



## Removal of hydrogen sulfide by immobilized *Thiobacillus thiooparus* in a biotrickling filter packed with polyurethane foam

Martín Ramírez<sup>a,\*</sup>, José Manuel Gómez<sup>a</sup>, Germán Aroca<sup>b</sup>, Domingo Cantero<sup>a</sup>

<sup>a</sup>Department of Chemical Engineering, Food Technology and Environmental Technologies, Faculty of Sciences, University of Cádiz, CP 11510 Puerto Real, Cádiz, Spain

<sup>b</sup>School of Biochemical Engineering, P. Catholic University of Valparaíso, Av. Brasil No. 2147, Valparaíso, Chile

### ARTICLE INFO

#### Article history:

Received 29 January 2009

Received in revised form 11 May 2009

Accepted 14 May 2009

Available online 5 June 2009

#### Keywords:

Biotrickling filter  
Hydrogen sulfide  
*Thiobacillus thiooparus*  
Polyurethane foam

### ABSTRACT

In the work described here, a biotrickling filter with *Thiobacillus thiooparus* (ATCC 23645) immobilized on polyurethane foam is proposed for the removal of hydrogen sulfide contained in air. The effect of surface velocity of the recirculation medium (5.9–1.2 m/h), sulfate concentration inhibition (3.0–10.7 g/L), pH (6.0–8.2), empty bed residence time (EBRT) (150–11 s) for constant loads of 11.5 and 2.9 g S/m<sup>3</sup>/h, and pressure drop of the system were investigated.

The total amount of biomass immobilized on the carrier was  $8.2 \pm 1.3 \times 10^{10}$  cells/g. The optimal values of the operating variables were: pH between 7.0 and 7.5, surface velocity of 5.9 m/h and sulfate concentration below 5 g/L. The critical EC value was 14.9 g S/m<sup>3</sup>/h (removal efficiency of 99.8%) and the EC<sub>max</sub> was 55.0 g S/m<sup>3</sup>/h (removal efficiency of 79.8%) for an EBRT of 150 s. For loads of  $2.89 \pm 0.05$  and  $11.5 \pm 0.1$  g S/m<sup>3</sup>/h, the removal efficiency was higher than 99% for an EBRT over 90 s.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is a colourless, toxic and flammable gas that has a characteristic odour of rotten eggs.

Both natural and anthropogenic sources contribute to the total emission of hydrogen sulfide. Hydrogen sulfide occurs naturally in the gases from volcanoes, sulfur springs, undersea vents, swamps, stagnant bodies of water in crude petroleum and natural gas and as a product of the biological degradation of organic matter (Lomans et al., 2002). Considerable amounts of hydrogen sulfide are also emitted from industrial activities such as petroleum refining, pulp and paper manufacturing, wastewater treatment, food processing, livestock farming, and natural gas processing.

The concentrations of hydrogen sulfide in gas emissions are usually very dilute and traditional physical–chemical technologies such as incineration, adsorption or chemical scrubbing tend to be costly and are associated with their own pollution problems. As a result, based on the cost of the equipment and operation, biological treatment is believed to be the most economical option for the removal of hydrogen sulfide.

Many microorganisms have been used for H<sub>2</sub>S removal, principally *Acidithiobacillus* and *Thiobacillus*. In these groups are acidophilic bacteria such as *Acidithiobacillus thiooxidans* (Aroca et al., 2007; Sercu et al., 2005), neutrophilic bacteria such as *Thiobacillus novellus* (Cha et al., 1999), *Thiobacillus thiooparus* (Chung et al., 2000;

Cox and Deshusses, 2002; Oyarzún et al., 2003) and *Thiobacillus denitrificans* (Ma et al., 2006). Other bacteria such as *Pseudomonas putida* CH11 (Chung et al., 2001), *Hyphomicrobium* sp. (Sercu et al., 2005) and haloalkaliphilic consortium (Gonzalez-Sanchez et al., 2008) have been used for the removal of H<sub>2</sub>S.

The major biological reactors for the treatment of dilute gases are biofilters, biotrickling filters, and bioscrubbers. These systems differ in the presence or absence of a carrier material, the phase of the biomass (suspended or fixed), and the state of the liquid phase (flowing or stationary).

In biofilters the most commonly used carriers are compost and peat, although some authors add other materials such as perlite and/or wood chips in an effort to avoid compaction of the bed (Wani et al., 1999). Activated carbons have also been used to remove H<sub>2</sub>S and these give very good performance (Chung et al., 2005; Ma et al., 2006). The active carbon allows the combination of adsorption and biological degradation.

The use of bioscrubbers to remove H<sub>2</sub>S is very unusual because the solubility of H<sub>2</sub>S in water is very low.

In biotrickling filters the most commonly used carriers are propylene rings (Jin et al., 2005), ceramics (Ruokojärvi et al., 2001) and lava rocks (Chitwood et al., 1999). However, some investigations have been carried out with polyurethane foam (Gabriel et al., 2004; Gabriel and Deshusses, 2003), but using active sludge as inoculum.

The objective of the work described here was to study the feasibility of treating air contaminated with H<sub>2</sub>S using a biotrickling filter packed with cubes of polyurethane foam inoculated with

\* Corresponding author. Tel.: +34 956016474; fax: +34 956016411.  
E-mail address: [martin.ramirez@uca.es](mailto:martin.ramirez@uca.es) (M. Ramírez).

pure culture (*T. thioparus*). *T. thioparus* was selected because this bacteria can oxidize other sulfur compounds and the optimal pH is neutral and therefore the hydrogen sulfide solubility will be greater.

## 2. Methods

### 2.1. Microorganism and cultivation medium

A pure culture of *T. thioparus* (ATCC 23645) was obtained from the American Type Culture Collection. The composition of the ATCC290:S6 mineral medium was (in grams per litre): 1.2 g of  $\text{Na}_2\text{HPO}_4$ , 1.4 g of  $\text{KH}_2\text{PO}_4$ , 0.1 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 g of  $(\text{NH}_4)_2\text{SO}_4$ , 0.03 g of  $\text{CaCl}_2$ , 0.02 g of  $\text{FeCl}_3$ , 0.02 g of  $\text{MnSO}_4$  and 10.0 g of  $\text{Na}_2\text{S}_2\text{O}_3$  and the final pH was adjusted to 7.0 using 2.0 N NaOH. Prior to preparation of the medium the iron solution was filtered (0.22  $\mu\text{m}$  filter) and the basalt salt solutions were autoclaved at 121 °C for 20 min and cooled. The two solutions were then mixed together.

### 2.2. Characteristics of the carrier material

Polyurethane foam cubes of 1  $\text{cm}^3$  were used as the carrier. Polyurethane foam is an inert material with good scale-up possibilities and a very low commercial cost. The principal relevant properties of this material are density (20  $\text{kg}/\text{m}^3$ ) and porosity (96%).

### 2.3. Growth kinetics and inoculum preparation

The propagation of *T. thioparus* was carried out in a liquid culture (100 mL of ATCC290:S6 medium) using a rotary shaker at 150 rpm and 30 °C (optimal temperature). The cells were collected and concentrated by centrifugation at 15,000 rpm (4 °C for 15 min). The pellet was resuspended in 5 mL of fresh culture medium. A volume of 100 mL of ATCC290:S6 medium was inoculated with 2 mL of the resuspension of cells and used for growth and inoculation of the biotrickling filter.

### 2.4. Experimental configuration

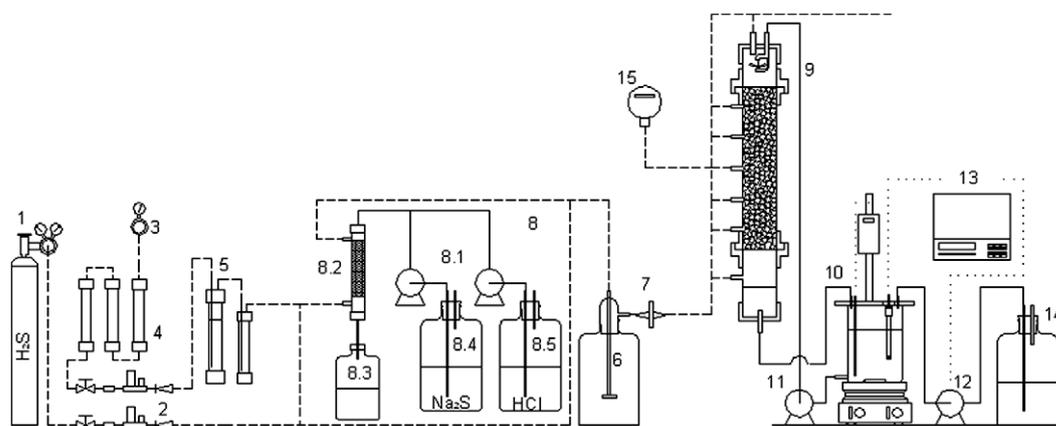
The experimental set up is illustrated in Fig. 1. A PVC tube with an external diameter of 63 mm and a thickness of 1.5 mm was used to build the biotrickling filter, which had a working volume of 1 L.

The air was supplied by an industrial compressor. Before entering the system, the air was passed through filters of silica gel, activated carbon and glass wool (diameter of 32 mm; packing height of 30 mm). The flow rates of each stream were regulated by mass flow rate controllers (Bronkhorst F-201C). A PVC desorption column packed with 5 mm glass spheres, with a packing height of 25 mm, was fed from the top of the column with two solutions of  $\text{Na}_2\text{S}$  and HCl to generate high hydrogen sulfide loads. An expansion tank with a capacity of 2.5 L was used to homogenize the input stream, and a 0.45  $\mu\text{m}$  filter was used at the end of the system to sterilise the input stream to the biofilter (Millipore Filter SLG05010). A solution of similar composition to ATCC290:S6 medium, but without the energy source (thiosulfate), was recirculated (centrifugal pump EHEIM 1046). The pH of the medium was controlled (only in the hydrogen sulfide gas removal study) by the addition of  $\text{NaHCO}_3$  (2.0 M) using a pH controller (Biocontroller ADI 1030, Applikon) and an electrode with a sleeve diaphragm (CRISON 5221). The temperature was maintained at 30 °C by heating the recirculation tank using a temperature controller (Heidolph EKT 3001) and an agitator (Agitamic-N agitator, J.P. Selecta).

### 2.5. Method for the immobilization and adaptation of *Thiobacillus thioparus*

The biotrickling filter was packed with 10 g of polyurethane foam in 1  $\text{cm}^3$  cubes and the initial volume of the packing was 1 L. The biomass was immobilized by attached growth (Cohen, 2001). A suspension of *T. thioparus* cells was fed onto the top of the column at a constant flow rate of 18.5 L/h (surface velocity of 8.6 m/h). The volume of the recirculation medium was 1 L, the temperature was controlled at 30 °C, and the medium was agitated at 200 rpm. In the first stage, 1 L of ATCC290:S6 medium was inoculated at 10% v/v with a culture of *T. thioparus* in the exponential growth phase. The culture was recirculated and the pH, thiosulfate concentration, sulfate concentration and biomass in suspension were monitored. When the thiosulfate concentration decreased to below 1.0 g/L, a total of 90% of the recirculation medium was drawn off in the first cycle (100% in subsequent cycles) and fresh medium was added. Successive cycles were performed until the maximum immobilized biomass was achieved.

In order to adapt the biofilm, the recirculation medium was replaced with a medium of identical formulation to ATCC290:S6 but without the energy source and, at the same time, the feed of



**Fig. 1.** Schematic diagram of the biotrickling filter. (1) Compressed gas cylinder ( $\text{H}_2\text{S}$ /synthetic air); (2) mass flow controllers; (3) air pressure regulator; (4) air prefilters; (5) humidifier and water trap; (6) expansion tank; (7) air filter; (8) system for  $\text{H}_2\text{S}$  generation by chemical reaction; (8.1) peristaltic pumps; (8.2) PVC column filled with glass spheres; (8.3) discharge tank; (8.4)  $\text{Na}_2\text{S}$  tank; (8.5) HCl tank; (9) biotrickling filter; (10) recirculation tank; (11) nutrient recirculation pump; (12) base addition pump; (13) biocontroller; (14)  $\text{NaHCO}_3$  tank; (15)  $\text{H}_2\text{S}$  sensor.

H<sub>2</sub>S in air was initiated. The empty bed residence time (EBRT) of the gas was 30 s, the surface velocity of the recirculation medium was 5.9 m/h, and the pH was controlled between 6.5 and 6.6.

### 2.6. Operation parameters effects

In the study of the operation parameters effects the initial values for the variables operations were as follows: surface velocity of the recirculation medium 7.9 m/h, EBRT 30 s, pH 7.0, inlet load  $11.5 \pm 0.1$  g S/m<sup>3</sup>/h and sulfate concentration < 5 g/L. The performance was monitoring during 112 days.

The experiments were carried out in the following sequence with the same biotrickling filter after the biofilm adaptation: effect of surface velocity of the recirculation medium, effect of pH, determination of the maximum elimination capacity, effect of EBRT and study of the pressure drop. The effect of the liquid velocity on the biotrickling filter performance was assessed varying the recirculation flow to obtain: 5.9, 3.5 and 1.2 m/h superficial velocities. Afterwards, the effect of sulfate concentration was evaluated from 3.0 to 10.0 g/L. Then the effect of pH on the removal efficiency was determined from 6.0 to 8.2. The maximum elimination capacity was obtained at EBRT of 150 s, and the effect of the EBRT from 150 to 11 s was studied at two H<sub>2</sub>S inlet loads of H<sub>2</sub>S of  $2.89 \pm 0.05$  g S/m<sup>3</sup>/h and  $11.5 \pm 0.1$  g S/m<sup>3</sup>/h.

### 2.7. Analytical techniques

A specific sensor from Crowcon (GASFLAG model, TXGARD-IS) was employed to analyse the H<sub>2</sub>S concentration in the gas phase. Sulfate concentration was analyzed by the turbidimetric method according to Standard Methods (APHA, 1998) and thiosulfate and H<sub>2</sub>S in the recirculation medium were determined by iodometric titration (Rodier, 1998). The quantity of immobilized biomass in the cells per gram of dry carrier was determined by counting the number of bacteria on a unit of the carrier material and dividing the total quantity of biomass by the weight of the polyurethane foam (Gomez et al., 2000).

The colony forming units (CFU) were measured by the Spread Plate method on ATCC290:S65-agar plates (1.5% w/v of agar) using serial 10-fold dilutions.

A U tube with a scale in mm was filled with water and this was used to measure the pressure drop.

## 3. Results and discussion

### 3.1. Growth kinetics

As can be observed in Fig. 2, the initial biomass concentration was  $1.6 \times 10^7$  cells/mL, with a growth maximum of  $5.7 \times 10^8$  cells/mL at 46 h. The substrate concentration decreased to zero at 70 h with a decrease in pH from 7.2 to 3.8. When the sulfate concentration was above 4.0 g/L, the elemental sulfur concentration increased (elemental sulfur measured by mass balance). A maximum specific growth rate ( $\mu$ ) of  $0.0971$  h<sup>-1</sup> with a linear regression coefficient of 0.993 was obtained.

### 3.2. Biomass immobilization

A total of 11 immobilization cycles were performed with a total duration of 310 h. The samples were taken in duplicate (A and B, Fig. 3) at the mid-point of the bed. The total quantity of biomass immobilized and substrate consumption rate in each cycle are shown in Fig. 3. The carrier material presented a wide variation in the number of bacteria immobilized. As a consequence of this heterogeneity in the immobilization, when the 4th cycle was completed it was decided to flood the column for 1 h before replacing the medium. The objective of this flooding was to homogenize the

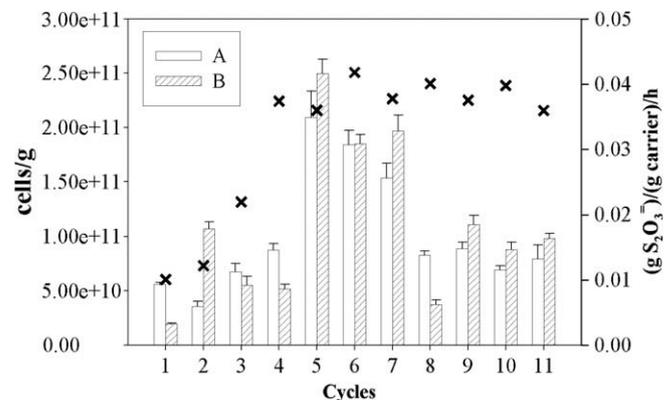


Fig. 3. Evolution of the immobilized biomass (A; B each sample) and consumption substrate rate in the immobilization process (x).

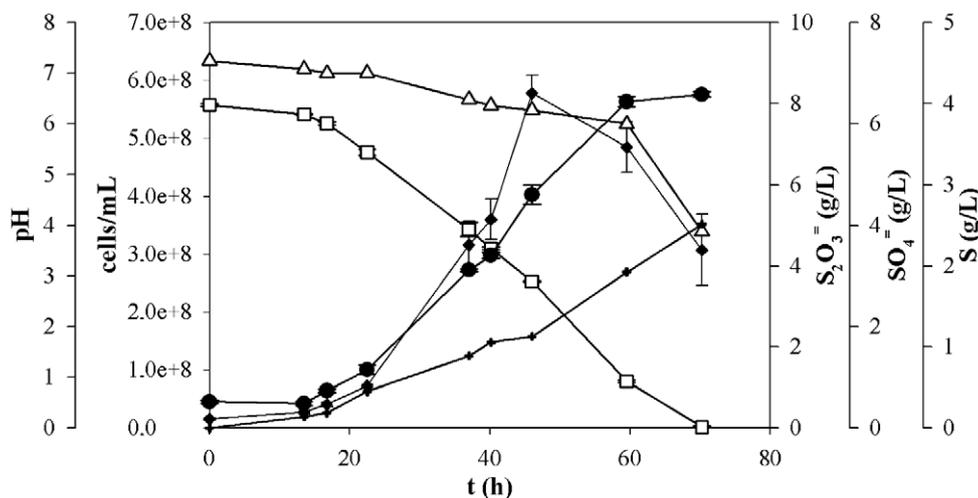


Fig. 2. Kinetic of *Thiobacillus thiooparus*. pH (Δ) and concentration of: biomass (◆), thiosulfate (□), sulfate (●) and sulfur (+) versus time.

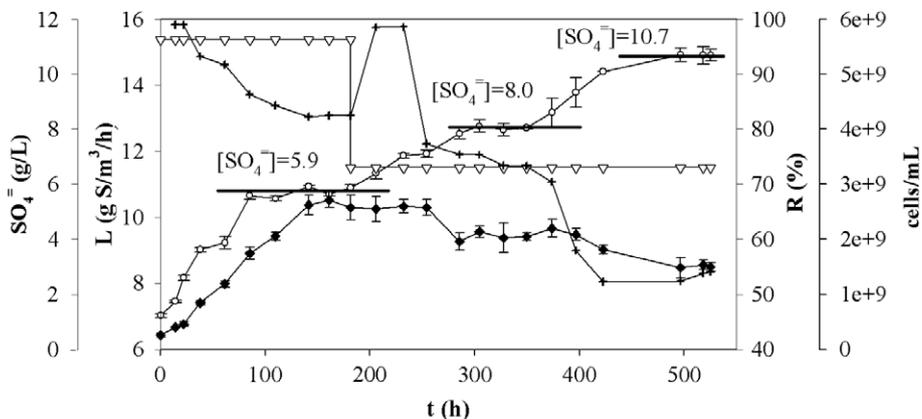


Fig. 4. Biofilm adaptation. Inlet load ( $\nabla$ ), removal efficiency (+) and concentrations of sulfate ( $\circ$ ) and biomass in the recirculation medium ( $\blacklozenge$ ) versus time.

system as a means of accelerating the immobilization process. This operation was repeated in the subsequent cycles.

The total quantity of biomass immobilized at the end of the cycles was  $8.1 \pm 1.3 \times 10^{10}$  cells/g dry carrier [ $1.1 \times 10^{10}$  CFU/g dry carrier].

In light of the results obtained, the substrate consumption rate could be taken as an indicator of the degree of immobilization and it could therefore be considered that, after 5 cycles (7–8 days), the maximum number of bacteria immobilized by this technique was reached.

### 3.3. Biofilm adaptation

High removal efficiency was achieved by replacing the energy source by  $H_2S$  from the initial time (Fig. 4). The biological removal of  $H_2S$  caused an increased in the sulfate concentration in the recirculation medium. When the sulfate concentration increased the  $H_2S$  removal efficiency decreased. The sulfate concentration increased to constant values of  $5.9 \pm 0.1$ ,  $8.0 \pm 0.2$  and  $10.7 \pm 0.3$  g/L. At these constant sulfate concentrations the removal efficiency did not decrease and it should therefore be considered that the total oxidation was to elemental sulfur, which is an intermediate oxidation product (Buisman et al., 1990). In fact, this behaviour is evident from Fig. 5 as the bacteria oxidized hydrogen sulfide to elemental sulfur within a short period and then the sulfate concentration increased.

Although the bacteria do achieve the oxidation of  $H_2S$  to sulfate, even at high sulfate concentrations, the removal efficiency decreased as the sulfate concentration increased. It was therefore very important to control the sulfate concentration in the recirculation

medium by replacing it with fresh medium (changed at 525 h). The biomass in the recirculation medium decreased with time.

### 3.4. Effect of surface velocity of the recirculation medium

The recirculation of the medium in a biotrickling filter enables the oxidation products to be removed easily. It also allows the thickness and humidity of the biofilm to be controlled and facilitates the absorption of the contaminant from the gas. The biotrickling filter was operated with a constant surface velocity of the recirculation medium of 5.9, 3.5 and 1.2 m/h (24 h for each surface velocity). The removal efficiency was  $83 \pm 1\%$ ,  $79 \pm 2\%$  and  $73 \pm 2\%$ , respectively. Thus the surface velocity was not a critical variable.

### 3.5. Effect of sulfate concentration

The recirculation medium was not changed during 12 days. In this period the sulfate concentration increased from  $3.0 \pm 0.1$  to  $10 \pm 0.2$  g/L and the removal efficiency decreased from  $78 \pm 4.9\%$  to  $54 \pm 2.8\%$ . This drop was more marked on decreasing the sulfate concentration from 5 g/L. As a result it was decided to use 5 g/L as the sulfate concentration limit for the subsequent experiments.

Koe and Yang (2000) maintained the sulfate level between 2 and 5 g/L; Jin et al. (2005) avoided concentrations above 1.9 g/L and Ruokojärvi et al. (2001) and Sercu et al. (2005) set a higher level of 15 g/L.

### 3.6. Effect of pH

The effect of pH on the  $H_2S$  removal was studied in the range from 6.0 to 8.2 (24 h for each value of pH). *T. thioparus* has an optimum growth at 28 °C at a pH between 6.6 and 7.2 (Kelly et al., 2005).  $H_2S$  can be removed from air by adsorption in the recirculation medium or by biological degradation. The elimination percentage due exclusively to the metabolism of the bacteria was calculated using the following equation, which was obtained from the  $H_2S$  mass balance of the system:

$$\begin{aligned} \text{Accumulation} &= \text{In} - \text{Out} \\ &\quad - \text{Reaction} (\text{Rate of } H_2S \text{ removal by biodegradation}) \end{aligned} \quad (1)$$

$$\text{Accumulation} = (A) = \frac{\Delta \bar{C}_L}{\Delta t} V_L \quad (2)$$

where  $\bar{C}_L$  (g S/m<sup>3</sup>) is the  $H_2S$  concentration in the recirculation medium and  $V_L$  (m<sup>3</sup>) is the volume of the recirculation medium.

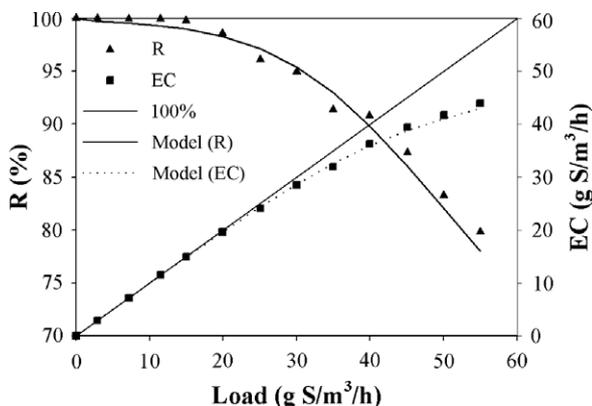


Fig. 5. Removal efficiency ( $\blacktriangle$ ) and elimination capacity ( $\blacksquare$ ) versus load. The lines represent the data predicted by the model.

$$\text{In} - \text{Out} = (I) - (O) = Q(\bar{C}_0 - \bar{C}_s) \quad (3)$$

Where  $Q$  ( $\text{m}^3/\text{h}$ ) is the gas flow rate,  $\bar{C}_0$  ( $\text{g S}/\text{m}^3$ ) is the inlet  $\text{H}_2\text{S}$  concentration and  $\bar{C}_s$  ( $\text{g S}/\text{m}^3$ ) is the outlet  $\text{H}_2\text{S}$  concentration.

Rearrangement and substitution into Eq. (1) gives the rate of  $\text{H}_2\text{S}$  removal by degradation:

$$(R) = (I) - (O) - (A) = Q(\bar{C}_0 - \bar{C}_s) - \frac{\Delta \bar{C}_L}{\Delta t} V_L \quad (4)$$

The biological removal efficiency will be the fraction of the  $\text{H}_2\text{S}$  removed by the biotrickling filter and this was expressed as a percentage:

$$(Rb) = \frac{(R)}{(E)} = \frac{Q(\bar{C}_0 - \bar{C}_s) - \frac{\Delta \bar{C}_L}{\Delta t} V_L}{\bar{C}_0 Q} \times 100 \quad (5)$$

For pH values greater than 7.5 the  $\text{H}_2\text{S}$  was accumulated in the recirculation medium as  $\text{HS}^-$  and the biological removal efficiency decreased. The values of biological removal efficiency was of  $88 \pm 2.0$ ,  $76 \pm 1.4$ ,  $72 \pm 1.8$ , and  $61 \pm 2.1$  for pH of 7.5, 8.2, 8.5 and 9.0, respectively.

### 3.7. Maximum elimination capacity

An experiment was performed at a constant EBRT of 150 s in order to minimize the mass transfer resistivity. The  $\text{H}_2\text{S}$  inlet load was increased from  $2.89 \pm 0.05$  to  $54.98 \pm 0.7$   $\text{g S}/\text{m}^3/\text{h}$  (Fig. 5). Each concentration was kept constant for at least 6 h. The steady-state was reached after 40 times the EBRT. The critical EC value was  $14.9$   $\text{g S}/\text{m}^3/\text{h}$  (removal efficiency of 99.8%) and the  $\text{EC}_{\text{max}}$  had a value of  $55.0$   $\text{g S}/\text{m}^3/\text{h}$  (removal efficiency of 79.8%). The experimental data can be modelled by the following equation (Cho et al., 1991; Chung et al., 2000; Wani et al., 1999):

$$\text{EC} = \frac{V_{\text{max}} \times C_{\text{In}}}{K_m + C_{\text{In}}} \quad (6)$$

where  $\text{EC} = [(C_0 - C_e) \times Q/V \times \beta]$  ( $\text{g S}/\text{m}^3/\text{h}$ ) is the elimination capacity,  $V_{\text{max}}$  ( $\text{g S}/\text{m}^3$ ) is the maximum elimination rate;  $K_m$  (ppmv) is the saturation constant;  $C_{\text{In}} = [C_0 - C_e]/\ln(C_0/C_e)$  (ppmv) is the log mean concentration;  $Q$  ( $\text{m}^3/\text{h}$ ) is the gas flow rate,  $C_0$  (ppmv) is the inlet  $\text{H}_2\text{S}$  concentration;  $C_e$  (ppmv) is the outlet  $\text{H}_2\text{S}$  concentration;  $V$  ( $\text{m}^3$ ) is the biofilter bed volume;  $\beta = [(M \times 10^{-3})/(22.4 \times (273 + T)/273)]$  is a conversion factor;  $M$  is the pollutant molecular weight and  $T$  the operating temperature ( $^{\circ}\text{C}$ ).

Rearrangement and multiplication by  $C_{\text{In}}$ :

$$\frac{C_{\text{In}}}{\text{EC}} = \frac{K_m}{V_{\text{max}}} + \frac{C_{\text{In}}}{V_{\text{max}}} \quad (7)$$

From the linear relationship between  $C_{\text{In}}/\text{EC}$  and  $C_{\text{In}}/V_{\text{max}}$ ,  $V_{\text{max}}$  and  $K_m$  were obtained from the slope and the intercept, respectively.

Plots of the elimination capacity and removal efficiency of the biotrickling filters versus inlet load are shown in Fig. 5. A good linear regression coefficient of 0.984 between experimental data

points and the predicted curves was found. The maximum elimination rate ( $V_{\text{max}}$ ) was  $56.7$   $\text{g S}/\text{m}^3/\text{h}$  and the saturation constant ( $K_m$ ) was  $295.7$  ppmv.

*T. thioparus* has been used in biotrickling filters and the following EC values were obtained;  $20$   $\text{g S}/\text{m}^3/\text{h}$  (91.3%) by Cox and Deshusses (2002) and  $14$   $\text{g S}/\text{m}^3/\text{h}$  (47%) by Aroca et al. (2007). Oyarzún et al. (2003) worked with a biofilter and obtained a maximum elimination capacity of  $55$   $\text{g S}/\text{m}^3/\text{h}$  (removal efficiency of 70%).

### 3.8. Effect of the EBRT

The effect that EBRT values of 150, 120, 90, 60, 30, 20 and 11 s had on  $\text{H}_2\text{S}$  removal was tested for two inlet loadings ( $2.89 \pm 0.05$  and  $11.50 \pm 0.15$   $\text{g S}/\text{m}^3/\text{h}$ ). Each EBRT was kept constant for at least 6 h. The  $\text{H}_2\text{S}$  concentration was measured throughout the bed in the sampling ports at bed heights of 0.060, 0.130, 0.205, 0.275 and 0.354 m. For these inlet loadings and EBRT values the inlet  $\text{H}_2\text{S}$  concentration ranged from  $7 \pm 0.2$  to  $94 \pm 1.1$  ppmv for  $2.89 \pm 0.05$   $\text{g S}/\text{m}^3/\text{h}$  and from  $27 \pm 0.4$  to  $372 \pm 3.7$  ppmv for  $11.50 \pm 0.15$   $\text{g S}/\text{m}^3/\text{h}$ .

From Eq. (6) the values of the constants  $V_{\text{max}}$  and  $K_m$  can be obtained for each biofilter height (Table 1).

In Eq. (6) a Monod-type substrate consumption rate is supposed:

$$(-r_b) = -\frac{V_{\text{max}} \times C}{K_m + C} \quad (8)$$

$V_{\text{max}}$  and  $K_m$  in Eq. (7) are intrinsic constants of the microorganism. Approximate values of these constants can be obtained in submerged culture when the substrate concentration is homogeneous. In this study the  $\text{H}_2\text{S}$  concentration measured did not correspond to the  $\text{H}_2\text{S}$  concentration in the biofilm and therefore the values of the constants obtained using Eq. (6) were apparent constants. The values of these constants are strongly influenced by the hydrodynamic conditions on the biotrickling filter.

$V_{\text{max}}$  and  $K_m$  decreased through the bed medium because the  $\text{H}_2\text{S}$  concentration decreased with increasing bed height and therefore the  $\text{H}_2\text{S}$  concentration gradient and the mass transfer also changed. The values of these constants allow us to predicted the hydrogen sulfide at any height of the bed.

The experimental data and the predicted curves are plotted in Fig. 6 for both loadings. For high EBRT the removal efficiency at different heights was very similar. So, the reduction in the removal efficiency as the flow rate increases, was not due to an insufficient contact time between  $\text{H}_2\text{S}$  and the biomass but is thought to be a problem related to gas diffusion and the low solubility of  $\text{H}_2\text{S}$  in the liquid phase. Sublette and Sylvester (1987) reported that  $\text{H}_2\text{S}$  can be metabolized by a pure culture of *Thiobacillus* within 1–2 s. Therefore, if the gas–liquid transfer can be improved the decrease in the removal efficiency will be less marked.

The biotrickling filter employed had some shortcomings in terms of hydrodynamic design and these lead to an increase in

**Table 1**  
Kinetic constants.

L	2.89 ( $\text{g S}/\text{m}^3/\text{h}$ )			11.50 ( $\text{g S}/\text{m}^3/\text{h}$ )		
	$V_{\text{max}}$ ( $\text{g S}/\text{m}^3/\text{h}$ )	$K_m$ (ppmv)	$r^2$	$V_{\text{max}}$ ( $\text{g S}/\text{m}^3/\text{h}$ )	$K_m$	$r^2$
0.060	172.4	369.2	0.986	100.7	179.2	0.992
0.130	14.9	23.6	0.987	71.7	168.8	0.998
0.205	12.8	22.2	0.967	50.6	125.2	0.994
0.275	5.2	5.2	0.899	37.0	90.0	0.990
0.354	3.5	2.4	0.992	34.5	95.8	0.989

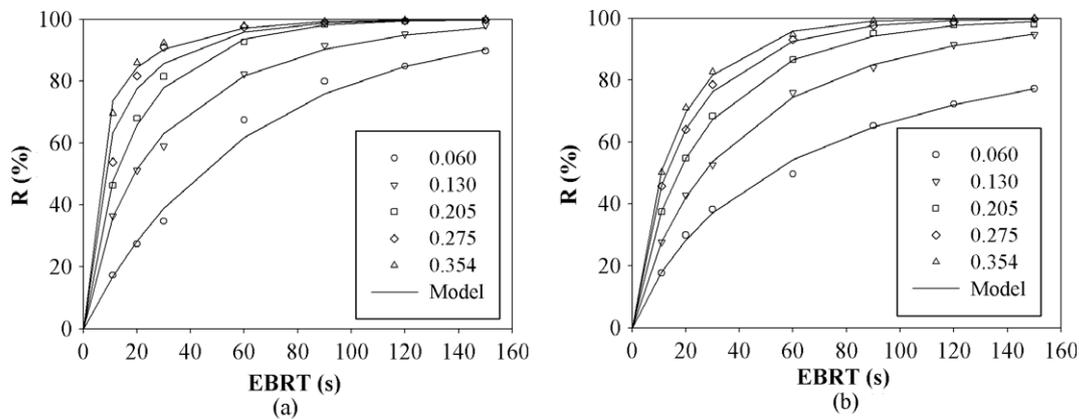


Fig. 6. Experimental data (icons) and data predicted by the model (lines) for loadings of 2.89 g S/m<sup>3</sup>/h (a) and 11.50 g S/m<sup>3</sup>/h (b).

mass transfer resistivity. Some of these shortcomings concerned the sprinkler system and the small diameter of the biotrickling filter.

### 3.9. Study of the pressure drop

The pressure drop in the biotrickling filter was measured before and after the immobilization in the study of the effect of the EBRT. The pressure drop increased from 5.65 to 6.50 cm H<sub>2</sub>O/m column for an EBRT of 11 s, and from 1.98 to 2.54 cm H<sub>2</sub>O/m column for an EBRT of 20 s for the system without and with biomass (biomass concentration in the middle of the bed of  $1.4 \pm 0.15 \times 10^{11}$  cells/g dry carrier), respectively.

As can be appreciated, the pressure drop per metre of column was increased slightly by having biomass present, according to the Ergun equation (1952):

$$\frac{\Delta P}{h \, v_g} = \alpha + \beta \, v_g \quad (9)$$

where  $\Delta P$  (Pa) is the pressure drop along the bed length,  $h$  (m) is the bed height,  $v_g$  (m/h) is the superficial gas velocity, and  $\alpha$  (Pa/h/m<sup>2</sup>) and  $\beta$  (Pa/h<sup>2</sup>/m<sup>3</sup>) the linear regression parameters.

Each surface velocity of the recirculation medium will have different values of the constants alpha and beta from the equation, since the Ergun equation is only applicable to the movement of a fluid phase (Ergun, 1952). Of the two constants (alpha and beta) the beta value had the greatest influence on the increase in the load loss since it is the slope of the line. The values found for the beta constant were 0.038 and 0.029 Pa/h<sup>2</sup>/m<sup>3</sup> for the biotrickling system with and without biomass, respectively (surface velocity of the recirculation medium of 5.9 m/h). The beta constant values obtained are comparatively much lower than those obtained with other carrier materials, as reported by Ramírez et al. (2003): 0.128, 1.642, 2.271, 4.167, 4.931 Pa/h<sup>2</sup>/m<sup>3</sup> for peanut shells, coconut husk, rice husk, maize stubble and bagasse, respectively.

## 4. Conclusions

The results obtained lead us to conclude that the parameters with the most influence on the performance of the biotrickling filter are the pH (optimal pH between 7.0 and 7.5) and the sulfate concentration (optimum < 5 g/L).

The critical EC value was 14.9 g S/m<sup>3</sup>/h (removal efficiency of 99.8%) and EC<sub>max</sub> was 55.0 g S/m<sup>3</sup>/h (removal efficiency of 79.8%) for an EBRT of 150 s. For loadings of  $2.89 \pm 0.05$  and  $11.5 \pm 0.1$  g S/m<sup>3</sup>/h, the removal efficiency was higher than 99% for an EBRT over 90 s.

The performance can be modelled by a Monod-type equation but the constants of the model should be considered apparent constants because these values are highly influenced by the hydrodynamic conditions.

Polyurethane foam has been shown to be a carrier material with a high capacity for the immobilization of *T. thioparus* and it also offers low resistance to the flow of gas, with the latter factor reducing the need for compression of the feed and the costs associated with this.

## Acknowledgement

The authors wish to thank the Ministry of Science and Technology for financing received under Project PPO2002-0217.

## References

- APHA, AWWA, WEF, 1998. Standard methods for the examination of water and wastewaters, 20th ed. American Public Health Association, American Water Works Associations, Water Environment Federation, Washington, DC.
- Aroca, G., Urrutia, H., Núñez, D., Oyarzún, P., Arancibia, A., Guerrero, K., 2007. Comparison on the removal of hydrogen sulfide in biotrickling filters inoculated with *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans*. Electron. J. Biotechnol. 10, 514–520.
- Buisman, C.J.N., Geraats, B.G., Ijspeert, P., Lettinga, G., 1990. Optimization of sulfur production in a biotechnological sulfide-removing reactor. Biotechnol. Bioeng. 35, 50–56.
- Chitwood, D.E., Devinny, J.S., Reynolds Jr., F.E., 1999. Evaluation of a two-stage biofilter for treatment of POTW waste air. Environ. Prog. 18, 212–221.
- Cha, J.M., Cha, W.S., Lee, J.H., 1999. Removal of organo-sulphur odor compounds by *Thiobacillus novellus* SRM, sulphur-oxidizing microorganisms. Process Biochem. 34, 659–665.
- Cho, K.S., Zhang, L., Hirai, M., Shoda, M., 1991. Removal characteristics of hydrogen sulphide and methanediol by *Thiobacillus sp.* isolated from peat in biological deodorization. J. Ferment. Bioeng. 71, 44–49.
- Chung, Y.C., Huang, C., Pan, J.R., Tseng, C.P., 2000. Biotreatment of H<sub>2</sub>S and NH<sub>3</sub>-containing waste gases by co-immobilized cells biofilter. Chemosphere 41, 329–336.
- Chung, Y.C., Huang, C., Tseng, C.P., 2001. Biological elimination of H<sub>2</sub>S and NH<sub>3</sub> from waste gases by biofilter packed with immobilized heterotrophic bacteria. Chemosphere 43, 1043–1050.
- Chung, Y.C., Li, Y.Y., Tseng, C.P., 2005. Removal of high concentration of NH<sub>3</sub> and coexistent H<sub>2</sub>S by biological activated carbon (BAC) biotrickling filter. Bioresour. Technol. 96, 1812–1820.
- Cohen, Y., 2001. Biofiltration – the treatment of fluids by microorganisms immobilized into the filter bedding material: a review. Bioresour. Technol. 77, 257–274.
- Cox, H.H.J., Deshusses, M.A., 2002. Co-treatment of H<sub>2</sub>S and toluene in a biotrickling filter. Chem. Eng. J. 87, 101–110.
- Ergun, S., 1952. Fluid flow through packed columns. Chem. Eng. Prog. 48, 89–94.
- Gabriel, D., Cox, H.H.J., Deshusses, M.A., 2004. Conversion of full-scale wet scrubbers to biotrickling filters for H<sub>2</sub>S control at publicly owned treatment works. J. Environ. Eng.-ASCE 130, 1110–1117.
- Gabriel, D., Deshusses, M.A., 2003. Retrofitting existing chemical scrubbers to biotrickling filters for H<sub>2</sub>S emission control. Proc. Natl. Acad. Sci. USA 100, 6308–6312.

- Gomez, J.M., Cantero, D., Webb, C., 2000. Immobilisation of *Thiobacillus ferrooxidans* cells on nickel alloy fiber for ferrous sulfate oxidation. *Appl. Microbiol. Biotechnol.* 54, 335–340.
- Gonzalez-Sanchez, A., Revah, S., Deshusses, M.A., 2008. Alkaline biofiltration of H<sub>2</sub>S odors. *Environ. Sci. Technol.* 42, 7398–7404.
- Jin, Y., Veiga, M.C., Kennes, C., 2005. Autotrophic deodorization of hydrogen sulfide in a biotrickling filter. *J. Chem. Technol. Biotechnol.* 80, 998–1004.
- Kelly, D.P., Wood, A.P., Stackebrandt, E., 2005. Genus II *Thiobacillus* Beijerinck 1904b, 597AL, second ed.. In: Brenner, D.J., Krieg, N.R., Staley, J.T., Garrity, G.M. (Eds.), *Bergey's Manual of Systematic Bacteriology*, vol. 2C Springer, New York, pp. 764–769.
- Koe, L.C.C., Yang, F., 2000. A bioscrubber for hydrogen sulfide removal. *Water Sci. Technol.* 41, 141–145.
- Lomans, B.P., Pol, A., Op den Camp, H.J., 2002. Microbial cycling of volatile organic sulfur compounds in anoxic environments. *Water Sci. Technol.* 45, 55–60.
- Ma, Y.L., Yang, B.L., Zhao, J.L., 2006. Removal of H<sub>2</sub>S by *Thiobacillus denitrificans* immobilized on different matrices. *Bioresour. Technol.* 97, 2041–2046.
- Oyazún, P., Arancibia, F., Canales, C., Aroca, G.E., 2003. Biofiltration of high concentration of hydrogen sulphide using *Thiobacillus thioparus*. *Process Biochem.* 39, 165–170.
- Ramírez, E.L., Corona, J.H., Dendooven, L., Rangel, P., Thalasso, F., 2003. Characterization of five agricultural by-products as potential biofilter carriers. *Bioresour. Technol.* 88, 259–263.
- Rodier, J., 1998. Análisis de las aguas. Aguas naturales, aguas residuales, agua de mar. Omega Ed., Barcelona, pp. 562–564.
- Ruokojärvi, A., Ruuskanen, J., Martikainen, P.J., Olkkonen, M., 2001. Oxidation of gas mixtures containing dimethyl sulfide, hydrogen sulfide, and methanethiol using a two-stage biotrickling filter. *J. Air Waste Manage.* 51, 11–16.
- Sercu, B., Van Langenhove, H., Nuñez, D., Aroca, G., Verstraete, W., 2005. Operational and microbiological aspects of a bioaugmented two-stage biotrickling filter removing hydrogen sulfide and dimethyl sulfide. *Biotechnol. Bioeng.* 90, 259–269.
- Sublette, K.L., Sylvester, N.D., 1987. Oxidation of hydrogen sulfide by *Thiobacillus denitrificans*: desulfurization of natural gas. *Biotechnol. Bioeng.* 29, 249–257.
- Wani, A.H., Lau, A.K., Branion, R.M.R., 1999. Biofiltration control of pulping odors – hydrogen sulfide: performance, macrokinetics and coexistence effects of organo-sulfur species. *J. Chem. Technol. Biotechnol.* 74, 9–16.