Alkaline Biofiltration of H_2S Odors

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Hydrogen sulfide (H_2S) is a very common odor nuisance which is best controlled by chemical or biological scrubbing. Under alkaline pH, the amount of H_2S that can be solubilized in a scrubbing liquid increases significantly, and therefore, gas−liquid mass transfer limitations can be reduced. To date, biological scrubbing of H_2S has been limited to neutral or acidic pH, despite the potential benefit of reduced mass transfer limitations at alkaline pH. In the present paper, an alkaliphilic sulfoxidizing bacterial consortium was deployed in a laboratory-scale biotrickling filter treating H_2S at pH 10. The gas contact time ranged from 1 to 6 s, and H_2S inlet concentrations, from 2.5 to 18 ppm_v. The results showed that under most conditions, H_2S removal exceeded 98% and the degradation end-product was sulfate. At the highest H_2S concentrations and shortest gas contact times, when the loading exceeded 30 g m^{-3} h^{-1}, the H_2S removal efficiency decreased significantly due to biological reaction limitation, and incompletely oxidized sulfides were measured in the trickling liquid. An analysis of the process demonstrated that operating the biotrickling filter at high pH results in an enhancement of the mass transfer by a factor of 1700−11 000. Overall, alkaline biotrickling filtration was shown to be very effective at low concentration of H_2S and very short gas contact time. This is the first demonstration of a biotrickling filter for air pollution control operated at high pH.

Introduction

Gaseous hydrogen sulfide (H_2S) is a very common odor nuisance. It is emitted from a variety of sources such a wastewater treatment plants, kraft mills, asphalt plants, and biogas production. Its distinct rotten eggs smell can be detected in air at levels lower than 1 ppb_v. H_2S emissions need to be controlled to avoid odor complaints by neighboring populations. Biological treatment in biofilters and biotrickling filters is widely used for H_2S control because it is effective and relatively economical (*1*−*4*). In biotreatment processes, gaseous H_2S is first absorbed (eq 1) into an aqueous scrubbing solution or an attached biofilm, where it is then converted by sulfide-oxidizing microorganisms to nonvolatile species, such as elemental sulfur and sulfate (eqs 2, 3) depending on the availability of dissolved oxygen. The pH in H_2S biotreatment systems usually ranges from near neutral to extremely acidic (*2, 4*). Gabriel and Deshusses (*2*) reported the successful removal of gaseous H_2S into a biotrickling filter operated at pH ∼2 with empty bed residence times (EBRTs) of 1.5 and 2.2 s for inlet concentration up to 30 ppm_v. Chemolithoautotrophic bacteria from the genera *Thiobacillae* and *Acidithiobacillae* have been reported to be the main organisms mediating the oxidation of dissolved sulfide (*5*). These bacteria are very sensitive to alkaline conditions, such as those found in spent caustic streams from oil refining operations (*6*).

Absorption:

$$H_2S_{gas} + OH^- \leftrightarrow HS^- + H_2O \quad (1)$$

Biological oxidation:

$$HS^- + \frac{1}{2}O_2 \rightarrow S^0 + OH^- \quad (2)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (3)$$

The pH is very relevant to H_2S gas treatment, since the amount of H_2S that can be absorbed in a scrubbing liquid increases with the pH because the chemical equilibrium favors the more soluble species, such as hydrosulfide (HS^-) or sulfide (S^{2-}). The pK_a for the $H_2S \leftrightarrow HS^-$ and the $HS^- \leftrightarrow S^{2-}$ equilibria are 6.9 and 12.75, respectively (*7*). Therefore, the saturation solubility of H_2S in aqueous solution at pH < 4, 20 °C, and ambient pressure is 0.1 M, whereas the solubility of Na_2S in 20 °C neutral pH water is as high as 2.4 M (*7*). Hence, performing H_2S biotreatment in alkaline conditions should be beneficial, in particular, for high air flow rates with low concentrations of H_2S, when mass transfer limitations may occur (*8, 9*).

One alkaline biotreatment approach has been developed for the removal of H_2S from biogas (*10, 11*). It consists of two steps: first, the absorption of gaseous H_2S in a caustic solution, followed by biodegradation of the dissolved sulfide to elemental sulfur in a separate bioreactor operating at pH 8 with *Thiobacillae*. Because the biological oxidation step is conducted under carefully controlled oxygen conditions, the dissolved sulfide is converted mainly to elemental sulfur (eq 2).

When higher pH values need to be used to foster H_2S absorption, different genera of bacteria capable of efficiently oxidizing dissolved sulfide at high pH are needed. These extremophiles are commonly grouped as alkaliphilic sulfoxidizing bacteria (ASB). Sorokin et al. (*12*) reported and characterized a large number of ASB strains, grouped within the *Thioalkalivibrio* and *Thioalkalimicrobium* genera, which are obligate or facultative chemolithoautotrophic, that grow between pH 9 and 11 and oxidize reduced sulfur compounds, such as sulfide, thiosulfate, polysulfide, tetrathionate, and thiocyanate, usually to sulfate or sulfur. Furthermore, ASB often grow in very saline environments with Na^+ concentrations ranging from 0.6 to 4.0 M.

The use of ASB was recently described for the removal of H_2S from synthetic sour gas. The process uses a gas lift bioreactor with the recycling of the gas operated under fed-batch regime at a pH around 10 and total sodium concentration of 2 mol L^{-1} (*11*). During biological oxidation of H_2S under alkaline pH conditions, it has been found that the abiotic spontaneous reaction rate of sulfide with dissolved oxygen is increased and intermediates, mainly pentasulfide, thiosulfate, and sulfite, are produced (*11, 13*). The formation

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of these intermediates has been shown to reduce the toxicity of sulfide, allowing further biological oxidation to sulfur or sulfate (*13*)

The aim of this work was to develop a one-step treatment process with an alkaliphilic sulfoxidizing bacterial consortium deployed in a single biotrickling filter reactor operated at high pH and to demonstrate effective control of low concentrations of H_2S in air at very short gas residence times (1−6 s).

Materials and Methods

Consortium Enrichment. A mesophilic consortium of ASB enriched from alkaline soils and soda lake sediments (pH between 9 and 11) in Mexico was used in this study (*13*). The consortium is obligately haloalkaliphilic and chemolithoautotrophic and consists of about seven different species as observed from denaturing gradient gel electrophoresis studies. The ASB consortium can oxidize sulfide, polysulfide, thiosulfate, elemental sulfur, and tetrathionate as the energy source, with oxygen as the final electron acceptor and carbon dioxide or dissolved carbonates as the carbon source. Its optimum growth conditions are a sodium concentration of 1 M, a pH of 8−10, and a temperature of 30 °C. It has a relatively slow growth rate ($\mu_{max} = 0.062\ h^{-1}$).

Laboratory-Scale Biotrickling Filter. A laboratory scale biotrickling filter was used for the experiments (Figure S1 in the Supporting Information). It had an internal diameter of 10 cm and a bed height of 60 cm. The packing material was an open-pore polyurethane foam (EDT, Germany) with a specific area 600 $m^2\ m^{-3}$, a density of 35 $kg\ m^{-3}$, and a porosity of 0.97. The foam cubes (4 × 4 × 4 cm) were fitted in the reactor. Air and trickling liquid flowed counter-currently. Intermediate ports for liquid and gas sampling were distributed along the height of the reactor. Due to the high air flow rates tested, prehumidification of the air was necessary to avoid both major loss of water by evaporation from the biotrickling filter and the adverse effects of evaporative cooling.

The mineral medium reported by Sorokin et al. (*14*) was used as the trickling liquid in the reactor. It contained ($g\ L^{-1}$) Na_2CO_3 (20); $NaHCO_3$ (10); NaCl (5); K_2HPO_4 (1.0); KNO_3 (1.0); $MgCl_2 \cdot 6H_2O$ (0.2), and 2 mL L^{-1} of a trace elements solution (*15*). Unless noted differently, the feeding rate of the mineral medium was 21 mL h^{-1}. The pH of the system was controlled at a value of 10 by automatic addition of 2 N NaOH.

Different air flow rates were applied to the biotrickling filter, ranging from 2.9 to 17.5 $m^3\ h^{-1}$, corresponding to EBRTs of 6−1 s. The main air stream was mixed with a metered stream of 50% (vol) H_2S in air, supplied using a peristaltic pump from a 20 L Tedlar bag. Different pumping rates were applied to reach H_2S inlet concentrations ranging from 2.5 to 18 ppm_v (0.0036 to 0.026 g m^{-3}). The liquid trickling rate was kept constant at 0.014 $m^3\ h^{-1}$, which corresponds to a linear velocity of 1.7 m h^{-1}. The liquid was uniformly dispersed on the bed using a PVC full cone spray nozzle (BETE Fog Nozzle, Inc., Greenfield, MA). The liquid volume (sump and holdup) in the biotrickling filter was about 1 L.

All experiments were performed at room temperature (20−22 °C). The biotrickling filter was inoculated with the ASB consortium from a 0.5 L shake flask batch culture. After inoculation, the biotrickling filter was initially fed thiosulfate as the sole energy source (24.8 $g\ L^{-1}\ Na_2S_2O_3 \cdot 5H_2O$ in mineral medium, with a feeding rate of 0.02 L h^{-1} and air flow rate of 2.9 $m^3\ h^{-1}$) for 10 days to build up a suitable biomass concentration. Thereafter, the biotrickling filter was fed with only gaseous H_2S in humid air and mineral medium. Subsequently, gradual increases of the H_2S loadings were imposed to determine the maximum elimination capacity of the biotrickling filter. The elimination capacity (EC) of biofilters and biotrickling filters is defined as EC = (inlet − outlet concentration ($g\ m^{-3}$)) × air flow/bed volume.

Analytical Methods. Periodic determinations of gaseous H_2S and of dissolved sulfur species concentrations were conducted during operation of the biotrickling filter to close the sulfur balance. Gas phase H_2S concentrations were measured using a Jerome 631X series meter (Arizona Instruments. Tempe, AZ). The detection limit was 1−3 ppb_v. Occasionally, an Odalog (App-Tek, distributed by Detection Instruments, Phoenix, AZ) was used for continuous measurements of H_2S. Sulfate was analyzed by ion chromatography (Dionex IC, Column AS16). A methylene blue spectrophotometric kit was used to quantify sulfide (Vacuvial, Chemetrics Inc. VA) (*16*). Thiosulfate was measured following a titrimetric method proposed by Kurtenacker (*17*). Elemental sulfur analysis was conducted as described by Schedel and Truper (*18, 19*). Polysulfides, which are frequently unstable, were not measured in this study. Biomass was determined indirectly by measuring total protein using the bicinchoninic acid method (*20*). From previous experiments, it was determined that 25% of dry cell weight was protein. Pressure drop across the bed was measured by a U tube water manometer.

The sulfide degrading activity of the suspended biomass and the biofilm was determined by oxygen uptake rate (OUR). The suspended biomass was collected periodically from the trickling liquid. At the completion of the biotrickling filtration experiments, the reactor was disassembled, and the biofilm was detached from the packing material and suspended into a known mineral medium volume so that determination of the total biomass content and its OUR activity was evaluated. Earlier research had shown that the activity of detached biomass was representative of the activity of the biofilm in the biotrickling filters (*21*). A 3.0 mL aliquot (previously aerated for 1 min) was added to a magnetically stirred miniature glass vessel fitted with a polarographic oxygen electrode (YSI 5331 Oxygen Probe, YSI Co., Yellow Springs, OH) and an oximeter (YSI 5300 Biological Oxygen Monitor, YSI Co., Yellow Springs, OH). Calculation of sulfide oxidation rate from OUR data was made assuming stoichiometric conversion of sulfide to sulfate (eq 3).

Results and Discussion

Performance of the Alkaline Biotrickling Filter. The experiments reported herein span over almost 5 months. Figure 1 shows the overall operation and performance during the entire experiment. Biomass build up of the ASB consortium with added liquid thiosulfate was maintained for the first 10 days to reduce the start-up period.

Immediately after starting the continuous feeding of gaseous H_2S, the biotrickling filter removed close to 80% of 18 ppm_v H_2S fed to the system at an EBRT of 6 s with corresponding production of sulfate (Figure 1). There was a subsequent growth of the ASB in the biotrickling filter between days 10 and 40. A relatively stable ASB culture was established in the biotrickling filter, as indicated by the protein−biomass measurements (Figure 1a). H_2S removal efficiency remained greater than 95%, and complete oxidation of H_2S to sulfate was reached for all H_2S loading rates tested at EBRTs of 6 and 4 s. On average, outlet H_2S concentrations at these EBRTs were less than 0.1 ppm_v. H_2S loading rates greater than 40 g $m^{-3}\ h^{-1}$ were tested on days 40−100 by shortening the EBRTs to 1 and 2 s. Pressure drop remained very low (below 2 cm of water column for all conditions), despite the high air velocity (up to ~2000 m h^{-1}). Because of the very short gas contact times (<2 s), the H_2S removal efficiency significantly decreased down to about 40%, and incomplete oxidation of sulfide was detected. This resulted in thiosulfate accumulation, as was measured in the liquid (Figure 1a), and probable production of polysulfides con-

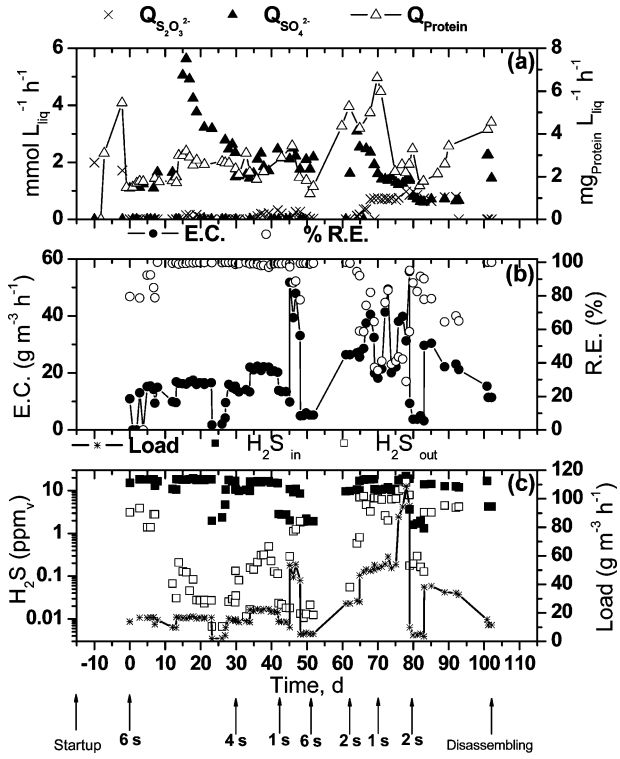

FIGURE 1. Overview of the performance and operation of the alkaline biotrickling filter during the experiment. Day 0 corresponds to the start of H_2S feeding. The vertical lines indicate the different EBRTs ranging from 6 to 1 s. $Q_{S_2O_3}$, Q_{SO_4}, $Q_{protein}$ are the volumetric production rates of thiosulfate, sulfate, and biomass (as protein), respectively. Note the logarithmic scale for the H_2S gaseous concentrations. RE = removal efficiency, EC = elimination capacity.

sistent with prior investigations on the degradation of sulfide by the same alkaliphilic sulfoxidizing bacterial consortium (*13*) and other reports (*11*). These intermediates have been shown to be produced mainly by the abiotic oxidation of HS^-. Biokinetic determinations and sulfur balances (see later) indicated that the biomass activity in the reactor was not sufficient to oxidize these intermediates further to sulfate; hence, the global performance of the biotrickling filter was controlled by biological reaction.

Figure 2 summarizes the performance of the biotrickling filter. Detailed examination of this figure reveals that the H_2S removal efficiency was greater than 95% at an EBRT as low as 1 s for the lowest H_2S inlet concentration (2.5 ppm_v). For H_2S inlet concentrations of 10 ppm_v and 18 ppm_v, the removal efficiency significantly decreased at lower gas contact time due to the biological limitation. With the exception of a few cases (*2, 3, 22*), the gas residence times reported for biofilters and biotrickling filters treating H_2S are usually 15−45 s. Thus, alkaline biotrickling filtration appears to offer many advantages for the treatment of low concentrations of H_2S. This has significant practical application because a large number of odor control equipment are exposed to H_2S concentrations not exceeding 10 ppm_v.

Figure 2 inset shows that the biotrickling filter had a critical H_2S loading rate (i.e., the loading at which removal falls below 95%) of around 30 g m^{-3} h^{-1} and a maximum elimination capacity of 40 g m^{-3} h^{-1}. Gabriel and Deshusses (*2*) reported some of the best performance for the removal of low concentrations of H_2S. A critical loading rate of 100 g m^{-3} h^{-1} at EBRTs of 1.5 and 2.2 s for H_2S inlet concentration of 30 ppm_v were reported for a H_2S degrading biotrickling filter operated under acidic conditions. The differences with the present work are due to the different metabolic activities

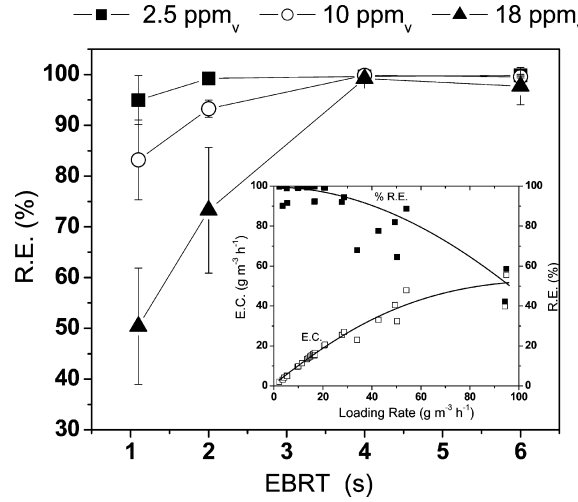

FIGURE 2. H_2S removal efficiencies in the alkaline biotrickling filter as a function of the EBRT and H_2S inlet concentration. Error bars are the standard deviations around the average RE. The inset shows EC and RE vs inlet loading (the lines are trend lines and not a model).

between alkaliphilic and acidophilic microorganisms (*12, 23*), the size scale (laboratory vs full scale), and the lower H_2S concentrations in the current study. As will be discussed later, alkaline biotreatment offers the advantage of inherent stability due to the efficient physical absorption of H_2S in alkaline solutions.

Removal and treatment of H_2S in alkaline biotrickling filters follows a two-step process. H_2S is first absorbed in the alkaline solution, resulting in dissolved sulfide, which reacts to form various dissolved polysulfides, of which pentasulfide (which is unstable) is probably the dominant species according to earlier studies (*13*). Then the dissolved sulfide and polysulfides are aerobically biodegraded by the ASB to sulfate. In parallel to the biotic degradation, chemical oxidation of the dissolved sulfide with oxygen occurs, resulting predominantly in thiosulfate. This abiotic process occurs at significant rates (*13*). It is estimated that an EC of 1.1 g m^{-3} h^{-1} (around 3% of the maximum experimental EC) was obtained for the highest H_2S inlet concentration tested just by the abiotic sulfide oxidation. The relative importance of the abiotic reactions may increase at even higher inlet H_2S concentrations (*13*), although this was not investigated.

The step limiting the rate of H_2S removal was further investigated. The biotrickling filter was operated at EBRTs of 2 and 4 s, corresponding to H_2S loading rates of 49 and 24 g of H_2S m^{-3} h^{-1}, and the liquid trickling rate was varied. The H_2S inlet concentration was constant at 18 ppm_v. At the lower H_2S loading rate, some mass transfer limitations were observed, as the outlet concentration of H_2S decreased, when increasing the trickling rate (see Figure S2 in the Supporting Information). At the highest H_2S loading rate, the biological reaction was the rate-limiting step, since the trickling rate did not affect the H_2S removal. This suggests that process optimization should focus on increasing biomass density and specific activity.

Analysis of the Mass Transfer Enhancement from the Alkaline Conditions. Overall, the results of Figures 1, 2, and S2 illustrate that some of the mass transfer limitations commonly reported in conventional biotrickling filter treating low concentrations of H_2S can be reduced in the alkaline biotrickling filter. This is because of fast chemical reaction of the absorbed H_2S in the alkaline scrubbing liquid (eq 1). This induces a significant enhancement of the H_2S absorption rate that can be evaluated from the enhancement factor E_A, as in eq 4 (*24*).

TABLE 1. Parameters for E_A Evaluation at 25°C

parameter	value	ref
D_A	1.48×10^{-5} ($cm^2\ s^{-1}$)	*24*
D_B	5.17×10^{-5} ($cm^2\ s^{-1}$)	*25*
H	9992 ($ppm_v\ mol^{-1}\ L$)[a]	-
A^*	$[H_2S]_{lm}/H$ ($mol\ L^{-1}$)	-
B_0	1×10^{-4} ($mol\ L^{-1}$)	-

[a] Based on the maximum dissolved H_2S concentration in the liquid that could be reached during the experiments. $A = H_2S$; $B = OH^-$

$$E_A = \sqrt{\frac{D_A}{D_B}} + \frac{B_0}{nA^*}\sqrt{\frac{D_B}{D_A}} \quad (4)$$

Quantification of the enhancement resulting from alkaline conditions was determined using the values of constants listed in Table 1. Since E_A depends on the gaseous concentration of H_2S and thus varies along the height of the biotrickling filter, it was evaluated using the logarithmic mean H_2S concentration ($[H_2S]_{lm}$) during the biotrickling filter operation. Thus, an average enhancement factor, $\bar{E}_A$, was calculated. First, the molar absorption rate of H_2S (Ja) with respect to the bed volume can be expressed (eq 5).

$$Ja = 1 \times 10^6 PK_G a([H_2S] - [H_2S]_{liq}H) = 1 \times 10^6 \frac{F_G}{S}\frac{d[H_2S]}{dz} \quad (5)$$

where

$$K_G a = \frac{1}{\frac{1}{k_G a} + \frac{H}{\bar{E}_A k_L a}} \quad (6)$$

As $\bar{E}_A$ increases, the liquid resistance decreases so that only the gas film resistance limits the rate of H_2S absorption into the aqueous phase. Next, $k_G a$ was determined from eq 7 (*24*), assuming insignificant resistance in the liquid phase and no reaction limitation. This was an approximate value, and to consider the maximum $k_G a$ value, the outlet H_2S concentration was set to 10^{-6} ppm_v; that is, a removal close to 100%.

$$k_G a = \frac{F_G}{SPL}\ln\left(\frac{[H_2S]_{in}}{[H_2S]_{out}}\right) \quad (7)$$

Kim and Deshusses (*26, 27*) reported experimental determinations and empirical correlations for $k_L a$ in biotrickling filters. For the same packing material and for conditions relatively close to those used here, a $k_L a$ value of 4.5 h^{-1} was obtained. $k_L a$ was found to be highly dependent on the rate of liquid trickling but varied only slightly with gas flow rate; hence, a constant value was used here for simplification. The impact of this assumption is minor.

Next, the maximum overall molar absorption rate of H_2S per volume of bed with and without chemical reaction (considering $E_A \gg 1$ and $E_A = 1$, respectively) can be evaluated from eq 8. This expression assumes no reaction limitation ($[H_2S]_{liq} = 0$), and its complete derivation can be seen in the Supporting Information.

$$Ja_{max} = 1 \times 10^6 \frac{F_G}{SL}[H_2S]_{in}\left(1 - \exp\left(\frac{-SP\langle K_G a|_{\bar{E}_A}\rangle L}{F_G}\right)\right) \quad (8)$$

Results for the calculated values of E_A, $k_G a$, $k_L a$ and $K_G a$ for each operating condition tested in the biotrickling filter are reported in Table 2. The data show the very significant enhancement of mass transfer caused by the alkaline conditions (E_A ranging from 1700 to 11 000). Remarkably, the enhancement is most important at low concentrations, for which operating a biotrickling filter at alkaline pH should be most economical.

Using the values reported in Table 2, the maximum absorption−reaction flux Ja was evaluated and compared to the corresponding H_2S elimination capacity reached during the biotrickling filtration experiments. The results are reported in Figure 3. At EBRTs greater than 1 s for an inlet concentration of 2.5 ppm_v H_2S and greater than 2 s, in the cases of 10 and 18 ppm_v, H_2S removal was essentially complete (see Figure 2), and therefore, the maximum flux Ja is roughly equal to the H_2S elimination capacity (Figure 3). At the shortest EBRT, the calculated Ja is significantly larger than the biotrickling filter elimination capacity, indicating that the biotrickling filter was kinetically limited. Figure 3 shows that the degree of kinetic limitation increases with increasing the H_2S concentration and decreasing the EBRT. It also indicates that an elimination capacity of up to 80 $g\ m^{-3}\ h^{-1}$ could possibly be obtained in the absence of kinetic limitation.

The enhancement of the H_2S absorption rate caused solely by the alkaline conditions was evaluated by calculating the molar mass transfer fluxes with and without reaction, that is, by taking the ratio of the fluxes when setting E_A to a large value, to the mass transfer flux for E_A equal to 1 (i.e., no reaction). The results (Figure 4) show that enhancement factors of about 15 were obtained at the longest EBRTs and that they were independent of concentration, whereas enhancement factors as high as 55−75, depending on the concentration, were obtained for EBRTs of 1 s. This figure adds further evidence that alkaline conditions are favorable for high performance treatment because they result in a considerable reduction in the liquid film mass transfer resistance.

Sulfur Balance. A sulfur balance was attempted to track the fate of the removed H_2S. Instantaneous H_2S consumption rates and sulfide/sulfate production rates were subject to significant fluctuations (Figure 5a) due to both experimental uncertainties and inherent reactor performance variations. Generally, there was a good correspondence between the H_2S removed and sulfate produced at the lower loadings, whereas at the higher loadings (days 40−100), the effects of kinetic limitations can be seen, resulting in lower than stoichiometric sulfate production. A better representation of the data is a cumulative mass balance, as shown in Figure 5b. During the first 40 days, the H_2S consumed in the biotrickling filter was converted mainly to sulfate, with a (SO_4^{2-}/H_2S) yield close to the theoretical value of 1.0. However, partial oxidation of sulfide and accumulation of intermediates occurred at higher loads after day 40. These intermediates include polysulfides, thiosulfate (see also Figure 1a), and elemental sulfur, which have been shown to be produced when the oxidation metabolism is overloaded (*11, 23*). Elemental sulfur was not observed in the present experiments, most probably because dissolved oxygen concentrations remained high.

Abiotic Operation. As discussed above, under most conditions, sulfate was the main sulfur compound from the biological oxidation of H_2S following the reaction shown in eq 3, and no detectable elemental sulfur was observed (eq 2). Thus, two protons were expected from the biodegradation of each molecule of H_2S. However, NaOH consumption during the operation of the biotrickling filter exceeded the value expected from the H_2S biodegradation rate. This was due to the absorption of CO_2 from the air, which is also favored at alkaline pH (*28*).

To determine the contribution of CO_2 absorption to the acidification of the trickling liquid, the biotrickling filter was operated as a H_2S (abiotic) scrubber, by replacing the air by nitrogen, thereby removing all oxygen from the system. This

TABLE 2. $\bar{E}_A$ and Mass Transfer Coefficients Estimated for Each Operating Condition Tested in the Biotrickling Filter[a]

EBRT (s)	$[H_2S]_{in}$ (ppm_v)	$\bar{E}_A$	k_La (h^{-1})	$k_Ga \times 10^5$	$K_Ga \times 10^5$ ($E_A \gg 1$)(mol h^{-1} m^{-3} atm^{-1})	K_Ga ($\bar{E}_A = 1$)
1.1	2.5	11006	4.5	12.0×10^5	5.82×10^5	103
2	2.5	11006	4.5	6.57×10^5	4.16×10^5	103
4	2.5	11006	4.5	3.29×10^5	2.55×10^5	103
6	2.5	11006	4.5	2.19×10^5	1.84×10^5	103
1.1	10	3011	4.5	13.07×10^5	2.51×10^5	103
2	10	3011	4.5	7.19×10^5	2.17×10^5	103
4	10	3011	4.5	3.60×10^5	1.67×10^5	103
6	10	3011	4.5	2.40×10^5	1.35×10^5	103
1.1	18	1734	4.5	13.55×10^5	1.58×10^5	103
2	18	1734	4.5	7.45×10^5	1.44×10^5	103
4	18	1734	4.5	3.73×10^5	1.21×10^5	103
6	18	1734	4.5	2.48×10^5	1.04×10^5	103

[a] K_Ga involves the effect of the instantaneous chemical reaction. See text for details.

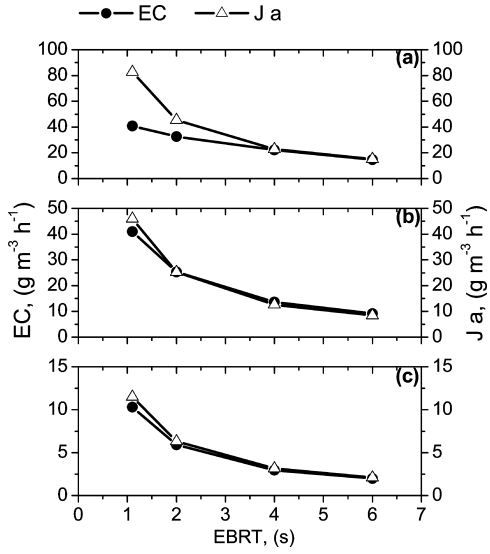

FIGURE 3. Comparison of the maximum Ja calculated from eq 8 and the experimental elimination capacity for each operating condition tested in the biotrickling filter: inlet H_2S concentration (a) 18 ppm_v, (b) 10 ppm_v, and (c) 2.5 ppm_v.

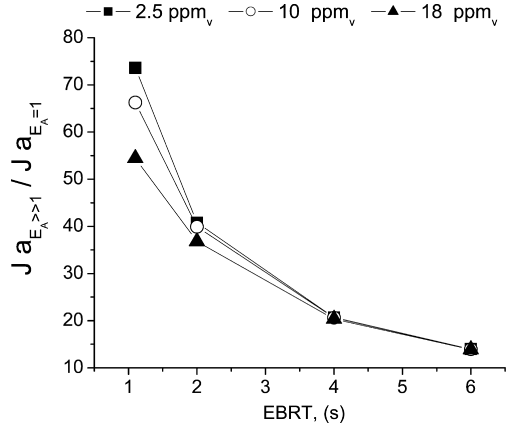

FIGURE 4. Enhancement of H_2S absorption rate due of alkaline conditions. The ratio of the H_2S molar absorption rate under alkaline conditions to absorption without reaction (when E_A=1) at different empty bed residence times is reported.

was meant to stop all abiotic oxidation and aerobic biodegradation. The experiment was conducted at an EBRT of 6 s and H_2S inlet concentration of 18 ppmv. Figure 6 shows the performance during the abiotic operation. The removal of H_2S rapidly decreased to 50% in the absence of oxygen, and dissolved sulfide accumulation increased as expected.

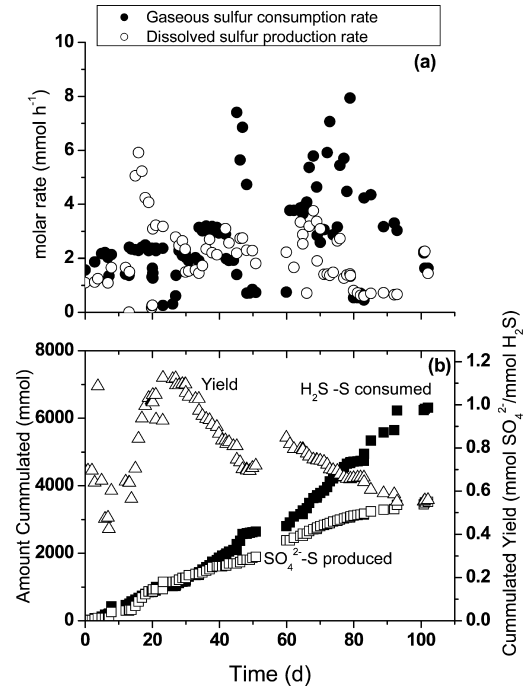

FIGURE 5. Sulfur balances: (a) instantaneous consumption and production rates and (b) cumulative mass balance.

By comparing the protons generated during the H_2S absorption process (abiotic operation) and during the overall H_2S absorption−oxidation process to sulfate (biotic operation), it was found that about 30% of the NaOH added to maintain a constant pH of 10 was used to neutralize the absorbed CO_2 and possibly other acid-forming molecules. This value is, of course, H_2S concentration-dependent. Only a small amount of carbonate is used for biomass formation.

The experiment also demonstrates that alkaline biotrickling filtration is inherently stable, that is, a significant fraction of H_2S will be removed, even if some catastrophic event completely inhibited the sulfide biodegradation process. This is a main advantage for treatment in the field, where there may be concerns of a slow startup or that a possible failure of the biology would result in odor emissions. Here, H_2S treatment would continue, although only by chemical scrubbing. Monitoring dissolved sulfides, sulfate, or the caustic consumption are some possible means to detect suboptimum biodegradation of sulfide in alkaline biotrickling filters.

Sulfide Degradation. Oxygen uptake rate was determined for the biomass attached as biofilm and for the suspended biomass to estimate their relative contribution to sulfide oxidation. Table 3 summarizes the main results. Surprisingly,

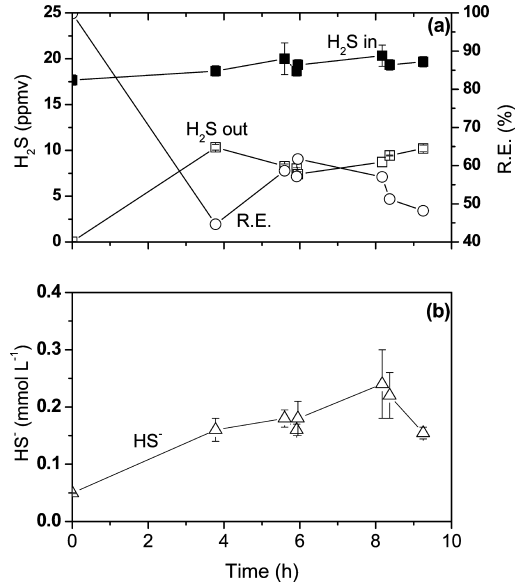

FIGURE 6. Abiotic operation of the biotrickling filter: H_2S absorption, at EBRT of 6 s; (a) gas phase performance; and (b) liquid phase performance. Oxygen-free operation was started at time 0.

TABLE 3. Determination of the Sulfide Degrading Activity in the Biotrickling Filter

biomass form	biofilm	suspended
biomass content (g_{Prot})	7.73	0.18
biomass density (g_{Prot} $m^{-3}_{reactor}$)	1590 (1280)[a]	37.6
specific OUR (mmol g_{prot}^{-1} min^{-1})	0.022 (0.081)[a]	0.054
O_2 consumption rate (mmol min^{-1})	0.167	0.010
E.C., O_2 (mmol m^{-3} min^{-1})	34.34	2.04
E.C., H_2S (g m^{-3} h^{-1})	35.03	2.08
sulfide degradation (%)	94.4	5.6
total $E.C_{max}$, H_2S (g m^{-3} h^{-1})	37.1	

[a] Values in parenthesis are those of acidophilic biotrickling filters estimated from Gabriel and Deshusses (*2, 3*).

the specific OUR of the suspended biomass was greater than that of the biofilm. However, the total volumetric oxygen consumption rate was much higher in the biofilm due to the large difference between suspended and attached biomass amounts. The H_2S elimination capacity of the biotrickling filter was assessed using the respective suspended and attached biomass amounts and the specific OURs. It was found that around 95% of the H_2S consumed was degraded in the biofilm. The total H_2S elimination capacity estimated from OUR was 37 g m^{-3} h^{-1}. This is similar to the H_2S maximum elimination capacity obtained in Figure 2 (40 g m^{-3} h^{-1}) and is in agreement with the observations that the reactor was operating under kinetic limiting conditions.

A comparison of the properties of previously studied acidophilic (*2, 3*) and the current alkaliphilic biotrickling filters (Table 3) reveals that biomass densities were approximately the same. This may be due to the fact that in addition to the pH, other very similar conditions (packing, trickling rates) were used in both systems. However, the specific sulfide degradation activity of acidophilic H_2S degraders was about 4 times greater than that of the alkaliphilic consortium. This explains that higher H_2S elimination capacities could be obtained in the previously studied acidic biotrickling filter.

This report is the first demonstration of a gas-phase bioreactor operated at high pH. Overall, the results demonstrate that extremophile alkaliphilic sulfoxidizing bacteria can be successfully deployed in biotrickling filters for highly efficient H_2S removal. The process is most suitable for the treatment of low concentrations of H_2S, which can be particularly challenging. Effective treatment could be accomplished at gas residence times as low as 1 s. This opens new possibilities for biotreatment of H_2S odors.

Appendix A

NOMENCLATURE

A^*	Dissolved H_2S concentration in equilibrium with corresponding gas phase H_2S concentration (mol L^{-1})
B_0	Bulk concentration of OH^- (mol L^{-1})
D_A	Diffusivity of dissolved H_2S in water (cm^2 s^{-1})
D_B	Diffusivity of OH^- in water (cm^2 s^{-1})
E_A	Enhancement factor (−)
EC	Elimination capacity (g m^{-3} h^{-1})
F_G	Molar air flow rate, (mol h^{-1})
H	Henry coefficient (ppm_v mol^{-1} L or atm mol^{-1} m^3)
$[H_2S]$	Gas phase H_2S concentration (ppm_v)
Ja	Molar absorption rate (mol m^{-3} h^{-1})
k_Ga	Gas film mass transfer coefficient (mol h^{-1} m^{-3} atm^{-1})
k_La	Liquid film mass transfer coefficient (h^{-1})
K_Ga	Overall gas phase mass transfer coefficient (mol h^{-1} m^{-3} atm^{-1})
L	Height of packed bed (m)
n	Number of moles of OH^- that reacts with 1 mol of dissolved H_2S
P	Total pressure (atm)
RE	Removal efficiency (%)
S	Cross section area of the biotrickling filter (m^2)
z	Axial coordinate (m)

SUBSCRIPT

in	inlet
liq	liquid
lm	log mean
out	outlet

Supporting Information Available

Additional figures and complete development of eq 8 are shown in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Janssen, A.; Ruitenberg, R.; Buisman, C. Industrial applications of new sulfur biotechnology. *Wat. Sci. Technol.* **2001**, *44*, 85–90.

(2) Gabriel, D.; Deshusses, M. A. Retrofitting existing chemical scrubbers to biotrickling filters for H_2S emission control. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 6308–6312.

(3) Gabriel, D.; Deshusses, M. A. Performance of a full-scale biotrickling filter treating H_2S at a gas contact time of 1.6 to 2.2 seconds. *Environ. Prog.* **2003**, *22*, 111–118.

(4) Smet, E.; Lens, P.; van Langenhove, H. Treatment of waste gases contaminated with odorous sulfur compounds. *Crit. Rev. Environ. Sci. Technol.* **1998**, *28*, 89–117.

(5) Islander, R. L.; Devinny, J. S.; Mansfeld, F.; Postyn, A.; Hong, S. Microbial ecology of crown corrosion in sewers. *J. Environ. Eng.-ASCE* **1991**, *117*, 751–770.

(6) Krishnakumar, B.; Majumdar, S.; Manilal, V. B.; Haridas, A. Treatment of sulphide containing wastewater with sulphur recovery in a novel reverse fluidized loop reactor (RFLR). *Wat. Res.* **2005**, *39*, 639–647.
(7) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill, New York, NY, 1999.
(8) Lobo, R.; Revah, S.; Viveros, T. An analysis of a trickle bed bioreactor: Carbon disulfide removal. *Biotechnol. Bioeng.* **1999**, *63*, 98–109.
(9) Kim, S.; Deshusses, M. A. Understanding the limits of H_2S degrading biotrickling filters using a differential biotrickling filter. *Chem. Eng. J.* **2005**, *113*, 119–126.
(10) Cline, C.; Hoksberg, A.; Abry, R.; Janssen, A. Biological process for H_2S removal from gas streams the Shell-Paques/Thiopaq gas desulfurization process *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, February 23−26, 2003.
(11) Bosch, P.; van Beusekom, O.; Buisman, C.; Janssen, A. Sulfide oxidation at halo-alkaline conditions in a fed-batch bioreactor. *Biotechnol. Bioeng.* **2007**, *97*, 1053–1063.
(12) Sorokin, D. Y.; Kuenen, J. G. Haloalkaliphilic sulfur-oxidizing bacteria in soda lakes. *FEMS Microbiol. Rev.* **2005**, *29*, 685–702.
(13) Gonzalez-Sanchez, A.; Revah, S. The effect of chemical oxidation on the biological sulfide oxidation by an alkaliphilic sulfoxidizing bacterial consortium. *Enzyme Microb. Technol.* **2007**, *40*, 292–298.
(14) Sorokin, D. Y.; Lysenko, A. M.; Mityushina, L. L.; Tourova, T. P.; Jones, B. E.; Rainey, F. A.; Robertson, L. A.; Kuenen, J. G. *Thioalkalimicrobium sibiricum* gen. nov., sp. nov., and *Thioalkalimicrobium aerophilum*, sp. nov., and *Thioalkalivibrio versutus* gen. nov., sp. nov., *Thioalkalivibrio nitratis*, sp. nov., and *Thioalkalivibrio denitrificans*, sp. nov., - novel alkaliphilic obligately chemolithoautotrophic sulfur-oxidizing bacteria from soda lakes. *Int. J. Syst. Evol. Microbiol.* **2001**, *51*, 565–580.
(15) Pfennig, N.; Lippert, K. D. Über das Vitamin B12-Bedürfnis phototropher Schwefelbacterien. *Arch. Microbiol.* **1966**, *55*, 245–256.
(16) Gilboa-Garber, N. Direct spectrophotometric determination of inorganic sulfide in biological materials and in other complex mixtures. *Anal. Biochem.* **1971**, *43*, 129–133.
(17) Kurtenacker, A. The aldehyde−bisulfite reaction in mass analysis. *Z. Anal. Chem.* **1924**, *64*, 56–61.
(18) Schedel, M.; Trueper, H. G. Anaerobic oxidation of thiosulfate and elemental sulfur in *Thiobacillus denitrificans*. *Arch. Microbiol.* **1980**, *124*, 205–210.
(19) Philip, L.; Deshusses, M. A. Sulfur dioxide treatment from flue gases using a biotrickling filter−bioreactor system. *Environ. Sci. Technol.* **2003**, *37*, 1978–1982.
(20) Smith, P.; Krohn, R.; Hermanson, G.; Mallia, A.; Gartner, F.; Provenzano, M.; Fujimoto, E.; Goeke, N.; Olson, B.; Klenk, D. Measurement of protein using bicinchoninic acid. *Anal. Biochem.* **1985**, *150*, 76–85.
(21) Cox, H. H. J.; Deshusses, M. A. Co-treatment of H_2S and toluene in a biotrickling filter. *Chem. Eng. J.* **2001**, *3901*, 1–10.
(22) Wu, L.; Loo, Y. Y.; Koe, L. C. A pilot study of a biotrickling filter for the treatment of odorous sewage air. *Wat. Sci. Technol.* **2001**, *44*, 295–299.
(23) Alcantara, S.; Velasco, A.; Muñoz, A.; Cid, J.; Revah, S.; Razo-Flores, E. Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: sulfur formation under oxygen limitation and removal of phenols. *Environ. Sci. Technol.* **2004**, *38*, 918–923.
(24) Danckwerts P. *Gas-Liquid Reactions*; Mc Graw-Hill: Columbus, OH, 1970.
(25) Cents, A.; Brilman, D.; Versteeg, G. CO_2 absorption in carbonate/bicarbonate solutions: The Danckwerts-criterion revisited. *Chem. Eng. Sci.* **2005**, *60*, 5830–5835.
(26) Kim, S.; Deshusses, M. A. Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control 1. Experimental results. *Chem. Eng. Sci.* **2008**, *63*, 841–855.
(27) Kim, S.; Deshusses, M. A. Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control 2. Development of mass transfer coefficients correlations. *Chem. Eng. Sci.* **2007**, *63*, 856–861.
(28) Zeng, A. Effect of CO_2 absorption on the measurement of CO_2 evolution rate in aerobic and anaerobic continuous cultures. *Appl. Microbiol. Biotechnol.* **1995**, *42*, 688–691.

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SUPPORTING INFORMATION
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Alkaline Biofiltration of H_2S Odors

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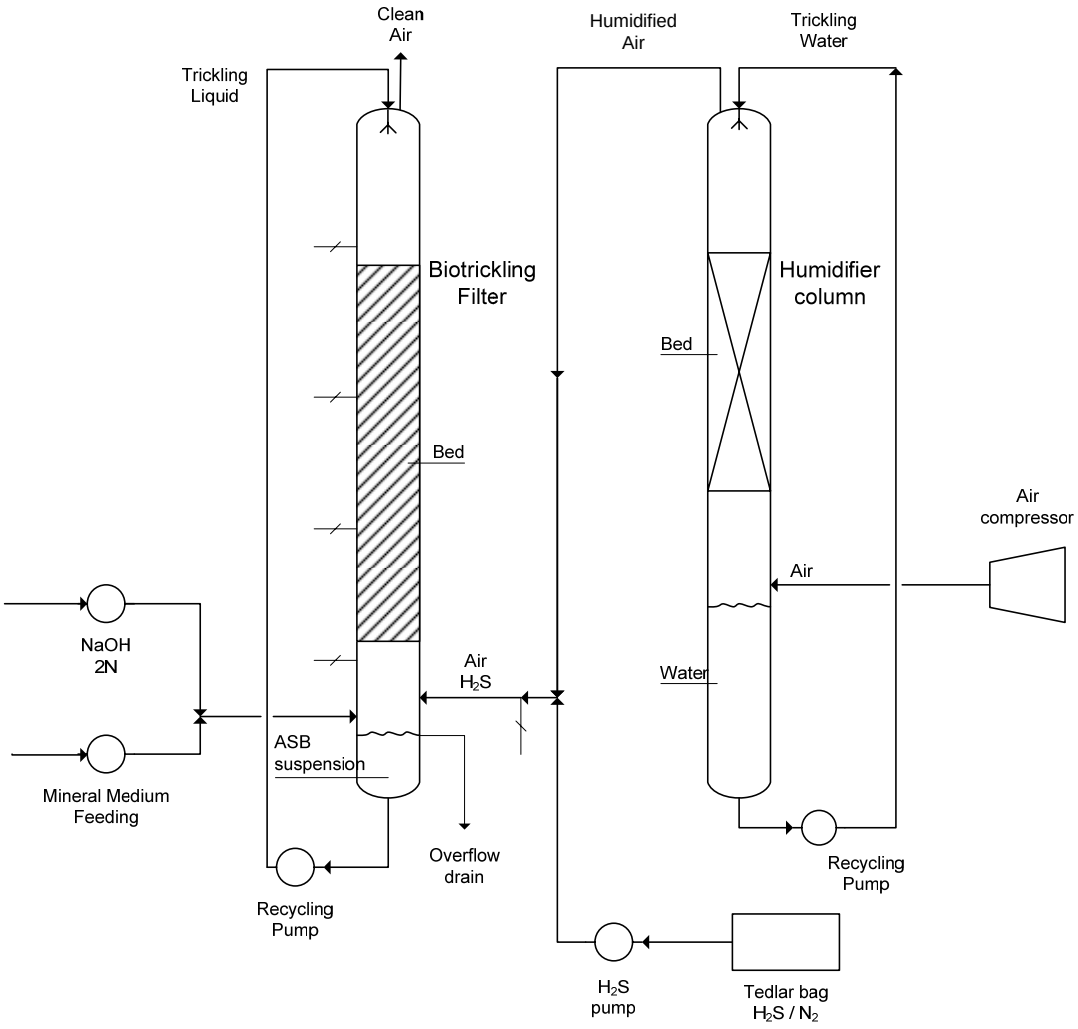

Figure S1. Schematic of the experimental system

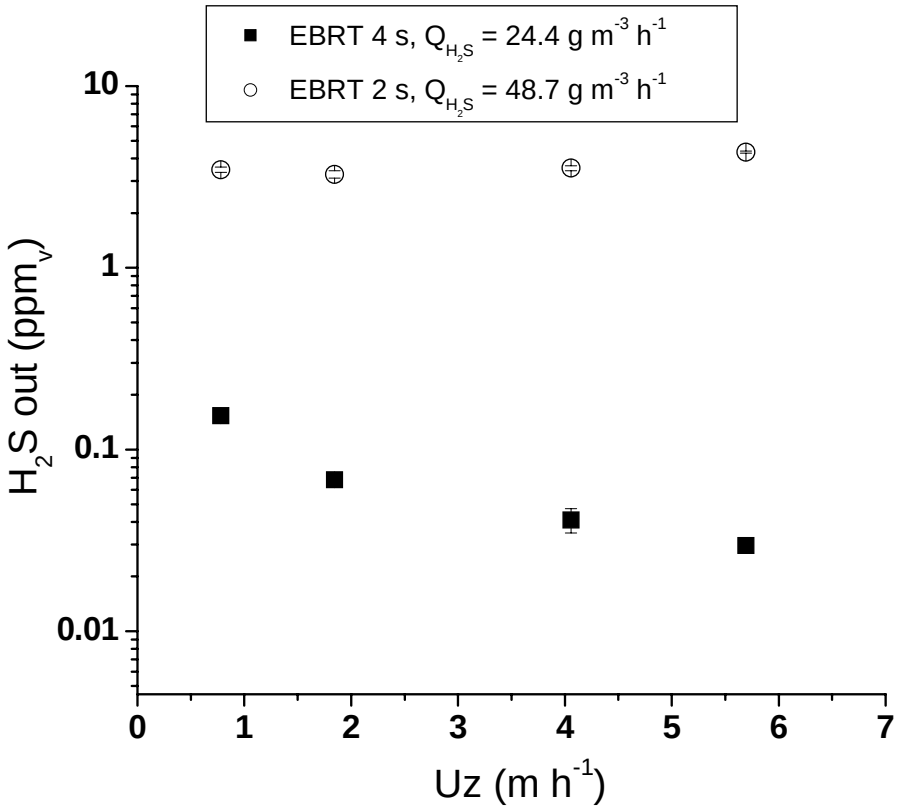

Figure S2. Effect of the liquid trickling rate on the H_2S outlet concentration. Inlet H_2S concentration was 18 ppm_v. Note the logarithmic scale for the H_2S concentration.

Derivation of Equation 8

From a differential balance of A in the gas phase:

$$-\frac{F_{gas}}{S}\frac{dy_A}{dz} = P\,K_G a(y_{Ab} - y_A^*)$$

Considering no reaction limitation ($C_{A,b} = 0$)

$$-\frac{F_{gas}}{S}\frac{dy_A}{dz} = P\,K_G a\,y_{Ab}$$

Integrating:

$$K_G a = \frac{F_{gas}}{S\,P\,z}\ln\left(\frac{y_{Aent}}{y_A}\right)$$

y_A can be obtained: as a function of column height (z)

$$y_A = y_{Aent}\exp\left[\frac{-S\,P\,K_G a\;z}{F_{gas}}\right]$$

Defining the maximal flux for each differential element z

$$\frac{1}{L}J\;\;a\,dz = \frac{F_{gas}}{S\,L}dy_A = \frac{P\,K_G a\,y_{Ab}}{L}dz$$

Integrating

$$\overline{J\;\;a} = \frac{P\,K_G a}{L}\int_0^L y_{Ab}\,dz$$

Then, substituting y_{Ab} definition and integrating

$$\overline{J\;\;a} = \frac{P\,K_G a}{L}y_{Ain}\int_0^L \exp\left[\frac{-S\,P\,K_G a\;z}{F_{gas}}\right]dz$$

$$\overline{J\;\;a} = -\frac{F_{gas}}{S\,L}y_{Ain}\int_0^L \exp w\;dw$$

$$\overline{J\;\;a} = -\frac{F_{gas}}{S\,L}y_{Ain}\left[\exp(w)\Big|_L - 1\right]$$

$$\overline{J_r\;a} = \frac{F_{gas}}{S\,L}y_{Ain}\left[1-\exp\left(\frac{-S\,P\,K_G a\;L}{F_{gas}}\right)\right]$$

$\overline{J\;a}$ is written as $J_r a$, which is the maximum overall molar absorption flux, but one should keep in mind that it is an average value along the column height.