As mentioned earlier, the model appears to be very sensitive to the diffusion coefficient of H_2S in the biofilm, so this sensitivity was investigated further. The results are reported in Figure 6a for a fixed H_2S initial concentration and variable air velocity, and in Figure 6b for a fixed air velocity and variable initial H_2S concentration. Examination of Figure 6a reveals that, at low air velocity, the process performance is not sensitive to the H_2S diffusion coefficient in the biofilm. This is because, under such conditions, the main bottleneck is the external mass transfer resistance. At higher linear velocities, as the external mass transfer resistance becomes less important compared to other rate limiting processes, a greater sensitivity to D is observed. This is a direct consequence of the very thin biofilm (23 μm) in the system and the high specific biodegradation rate of H_2S. Under these conditions, the present model reduces to a traditional biofilter diffusion-reaction model in which the observed H_2S removal rate solely depends on the concentration gradient at the biofilm interface [27]. This is further illustrated in Figure 6b, where one sees that the higher the H_2S concentration, the higher the sensitivity to its diffusion. This is linked to the increase of H_2S concentration gradient at the interface, and the faster biodegradation kinetics, as H_2S concentration is increased.

The sensitivity of the biotrickling filter model to H_2S maximum biodegradation rate R_m and half-saturation constant Ks is reported in Figures 7 and 8, respectively. The results illustrate that EC_{max} is a clear function of the specific maximum biodegradation rate and concentration, as is expected for a system limited by both the biological kinetics and by diffusion. It is interesting to see that the model is somewhat sensitive to K_s (~20% variation, see Figure 8). This—as well as other direct dependency on biokinetic parameters—was not expected because of the high concentration considered for the simulation. The reason for such sensitivity is clearly linked to the fact that the process was, in part, diffusion limited, which resulted in the depletion of H_2S within the biofilm, in turn creating first order microkinetics (i.e., dependent on K_s) in the deep portions of the biofilm.

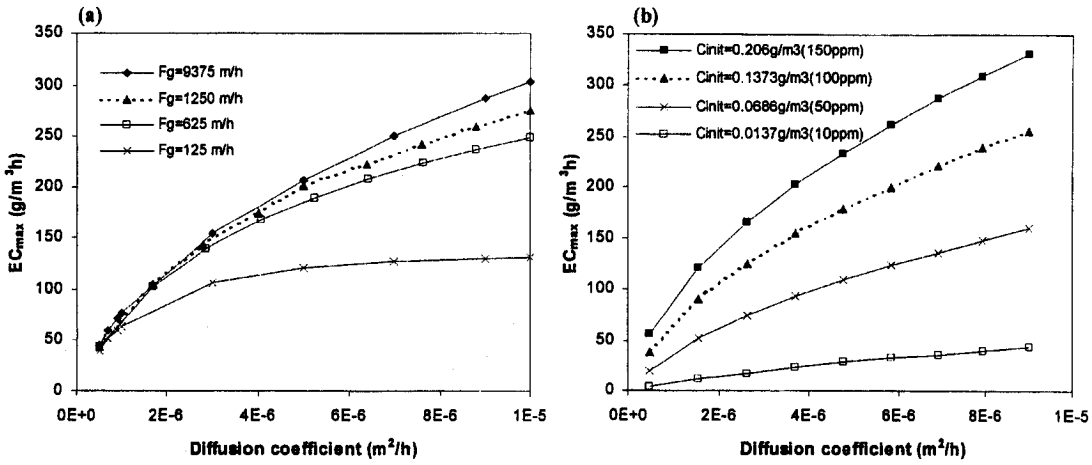

Figure 6. Effect of diffusion coefficient (D) on simulated H_2S maximum elimination capacity (EC). (a) fixed initial H_2S concentration (116 ppm_v) and effect of gas velocity; (b) fixed air velocity (9,400 m h^{-1}) and effect of initial H_2S concentration.

Effect of Air Velocity on H_2S Elimination Capacity

A primary motivation for the study was to explain why such high H_2S removal rates were obtained in the biotrickling filter at OCSD [3], when extrapolation from laboratory biotrickling filtration tests or other biotrickling filters predicted a much lower performance. A series of experiments of the type reported in Figure 3 was conducted in which the air flow rate through the biotrickling filter was varied so that the external mass transfer characteristics would be changed. The maximum elimination capacity of H_2S was determined in each experiment, and the data were reported as a function of the air velocity in Figure 9. To account for the variability of biomass density in the foam cubes used for the experiments, the results were normalized by the amount of biomass. This reduced scattering of the data, but hid the fact that extremely high performance (EC of 200-260 g m^{-3} h^{-1}) was obtained. The data confirm that the elimination capacities values predicted by the model in Figures 5-8 were not unreasonable.

Besides the very high performance, the results show a behavior that has not been commonly observed. They show an increase in the elimination capacity of H_2S as the air velocity is increased, proving that some degree of external mass transfer limitation was occurring in the biotrickling filter. This does not contradict the claim of diffusion and reaction limitations discussed earlier because the velocities tested experimentally were much lower than the one used for computing Figures 5-8. At the moment, the model only qualitatively predicts the increasing trend in H_2S elimination capacity with increasing air velocity (not shown). Still, further adjustments in the mass transfer correlation, and possibly the value of key parameters, such as diffusion coefficient, may help to improve the accuracy of the model over a wide range of air velocities and H_2S concentrations.

It is difficult to generalize from the results obtained with one packing, for one set of experimental conditions, to the wide variety of H_2S-degrading reactors and

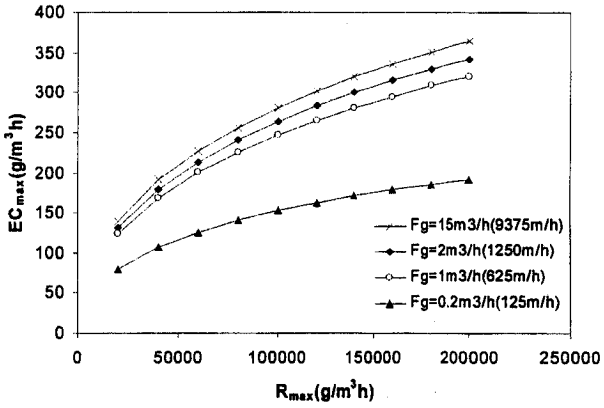

Figure 7. Effect of maximum reaction rate (R_m) on elimination capacity (EC) at various linear gas velocities (initial H_2S concentration: 116 ppm_v). Note that unit of R_m is g of H_2S degraded per unit volume biofilm per hour.

operating conditions that exist. The foam packing used in the present study has smaller pores than most biotrickling filter packing, meaning that the air is closer to the packing surface. Further, the foam packing has better connections through the pores, suggesting that the air may flow in less tortuous paths, perhaps reducing the turbulence that moves the contaminant to the surface. Thus, it is possible that the air-phase resistance noted is also partly a result of the particular packing used. On the other hand, the mathematical model presented uses very general mass transfer correlations not specific to the packing, and yet, still qualitatively predicts the increasing performance trend. Thus, it is reasonable to believe that external mass transfer limitations may exist in other H_2S-degrading biotrickling filters. This finding has wide implications, since most H_2S-degrading biofilters or biotrickling filters operate at gas contact times of 15-45 s, in beds that are usually

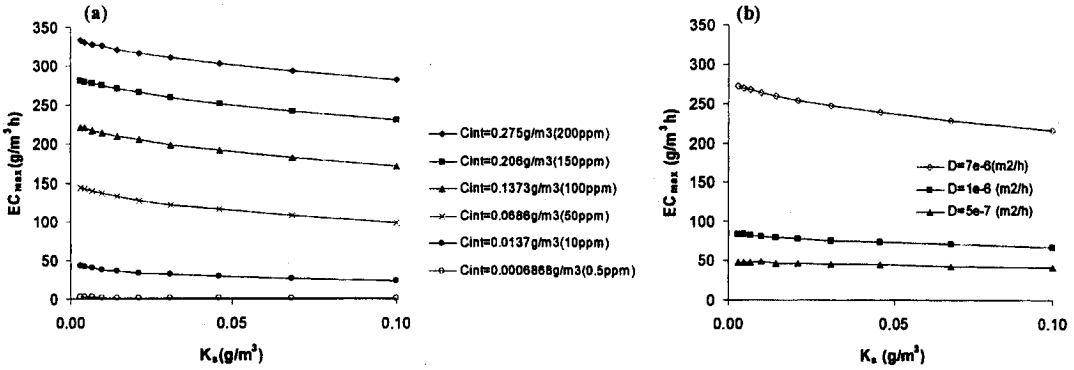

Figure 8. Effect of Michaelis-Menten Constant (K_s) on H_2S elimination capacity at (a) varying H_2S initial concentration (0.5 ~ 200 ppm_v); (b) varying diffusion coefficients (5 x 10^{-7} ~ 7 x 10^{-6} m^2 h^{-1}) but fixed initial H_2S concentration (116 ppm_v).

1-1.5 m deep. This corresponds to air velocities of 80 to 360 m h^{-1}, i.e., velocities that are markedly lower than those reported in Figure 9. The present findings suggest that those bioreactors may be heavily limited by external mass transfer, and, therefore, that the full capabilities of H_2S degrading biotrickling filters have not yet been exploited.

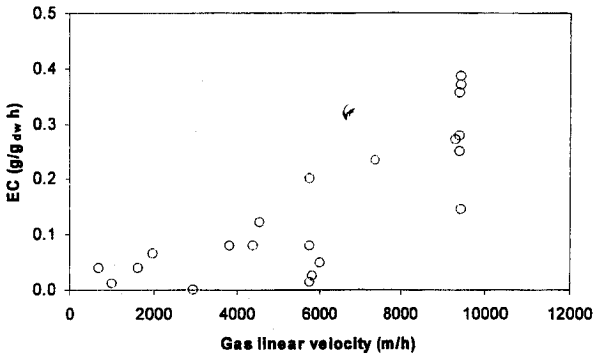

Figure 9. Experimental data for the normalized EC (g H_2S per g dry biomass per h) as a function of air linear velocity. All other parameters were kept constant. Initial concentrations of H_2S were between 50 and 120 ppm_v. The biomass content in each foam cube varied, but was on average about 0.7 kg_{dw} m^{-3}.

NOMENCLATURE

A	interfacial area (m^2)
A_{nw}	non-wetted area (m^2)
A_w	wetted area (m^2)
a	specific interfacial area (m^2 m^{-3})
a_b	cross sectional area of bed (m^2)
C_g	H_2S gas concentration (g m^{-3})
C_{gi1}	H_2S gaseous concentration at gas-liquid interface (g m^{-3})
C_{gi2}	H_2S gaseous concentration at gas-liquid interface (g m^{-3})
C_L	H_2S concentration dissolved in liquid (g m^{-3})
C_{Li2}	H_2S concentration in liquid at liquid-biofilm interface (g m^{-3})
C_{nwb}	H_2S concentration in non-wetted biofilm (g m^{-3})
C_{wb}	H_2S concentration in wetted biofilm (g m^{-3})
D	diffusivity of H_2S in liquid (m^2 h^{-1})
D_g	diffusivity in gas (m^2 h^{-1})
D_p	nominal size of packing (m)
EC	elimination capacity (g m^{-3} h^{-1})
EC	elimination capacity normalized per volumetric biomass content (g g_{dw}^{-1} h^{-1})
F_g	volumetric flow rate of gas (m^3 h^{-1})
F_L	volumetric flow rate of liquid (m^3 h^{-1})
Fr	Froude number, $aL^2/g_c/\rho_L^2$
FT	biofilm thickness (m)
G	superficial mass velocity of gas, $F_g\rho_g/a_b$ (kg m^{-2} h^{-1})
g_c	gravitational constant (m h^{-2})
H	Henry's Constant (-)
i, j	index for finite elements in the dynamic model
k_{g1}	mass transfer coefficient from gas to liquid (m h^{-1})
k_{g2}	mass transfer coefficient from gas to non-wetted biofilm (m h^{-1})
k_L	mass transfer coefficient in liquid (m h^{-1})
K_s	Michaelis-Menten Constant (g m^{-3})
L	superficial mass velocity of liquid, $F_L\rho_L/a_b$ (kg m^{-2} h^{-1})
N	number of layer subdivision
nb	number of biofilm layers
nvs	number of vertical segments along the biotrickling filter height
Re	Reynolds number, $L/a/\mu_L$
R_m	maximum reaction rate (g m^{-3} h^{-1})
R_{nwb}	reaction rate in non-wetted biofilm (g m^{-3} h^{-1})
R_{wb}	reaction rate in wetted biofilm (g m^{-3} h^{-1})
V_g	volume of gas phase (m^3)
V_L	volume of liquid phase (m^3)
We	Weber number, $L^2/\rho_L/\sigma/a$