Effects of pH, CO$_2$, and flow pattern on the autotrophic degradation of hydrogen sulfide in a biotrickling filter

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Abstract

In this study, the effects of pH, CO$_2$, and flow pattern on the performance of a biotrickling filter (BTF) packed with plastic Pall rings and treating a H$_2$S-polluted waste gas were investigated to establish the optimum operating conditions and design criteria. The CO$_2$ concentration had no effect on the biodegradation at H$_2$S concentrations below 50 ppm. In the range of 50–127 ppm H$_2$S, CO$_2$ concentrations between 865 and 1,087 ppm enhanced H$_2$S removal, while higher concentrations of 1,309–4,009 ppm CO$_2$ slightly inhibited H$_2$S removal. The co-current flow BTF presented the advantage of a more uniform H$_2$S removal and biomass growth in each section than the counter-current flow BTF. Examination of the pH-effect in the range of pH 2.00–7.00 revealed optimal activity for autotrophs at pH 6.00. Under optimal conditions, the elimination capacity reached 31.12 g H$_2$S/m^3/h with a removal efficiency exceeding 97%. In the present research, autotrophic biomass was developed in the BTF, performing both a partial oxidization of H$_2$S to elemental sulfur and a complete oxidization to sulfate, which is favorable from an environmental point of view. Results showed that around 60% of the sulfide concentration fed to the reactor was transformed into sulfate. Such autotrophic trickling filters may present other advantages, including the fact that they do not release any CO$_2$ to the atmosphere. Besides, the limited growth of autotrophs avoids potential clogging problems. Experimental performance data were compared with data from a mathematical model. Comparisons showed that the theoretical model was successful in predicting the performance of the biotrickling filter.

Keywords:

INTRODUCTION

Hydrogen sulfide (H_2S) is a toxic, colorless, flammable gas heavier than air, with an odor threshold of about 0.47 ppb. It is released to the atmosphere as a byproduct of industrial processes including, among others, sour gas flaring, petroleum refining, wastewater treatment, food processing, and pulp and paper manufacturing. The removal of H_2S from waste gases is necessary because it is harmful for living organisms, that is, its MAC value is 10 ppm, it has a low odor threshold concentration, and it contributes to the deterioration of the environment. Furthermore, the oxidation products of H_2S, namely SO_2 and SO_3, are considered to be major contributors to acid rain. Therefore, strict regulations are necessary for controlling the emission levels. A host of methods has been developed to purify gas streams containing H2S. Compared with physical and chemical processes, such as activated carbon adsorption, ozone oxidation, incineration, and scrubbing, biofiltration is considered economical, cleaner and greener because of its low operation costs, absence of residuals, and emission of no NOx and quite less CO_2 than thermal oxidation. Biofiltration is a viable and cost-effective alternative to conventional technologies for the treatment of low-concentration polluted air streams (Jin and Chen, 2001; Kennes and Thalasso, 1998; Kennes and Veiga, 2001; Wani et al., 1997). Under optimal conditions, biodegradable contaminants are rapidly converted to harm-less end-products without the accumulation of intermediates or dead-end metabolites.

The biological removal of H_2S has been studied by a number of researchers, mainly under heterotrophic conditions in presence of organic carbon substrates (Chitwood et al., 1999; Chitwood and Devinny, 2001; Chung et al., 1996, 1998; Cox and Deshusses, 2002; Gabriel and Deshusses, 2003; Koe and Yang, 2000; Yang and Allen, 1994a,b). However, hardly any reports have been published on the autotrophic removal of H_2S from polluted air, nor on the effects of process conditions as pH, CO_2 concentration, or flow pattern on its efficiency. The heterotrophic removal of H_2S from polluted air requires the presence of an external organic carbon source which may sometimes be available, for example when treating waste air from wastewater treatment plants and using such wastewater as trickling phase. Never the less, whenever an external carbon source is not directly available, the autotrophic removal of H_2S will be cheaper and more advantageous since it is based on the use of CO_2 from air as a carbon source. Another advantage of fomenting the activity of autotrophic rather than heterotrophic biocatalysts is that the slower biomass growth and build-up of the former will avoid clogging problems, quite typical in heterotrophic systems. Autotrophs are also interesting because of their low nutritional requirements. It is interesting to note that autotrophic microorganisms do not produce any CO_2 as happens with heterotrophs. Since they fix CO_2 during the removal of H_2S, the CO_2 concentration could presumably have an influence on the biodegradation rate of H_2S and the bacteria's growth rate. H_2S and CO_2 may coexist in a variety of polluted gas streams, for example, pressurized natural gas, synthesis gas, biogas, as well as polluted air released from wastewater treatment plants, pulp and paper industries, or refineries. Different authors (Haddadin et al., 1993; Torma et al., 1972) mentioned the influence of carbon dioxide on bacterial growth, biomass concentration as well as on the rate of sulfide oxidation. They suggest that the CO_2 concentration may play an important role in sulfide biooxidation. There- fore, the effect of CO_2 on the removal efficiency of H_2S may provide important information to develop efficient biotech- nological processes for field application.

Sulfur compounds, when biologically degraded in gas-phase bioreactors, generate sulfate leading to a substantial drop in pH with a concomitant reduction in biological activity and thus in H_2S removal. Yang and Allen (1994a,b) observed removal efficiencies exceeding 99% under a wide range of heterotrophic conditions in a compost biofilter. However, a rapid pH decrease led to a reduced removal efficiency. Cox and Deshusses (2002) observed that operating a bioreactor at either pH 4.5 or 7.0 did not significantly affect the biotrickling filter's performance, when feeding H_2S and toluene simultaneously. However, they found that at pH

4.5, the start-up phase for toluene degradation was relatively long and that a sudden pH drop may cause a temporary poor removal of H_2S and toluene. Although numerous studies have been published on biofiltration of H_2S, only few focused on the pH-effect on performance.

Biofilters may be operated either with co-current flows, when both the gas and aqueous nutrient streams are introduced through the top of the biofilter, or with counter-current flows, when the gas stream is introduced at the bottom while the liquid is fed through the top of the reactor. It is not clear which configuration would be superior. However, some possible advantages of co-current flow would be a better moisture control and nutrient distribution, and less stripping effect. Nevertheless, some studies (Diks and Ottengraf, 1991; Hartmans and Tramper, 1991) have suggested that there is no significant difference in biofilter performance irrespective of the flow pattern. Still others describe success stories of biofilters operated with counter-current fluid flows (Devinny et al., 1999; Lu et al., 2002; Mpanias and Baltzis, 1998). It is still not well understood how the flow pattern may affect the efficiency of biotrickling filters used for air pollution control. Data of one of our previous recent studies have shown that the treatment of H_2S-containing waste gases is feasible with autotrophic microorganisms (Jin et al., 2005). The overall goal of the present study was to develop and optimize the operation of a biotrickling filter for potential use for the biological autotrophic removal of H_2S from polluted air of wastewater treatment plants and chemical industries. The specific tasks were to determine the effect of operation parameters as pH, CO_2 concentration, and flow pattern, and to briefly evaluate solutions that make the treatment technology more environmental friendly by minimizing the waste discharge, that is, S^0 recovery and SO^{2-} reuse. The information gained from these specific tasks will be very beneficial for the subsequent application of biofiltration to the removal of H_2S from waste gases under optimal conditions.

MATERIALS AND METHODS

Microorganisms and Cultivation

An autotrophic H_2S-degrading culture obtained from the activated sludge of the full-scale wastewater treatment plant of a resin-producing industry was enriched in a biofilter. The characteristics of the sludge have been described elsewhere (Prado et al., 2004). The biomass was acclimized to sulfur compounds in a sodium thiosulphate mineral medium without addition of any external organic carbon source. The composition of the liquid medium used was (in g/L):
KH_2PO_4, 2; K_2HPO_4, 2; NH_4Cl, 0.4; $MgCl_2 \cdot 6H_2O$, 0.2; $FeSO_4 \cdot 7H_2O$, 0.01; and $Na_2S_2O_3 \cdot 5H_2O$, 8 (Jin et al., 2005).

Experimental Setup

The schematic of the biotrickling filter used in this study is shown in Figure 1 and has been described previously in detail (Jin et al., 2005). It is a cylindrical packed bed reactor made of glass, 75 mm in diameter and 700 mm in height. The packed column was filled with polypropylene Pall rings of a nominal height of 15 mm. The total height of the packed bed was 640 mm. The Pall ring bed had an initial porosity of 91% and a specific surface area of 350 m^2/m^3. The glass column contained four equidistant sampling ports. All fittings, connections and tubings were made of Teflon. H_2S was introduced by passing the air stream over a H_2SO_4 solution into which a solution of Na_2S was dripped. Gas phase H_2S concentrations ranging from 0 to 190 ppm were obtained by changing the Na_2S concentration and/or dripping rate. The resulting synthetic waste gas was introduced either through the bottom or the top of the column respectively for counter- current flow or co-current flow operation. Initially, the gas flow rate was maintained constant at 7 L/min, corresponding to an empty bed residence time of 24 s. The aqueous mineral medium described above, without $Na_2S_2O_3$ nor any external carbon source, was continuously recirculated over the packed bed using a peristaltic pump (model 323E/D, Watson- Marlow Limited, Falmouth Cornwall, England) at a constant volumetric flow rate of 2.77 L/h. The nutrient solution of the biotrickling filter was renewed every day. The pH of the nutrient solution was measured and controlled with an automatic pH regulator (pH-METROS DO9765T, LabProcess, Barcelona, Spain). During the experimental study on the effect of CO_2, carbon dioxide from a gas cylinder flew first through a pressure gauge (RBDE-30/PS-3.5, Carburos Metalicos S.A., La Corun˜a, Spain) and then through a flowmeter (Model VCD 1000 flow controller, Porter Instrument Co., Inc., Hatfield, PA) in order to reach the expected CO_2 concentration in the inlet gas. During most of the experiments, the biotrickling filter was operated in countercurrent mode without extra CO_2 addition nor pH regulation, unless otherwise specified.
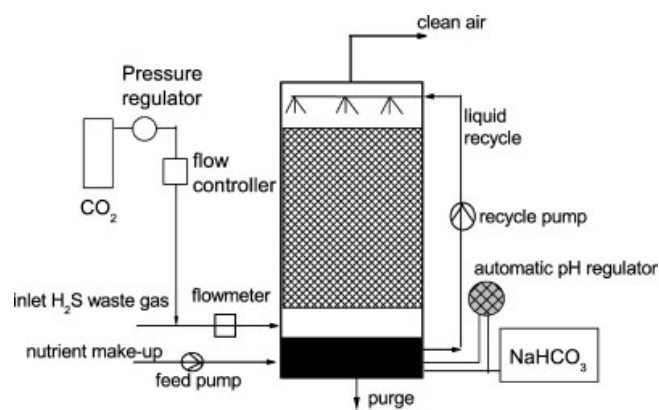

Figure 1. Scheme of the biotrickling filter.

## Analytical Methods

Inlet and outlet H_2S concentrations were determined using a gas sensor (Dräger Sensor XSEC H_2S HC6809180). Gas- phase CO_2 concentrations were measured by gas chromatography on a HP-5890 GC equipped with a thermal conductivity detector and a Porapack Q-column W80/100. SEM photographs and chemical microanalysis of the filter beds were done, respectively, with a JEOL JSM-6400 SEM, working at a voltage of 20 kV and a working distance of 15 mm, and Oxford Instruments EDX equipment. Before the SEM analysis, the samples were dried for 24 h, placed on a metallic stub and

covered with gold by means of a Balzers SCD-004 sputter coater. Sulfate concentrations were determined as described by Jin et al. (2005).

RESULTS AND DISCUSSION

Influence of CO_2 on Performance In this experiment a biotrickling filter was fed H2S-polluted air enriched with different CO_2 concentrations. According to the data shown in Figure 2, it appeared that in the lower range of H_2S concentrations, that is, <50 ppm, the CO_2 concentration had no visible effect on the removal efficiency ofH2S. However, a non-negligible enhancement of H_2S removal was found when gradually increasing the content of CO_2 to 4,009 ppm, at H_2S concentrations higher than 50 ppm. This indicated that at lowerH_2S concentrations, the inherentCO_2 in the waste gas did not limit the degradation rate, but at high H_2S concentrations the pollutant's removal rate was limited by the availability of CO_2, probably due to the mass transfer rate of CO_2 from the gas phase to the liquid biofilm. When the CO_2 concentration was slightly increased from 865 ppm to 1,087 ppm, no detectable difference in H_2S removal was observed. However, the removal efficiency decreased as the CO_2 concentration was further increased to 1,309 ppm or more. This means that higher CO_2 concentrations can enhance the removal of H_2S at CO_2 concentrations ranging between ambient levels and 1,087 ppm. However, higher concentrations of CO_2, for example >1,309 ppm, did not further improve the degradation of H_2S.
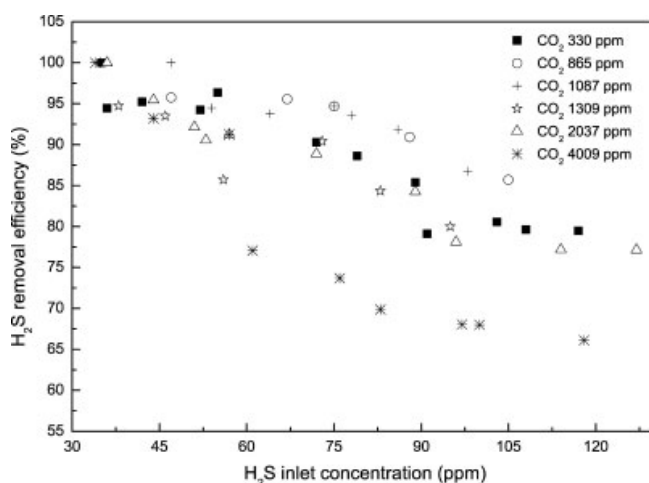
In order to get more insight in this phenomenum, gas and liquid film mass transfer coefficients, and wetted area were determined experimentally for the packing material and conditions of the biotrickling filtration experiments. The Onda correlations, which are widely used in chemical scrubbers, were selected for the determination of mass transfer coefficients and wetted area in the biotrickling filter.
The Onda model consists of three separate equations for the calculations of the local individual liquid, and gas phase mass transfer coefficients, k_L and k_G, as well as the wetted specific interfacial surface area for mass transfer, a_W. The Onda model is given by the following equations (Onda et al.,1968):

$$k_L = 0.0051 \left(\frac{L_f}{a_w \mu_L} \right)^{2/3} (Sc_L)^{-1/2} (E_r)^{-0.4} (Sh_L)^{-1/3} \quad (1)$$

$$\frac{k_G}{a_t D_G} = c(R_G)^{0.7} (Sc_G)^{1/3} (E_r)^2 \quad (2)$$

$$a_w = a_t \left\{ 1 - \exp \left[-1.45 \, (R_L)^{0.1} (F_L)^{-0.05} (We_L)^{0.2} (M_C)^{0.75} \right] \right\} \quad (3)$$

After searching for the values of the different parameters as indicated in Table I (Knudsen et al., 1997; Thibodeaux,1996), the Onda model can be used to calculate the individual mass transfer coefficients in the liquid phase and in the gas phase, as well as the wetted specific surface area of the packing.

Table I. Known value of parameters.

Parameter	Value
a_t (m^2/m^3)	350
L_f (kg/m^2/s)	0.1737
G_f (kg/m^2/s)	0.03131
ρ_L (kg/m^3)	996.95
ρ_G (kg/m^3)	1.185
d_p (m)	0.015
g (m/s^2)	9.81
C	5.23
μ_L (kg/m/s)	1.006×10^{-3}
μ_G (kg/m/s)	18.1×10^{-6}
σ_C (kg/s^2)	0.04
σ_L (kg/s^2)	0.0728
$D_{H_2S,L}$ (m^2/s)	1.36×10^{-9}
$D_{H_2S,G}$ (m^2/s)	1.66×10^{-5}
m_{H_2S} (dimensionless g/aq)	0.4088
$D_{CO_2,L}$ (m^2/s)	1.77×10^{-9}
$D_{CO_2,G}$ (m^2/s)	1.64×10^{-5}
m_{CO_2} (dimensionless g/aq)	1.202
$D_{O_2,L}$ (m^2/s)	2.35×10^{-9}
$D_{O_2,G}$ (m^2/s)	2.06×10^{-5}
m_{O_2} (dimensionless g/aq)	31.44

Besides, the two-phase resistance theory postulates that the overall resistance to interfacial mass transfer is equal to the sum of the individual liquid- and gas-phase resistances, therefore,

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}$$

From the results shown in Table II, it appears that the mass transfer coefficients of H2S and CO2 are somewhat different, but still of the same order of magnitude. However, the mass transfer for O2 is two orders smaller. We derived the stoichiometric equation given below as the net relationship describing growth of autotrophic bacteria on sulfide as an energy source and oxygen as a terminal electron acceptor.

$$0.444H_2S + 0.4HS^- + 1.2555O_2 + 0.0865H_2O$$
$$+ 0.346CO_2 + 0.0865HCO_3^-$$
$$+ 0.0865NH_4^+ \rightarrow 0.844SO_4^{2-}$$
$$+ 0.0865C_5H_7O_2N(\text{biomass}) + 1.288H^+$$
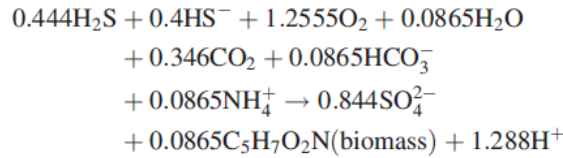
The formula $C_5H_7O_2N$ utilized for the biomass composition is generally valid for most bacteria (Sublette and Sylvester, 1987). According to the ratio of H_2S to CO_2 fed to the reactor, the CO_2 concentration in the gas phase should be sufficient for the biodegradation of H_2S in the experiment over all the concentration range studied. However, the removal of H_2S increased with the CO_2 concentration, which could be explained by the fact that the mass transfer rate of CO_2 is lower (about 2.5 times) than for H_2S. A high concentration of CO_2 generates a high gradient between the gas phase and the liquid phase increasing the driving force and the mass transfer rate. When the CO_2 concentration was higher than 1,309 ppm, the removal of H_2S was no longer enhanced by the CO_2 concentration. Therefore, other factors than the CO_2 concentration should be considered to be limiting the removal. In this case, O_2 may become the limiting factor, due to its mass transfer rate two orders of magnitude lower than for the other two compounds (Table II). In addition, high concentrations of CO_2 might even inhibit the activity of bacteria.

Table II. Mass transfer parameters.

Parameter	H_2S	CO_2	O_2
a_w (m^2/m^3)	37.06	37.06	37.06
k_L (m/s)	2.187×10^{-5}	2.495×10^{-5}	2.874×10^{-5}
k_G (m/s)	3.281×10^{-3}	3.255×10^{-3}	3.790×10^{-3}
K_G (m/s)	5.263×10^{-5}	2.062×10^{-5}	9.141×10^{-7}

The results obtained in this experiment provide an experimental evidence for the potential effect of carbon dioxide on H_2S removal. Recently, Gabriel and Deshusses (2003) suggested the possible influence of CO_2 on H2S removal as a hypothesis. They supposed that the high concentration of CO_2 of more than 4,000 ppm in foul air treated in a BTF contributed to the efficiency of the process culture such that it was never limiting the degradation of H_2S, leading to a high reactor performance. Nevertheless, this hypothesis was not confirmed experimentally, and no study has ever been published on the effect of the CO_2 concentration on a biotrickling filter's performance. In that study, the secondary effluent of a wastewater treatment plant was used as trickling phase and carbon-containing compounds as CS_2, CH_3SH, COS, and odor-compounds were removed simultaneously to H_2S resulting in the presence of heterotrophic organisms.

Effect of pH on H_2S Removal
The complete biodegradation of H_2S produces sulfuric acid. Since there is no biotransformation consuming the acid, the latter will accumulate very fast in the recirculated trickling phase, and the pH will drop down to the point where the microbial populations become inhibited.
The effect of the pH on the removal of H_2S was examined over a pH range of 2.00–7.00. The pH of the trickling liquid was measured online and was actually controlled and maintained at the desired value through the automatic addition of a diluted solution of $NaHCO_3$ when necessary. Each specific pH value was kept for two consecutive days.

Figure 3 represents the removal efficiencies and elimination capacities at the different pH.
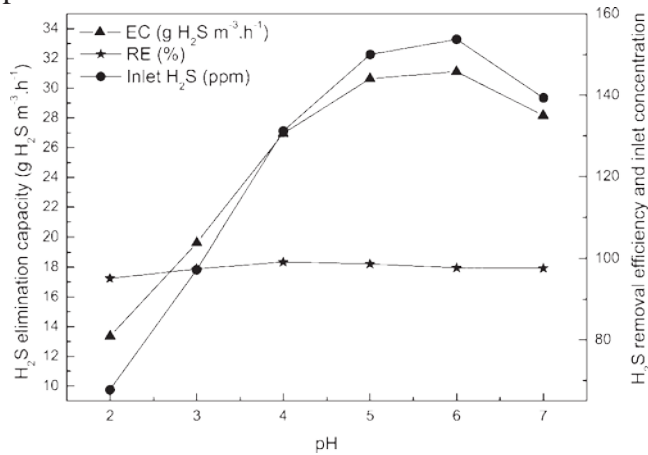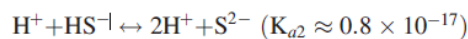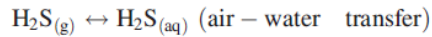

Figure 3.   Elimination capacities of the biotrickling filter as a function of pH.

At each pH value, the maximum elimination capacity allowing reaching near 100% removal efficiency was evaluated. Therefore, as can be observed from the data in Figure 3, the removal efficiency was maintained at a high value around or slightly above 97% between pH 3.00 and 7.00, and around 95% at pH 2.00. The H_2S elimination capacity increased from 13.35 to 31.12 g H_2S/m3/h when increasing the pH from 2.00 to 6.00, and then slightly dropped to 28.17 g H_2S/m3/h at pH 7.00. These results confirm our former preliminary results (Jin et al., 2005). In the preliminary study the pH was adjusted manually every 30 min and measured offline which made it difficult to maintain a strictly constant pH. In the present case, the online measurements and instantaneous automatic pH regulation improved the accuracy of the data. The optimal desulfurizing capability was obtained when the pH was regulated at a value of 6.00. This may be due to two main reasons. On the one hand, it has been shown that different autotrophic microbial groups and activities dominate at different pH. It is known that the autotrophic Thiobacillus group includes both acidophobic bacteria that prefer a near neutral pH and acidophilic bacteria that grow at low pH values (Smet et al., 1998). On the other hand, the substrate HS⁻ is more available for bacteria at a higher pH in the wet biofilm where the biodegradation takes place. The fact that hydrogen sulfide incompletely dissociates in the water phase, resulting in the coexistence of the ionized and unionized forms, complicates the description of hydrogen sulfide removal (Yongsiri et al., 2004). The existence of different sulfide species in sewer networks can be illustrated by the following equations, at 208C:

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \ (air - water \quad transfer)$$

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \ (K_{a1} \approx 1.0 \times 10^{-7})$$

$$H^+ + HS^{-|} \leftrightarrow 2H^+ + S^{2-} \ (K_{a2} \approx 0.8 \times 10^{-17})$$

where K_{a1} and K_{a2} are equilibrium constants, which are weakly dependent on temperature and conductivity. Because of the low K_{a2} value, the sulfide ion (S^{2-}) is, in practice, present in insignificant amounts in typical domestic wastewater and in aqueous media in general, as biofilms in gasphase trickling filters. Based on the Ka1 value of approximately $1.0*10^{-7}$, 50% of the total dissolved sulfide ($H_2S(aq)+HS^-$) is in the

unionized form as $H_2S(aq)$ at pH 7. This means that HS^- rather than S^{2-} will be preferentially taken up by the bacteria.

S^0 Recovery and $SO_4{}^{2-}$ Reuse

The biodegradation of H_2S results in medium acidification and production of sulfate ions, which may accumulate and poison the degrading microorganisms. To assure a continued, high microbial activity in biotrickling filters treating H_2S polluted air, some actions are possible to keep the operating conditions within an adequate range, as briefly described hereafter.

Some researchers used effluent sewage from municipal wastewater treatment plants as the recycling liquid to provide the nutrients for the bacteria but also to remove sulfate ions as soon as they form. Sulfate ions are converted to H_2S, which is emitted into the air again. Afterwards, the purge from the biotrickling filter is continuously discharged to the wastewater treatment plant again. This is a cycle in which pollutants are continuously transferred from one phase to another. In order to avoid this dilemma and make biotrickling filters environmental friendly, S recovery and sulfate reuse were considered in the present study.

In this experiment, the pH of the trickling phase was initially 6.78. It was then allowed to vary naturally in the reactor. In such a case, the pH of the liquid phase dropped steadily to a value of around 3.00. Afterwards, it continued decreasing, but much more slowly, to about 2 over a period of several hours. Throughout that complete period, the H_2S elimination rate remained basically constant in the reactor (Fig. 4). Meanwhile, the SO_4^{2-} generation rate gradually decreased to finally stabilize once the pH reached a nearly constant value of about 2. The SO_4^{2-} concentration in the recycled trickling nutrient solution suggested partial oxidation of H_2S to elemental sulfur (S^0) instead of sulfate (SO_4^{2-}).
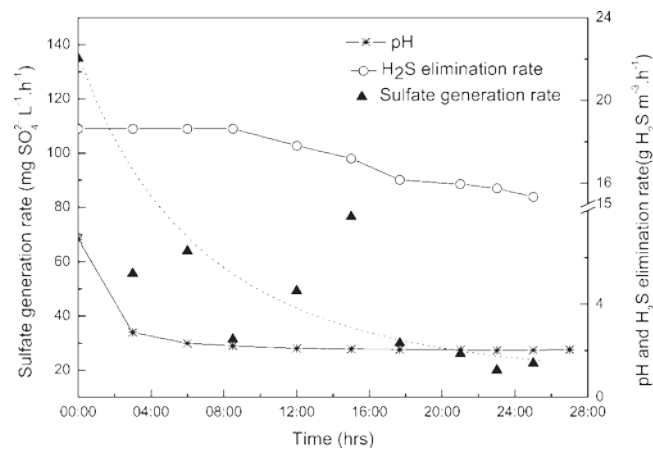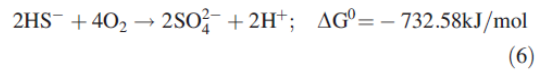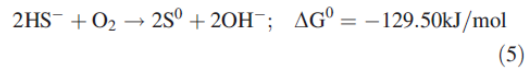

Figure 4. Changes of pH, H_2S elimination rate, and sulfate generation rate with time in a continuous biotrickling filter without pH regulation.

The sulfur balance showed that around 60% of sulfide was converted into sulfate. This seems to clearly indicate that once the pH stabilized around 2, part of the H2S was only partially oxidized to sulfur instead of sulfate. This hypothesis was confirmed at the end of the experiment by SEM photographs of samples of the Pall rings taken from regions located at middle height in the bioreactor. Figure 5 shows both fresh Pall rings and spent Pall rings. The rod-shaped elements in the spent Pall rings, not found in fresh rings, was mainly condensed elemental sulfur, as was also confirmed by the subsequent elemental analysis (data not show).

Sulfur production from the partial oxidation of sulfide instead of the complete oxidation to sulfate has interesting environmental implications, as elemental sulfur can easily be removed by sedimentation. Additionally, lower energy consumption is required because the oxidation to sulfur requires four-fold less oxygen than the conversion to sulfate according to the following reactions:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^-; \quad \Delta G^0 = -129.50 \text{kJ/mol}$$
$$(5)$$
$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+; \quad \Delta G^0 = -732.58 \text{kJ/mol}$$
$$(6)$$

According to the stoichiometry of the aerobic biological sulfide oxidation, oxygen is the key parameter that controls the level of oxidation. This is also confirmed from the results of the experiments on the effect of CO_2.

The sulfate formed during the process could be removed through precipitation in a settling tank coupled to the biotrickling filter, rather than being treated and eventually converted again to H_2S in a wastewater treatment plant. In order to precipitate SO_4^{2-} to form $CaSO_4$ in the used nutrient solution, the effect of the addition of either CaCO3 or CaO was tested. Twenty-five milliliters of used nutrient solution was introduced in three glass tubes. The first one acted as reference and in the other two either CaO or $CaCO_3$ was added. The generated $CaSO_4$ settled down much faster in the presence of CaO (Fig. 6). Using this method, the treated nutrient solution leached from the biotrickling filter can be reused for reclamation of alkali soils. This will generate $CaSO_4$ and reduce the wastewater discharge.
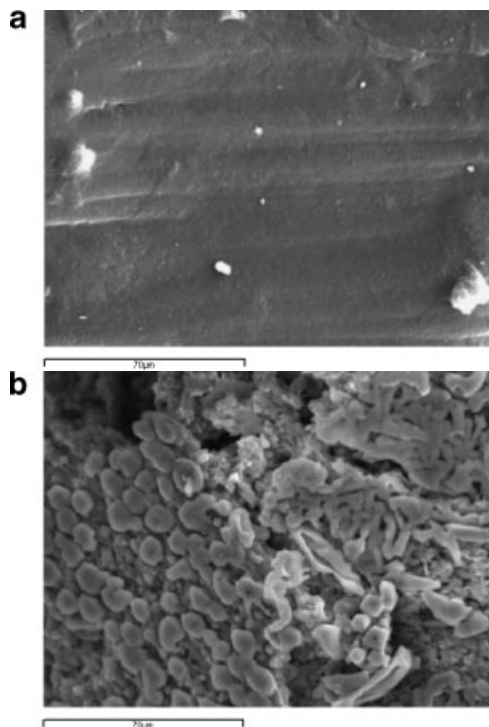

Figure 5.   Scanning electron microphotographs of packing material taken from inside the biotrickling filter, top: fresh Pall ring; bottom: spent Pall ring.
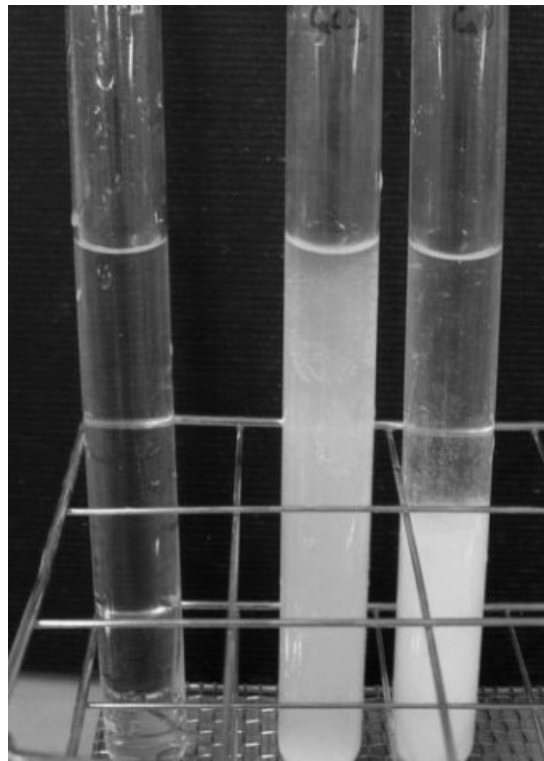
Figure 6.   Precipitation of CaSO4 using CaCO3 or CaO (left: no addition; middle: CaCO3 addition; right: CaO addition).

Effect of the Flow Pattern on Performance

In most of our studies, counter-current operation was used for the reactor. The performance of a biotrickling filter operated with either co-current or counter-current flows throughout the parameter range of practical interest was investigated during this experiment. The performance curves were determined at a liquid flow rate of 2.77 L/h and a gas flow rate of 7 L/min for both modes of operation (Fig. 7).

In co-current operation, the removal of H_2S was almost linear with the distance in the reactor. The higher the inlet concentration, the lower the percent removal in the first section of the bioreactor. This may be due to the sparse concentration. Although slow growing autotrophic microorganisms colonize the filter bed, a somewhat higher amount of biomass is present near the inlet of the reactor resulting in somewhat higher removal rates. The other factor is that at low substrate concentrations, the amount of H2S reaching the outlet section of the biofilter is low and induces diffusion limitations resulting in decreasing removal rates leading to a curve rather than a straight line at such low concentrations. These profiles can be explained as discussed hereafter by using Ottengraf's model illustrated in Figure 8 (Ottengraf and van den Oever, 1983).

(1) If there is no diffusion limitation in the biofilm on the surface of the packing, the overall elimination rate is only controlled by the kinetics of biodegradation (reaction limitation). In this case, the H_2S loads exceed the critical load. The decrease of H_2S concentration is linear along the height of the bioreactor. The relationship between the H_2S concentration in the gas phase and the height of the bioreactor bed is described by:

$$\frac{C_g}{C_{g,in}} = 1 - \frac{k_0 A_s \delta H}{U_g C_{g,in}}$$

Figure 7 shows the H_2S concentration profiles along the bioreactor's height. At the highest loads (i.e., highest H_2S concentration), the removal profile is close to a linear variation in concentration (Fig. 7b).

(2) Diffusion limitation occurs when the H_2S concentration in the gas phase falls below a critical value. The overall elimination rate is controlled by the rate of diffusion and the theoretical dependence of Cg with respect to the height is given by:

$$\frac{C_g}{C_{g,in}} = \left(1 - \frac{A_s H}{U_g} \sqrt{\frac{k_0 D_{eff}}{2 C_{g,in} m}}\right)^2$$

At low loadings, a clear non-linear variation of concentration versus height was observed in the upflow reactor (Fig. 7b).
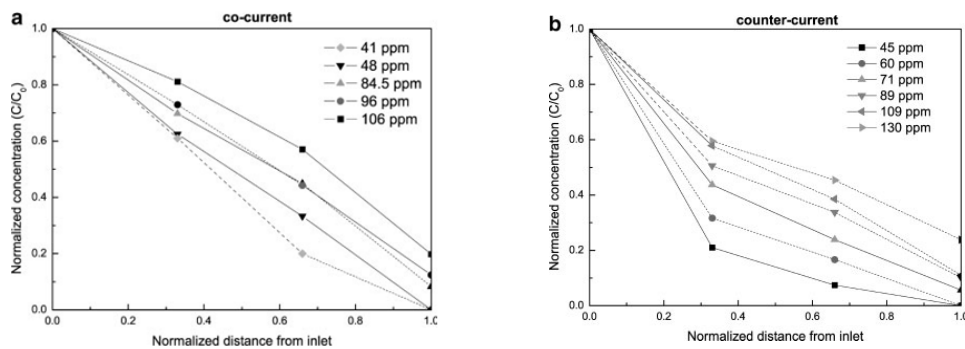

Figure 7. H_2S removal profiles along the biotrickling filter with either (a) co-current or (b) counter-current flows.
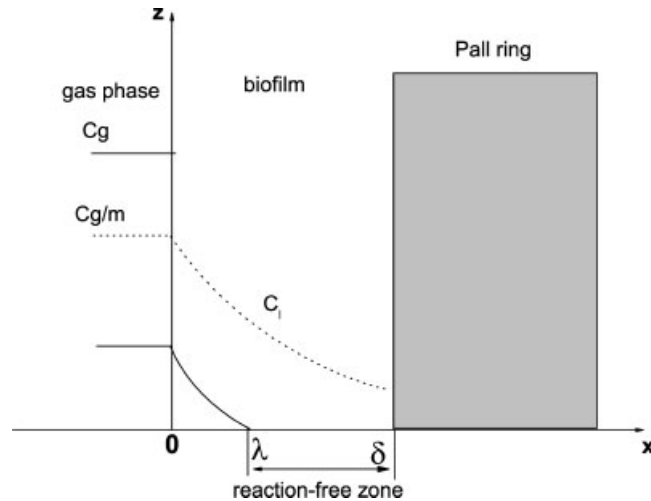
Figure 8. The biophysical model for the biotrickling filter; x is the distance into the biofilm, d is the biofilm thickness, l is the penetration thickness of H2S within the biofilm.

Mathematical Model Application

In order to predict the performance of a biofilter, some theoretical models have been developed based on the appropriate assumptions for the experimental conditions under consideration (Kennes and Veiga, 2001). In the present study, experimental and model data were compared. In addition to their simplicity, the equations used in the present study are based on a model that has proven to be adequate and suitable for describing the behavior of many biofilters (Delhomenie et al., 2002; Ottengraf and van den Oever, 1983).The following solutions can be derived from Ottengraf's model (Delhomenie et al., 2002):

(i) Under reaction limitation, the biofilm layer is fully active and H_2S concentration at the outlet of the bioreactor is a function of inlet concentration according to:

$$c_{g,out} = c_{g,in} - k_0 \frac{V}{Q}$$

Where $k_0 = k \delta A_s$

Then the elimination capacity in the reaction limitation regime can be expressed as:

$$EC = \frac{Q}{V}\left(c_{g,in} - c_{g,out}\right) = k_0$$

(ii) Under diffusion limitation, the biodegradation of the pollutant takes place only over part of the total biofilm thickness, namely l. In this case, the H2S concentration Cl vanishes at the position x equal to l. The H2S concentration at the outlet of the bioreactor is a function of inlet concentration according to:

$$\sqrt{c_{g,out}} = \sqrt{c_{g,in}} - k_1 \frac{V}{Q}$$

Where $k_1 = A_s \sqrt{\dfrac{k_0 D_{eff}}{2m}}$

Hence, the elimination capacity in the diffusion limitation regime takes the following form:

$$EC=IL\left[1-\left(1-k_1\sqrt{\frac{V}{Q*Il}}\right)^2\right]$$

Thus, the elimination capacity is an increasing function of the inlet load in the diffusion limitation regime, but constant and independent of IL in the reaction limitation regime, indicating that there is a critical inlet load value IL_{cri} at which the system switches from one regime to the other.

When the expressions given by Equations 10 and 12 are combined, one gets:

$$IL_{cri}=\frac{k}{4V}\left(\frac{k_0}{k_1}+\frac{k_1V}{Q}\right)^2$$

As a first step, the validity of the mathematical model needs to be proven for the present experimental study. For that purpose, the measurements of the inlet and outlet H2S concentrations in the gas phase were used to verify the theoretical relationships given by Equations 9 and 11. In the case of the reaction limitation regime, $C_{g,out}$ is plotted against $C_{g,in}$ as shown in Figure 9, whereas in the case of the diffusion limitation regime, $\sqrt{c_{g,out}}$ is plotted against $\sqrt{c_{g,in}}$ as in Figure 10. In both plots, the experimental data are adequately fitted with a straight line having a slope nearly equal to unity, in agreement with the theory. The slopes of the linear correlations were 0.86 and 1.09 with a regression coefficient equal to 0.95 and 0.82, respectively. Therefore, the present model is appropriate for describing the behavior of the biofilter under consideration. Moreover, the parameters K_0*V/Q and K_1*V/Q are estimated as 0.165 g/m^3 and 0.329 g$^{1/2}$/m$^{3/2}$, giving a value of 24 g/m^3/h and 47.9 g$^{1/2}$/m$^{3/2}$/h for K_0 and K_1, respectively. Figure 11 shows the experimental results along with the theoretical predictions of the elimination capacity versus the inlet load. Comparison between the mathematical model and experiments reveals that the laboratory measurements are in good agreement with the theory. The transition between the diffusion and reaction limitation regimes takes place at a critical inlet load of 25.1 g/m^3/h. Furthermore, the experimental data show a maximum elimination capacity of 22.78 g/m^3/h, in contrast to a value of 24 g/m^3/h predicted by the model, corresponding to a discrepancy of only 5%. For relatively smaller values of IL, the agreement between the theory and the experimental data is highly satisfactory. Hence, taking into consideration measurement errors, the theoretical model is suitable for the prediction of the biofiltration unit's performance.
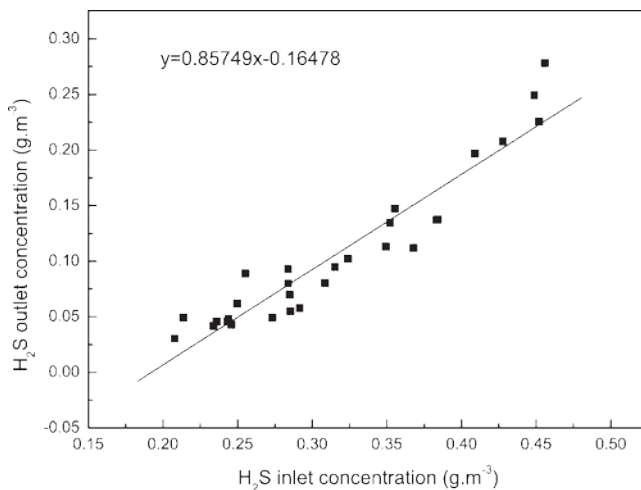

Figure 9. H2S outlet concentration versus H2S inlet concentration (reaction limitation regime).

CONCLUSIONS

The following conclusions can be drawn from the results presented in this study:

(1) The CO_2 concentration has no significant effect on the BTF's performance in the low range of H_2S concentrations, that is, <50 ppm. When the H_2S concentration is increased above this level, the CO_2 concentration seems to improve the BTF's performance at moderate CO_2 concentrations, below 1,309 ppm.

(2) The counter-current flow BTF removed 40%–80% of the H_2S load near the inlet section. Conversely, the removal in the different parts of the bioreactor were mostly linear in the co-current mode of operation.

(3) The pH of the trickling nutrient solution had pronounced effects on the BTF's performance for H_2S

removal. The H_2S removal efficiency increased as the pH of the nutrient feed increased in the pH range of 2.00–6.00. However, an opposite trend was observed for the pH between 6.00 and 7.00. The optimum pH for the autotrophic population was near 6.00.

(4) The experimental data showed that some of the H_2S was converted to sulfur instead of sulfate, without pH regulation. From the sulfur balance, around 60% of sulfide was transformed into sulfate. The SO_4^- in the trickling liquid can easily be precipitated by CaO and the generated $CaSO_4$ can be reused for reclamation of alkali soils. This post-treatment, together with the BTF, makes this technology a zero-waste discharge. Besides, the autotrophic biotrickling filter not only emits no extra CO_2, but also uses the CO_2 as the carbon source.

(5) The experimental data were compared with the predictions of a simple model. The model proved to be suitable for the description of the behavior of the BTF.The mathematical model predicted a maximum elimination capacity of 24 g $H_2S/m^3/h$, compared to an experimental value of 22.78 g $H_2S/m^3/h$.
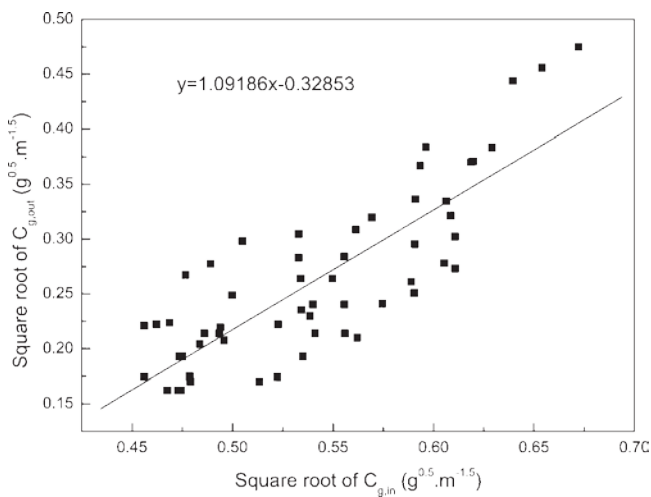

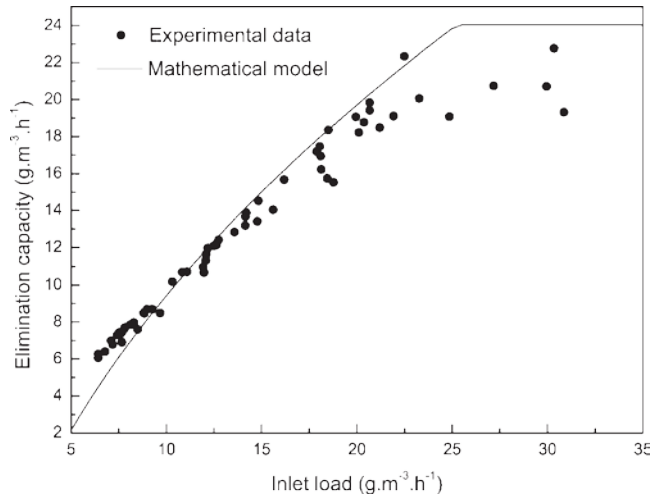Figure 10. Square root of H2S outlet concentration versus square root ofH2S inlet concentration (diffusion limitation regime).

Figure 11. Comparison of theoretical and experimental performance of the biotrickling filter.

NOMENCLATURE

a_t	total specific surface area of the packing (m_2/m_3)
a_w	wetted specific surface area of the packing (m_2/m_3)
c	c=2 if d_P<15 mm, otherwise c=5.23;
C_g	the concentration in the gas phase (g/m_3)
$C_{g,in}$	H_2S inlet concentration (g/m_3)
$C_{g,out}$	H_2S outlet concentrations (g/m_3)
C_l	H_2S liquid phase concentration (g/m_3)
D_{eff}	effective diffusion coefficient of H_2S in the biofilm (m_2/h)
D_G	gas diffusion coefficient (m_2/s)
D_L	liquid diffusion coefficient (m_2/s)
d_p	nominal packing diameter (m)
EC	elimination capacity of H_2S ($g/m_3/h$)
$E_r=1/a_t d_p$	packing efficiency number
$Fr_L=\frac{L_f^2 a_t}{\rho_L^2 g}$	liquid-phase Froude number
g	gravitational constant (m/s_2)
G_f	gas mass flux ($kg/m_2/s$)
H	height of the packed bed (m)
IL	inlet load of H_2S ($g/m_3/h$)
IL_{cri}	the critical inlet load of H_2S ($g/m_3/h$)
k_0	a zeroth-order reaction rate constant ($g/m_3/h$)
K_0	parameter of the model ($g/m_3/h$)
K_1	parameter of the model ($g_{1/2}/m_{3/2}/h$)
k_G	local gas-phase mass transfer coefficient (m/s)
K_G	the overall (gas-phase-based) mass transfer coefficient (m/s)
k_L	local liquid-phase mass transfer coefficient (m/s)
L_f	liquid mass flux ($kg/m_2/s$)
m	Henry's law constant expressed as the ratio of the mass concentration in the gas phase to that in the liquid phase (dimensionless)
$M_c=\sigma_c/\sigma_L$	wettability number
N	the substrate flux into the biolayer ($g/m_2/h$)
Q	the waste gas flow rate (m_3/h)
$R_G=G_f/a_t\mu_G$	gas-phase Reynolds number
$R_L=L_f/a_t\mu_L$	liquid-phase Reynolds number
$Sc_G=\mu_G/\rho_G D_G$	gas Schmidt number
$Sc_L=\mu_L/\rho_L D_L$	liquid Schmidt number
$Sh_L=\rho_L/\mu_L g$	liquid Sherwood number
U_g	the superficial velocity of air (m/h)
V	the volume of the biofilter bed (m_3)
$We_L=L_f^2/a_t\rho_L\sigma_L$	liquid-phase Weber number
x	the distance coordinate (m)
z	the height coordinate (m)

Greek Symbols

δ	the thickness of the biofilm (m)
λ	thickness of the active portion of the biofilm (m)
μ_G	gas dynamic viscosity (kg/m/s)
μ_L	liquid dynamic viscosity (kg/m/s)
ρ_G	density of the gas (kg/m3)
ρ_L	density of the liquid (kg/m3)
σ_c	surface tension of the packing material (kg/s2)
σ_L	surface tension of the liquid (kg/s2)

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