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Performance evaluation of packing materials in the removal of hydrogen sulphide in gas-phase biofilters: Polyurethane foam, sugarcane bagasse, and coconut fibre

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ABSTRACT

The main objective of this work was to investigate three packing materials (polyurethane foam, sugarcane bagasse, and coconut fibre) for biofiltration of a gaseous mixture containing hydrogen sulphide (H_2S). Mixed cultures were obtained from two sources, aerated submerged biofilters and activated sludge, and were utilised as inoculums. Biofilters reached 100% removal efficiency after two days of operation. The empty bed residence time was 49 s for each of the biofilters. The reactors were operated simultaneously, and the inlet concentrations of H_2S varied between 184 and 644 ppmv during the long-term continuous operation of the biofilters (100 days). Average removal efficiencies remained above 99.3%, taking into consideration the entire period of operation. Average elimination capacities reached by the biofilters packed with polyurethane foam, coconut fibre, and sugarcane bagasse were in the range of 17.8–66.6; 18.9–68.8, and 18.7–72.9 $g\,m^{-3}\,h^{-1}$, respectively. Finally, we concluded that the packing materials tested in this work are appropriate for the long-term biofiltration of hydrogen sulphide.

1. Introduction

It is widely known that hydrogen sulphide (H_2S) has high toxicity, corrosive action, and an undesirable smell. Its odour threshold is about 0.00047 ppmv, and the value of the Henry's Law constant for the water–hydrogen sulphide system at 25 °C is 545 atm mol^{-1} fraction [1].

Considerable amounts of H_2S are emitted from industrial activities such as food and rubber processing, leather manufacturing, petroleum refining, and pulp and paper manufacturing [2,3]. This compound can also be found in landfill biogas and is the principal odorous component in off-gases from wastewater collection and treatment facilities [4]. The concentration of hydrogen sulphide in biogas depends on the feedstock and varies between approximately 0.1 and 2% [5], which can cause many health and environmental problems.

To remove this highly toxic gas from gaseous emissions, many different physical and chemical processes have been established. These techniques can efficiently remove H_2S and provide sulphur recovery. However, the current treatment systems based on these conventional techniques to control emissions are energy intensive, have high chemical consumption, or have operational complexities [5,6]. To overcome these inconsistencies, biological treatment has been proposed as a convenient alternative for treating gaseous emissions containing hydrogen sulphide and reduced sulphur compounds [1,6]. There are three types of technology for biological treatment: biofilters, biotrickling filters and bioscrubbers. Although all these techniques operate using the same degradation mechanism, they differ in their design, parameter control, and flexibility of operation and in some operational parameters [7].

Biofiltration has been chosen by many researchers because of its peculiar characteristics. According to Ma et al. [8], this method has low capital and operating costs for its regeneration and recirculation and low energy requirements, with no need (in many cases) for additional chemicals or fuels. It also has an absence of residual products that require further treatment or disposal and, above all, public acceptance as an "environmentally friendly" process for reducing secondary pollution.

Biofiltration is an unconventional application of biotechnology in environmental engineering that, instead of transferring contaminants from one medium to another or using large amounts of energy to remove pollutants, utilises the efficiency of microorganisms to degrade the pollutants [3,9]. Many important factors,

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such as packing material conditions, microbial diversity, and nutrients, associated with the fluid dynamics conditions are crucial points that determine the performance of biofiltration systems [10,11].

Among these relevant factors for biofilter performance, the packing material is considered to be the "heart" of the biofiltration system, especially when it also provides the active biomass [12]. According to Maestre et al. [13] and Gaudin et al. [14], the main characteristics to consider in the selection of an appropriate packing material are its specific surface area, density, porosity, pH, water-holding capacity, buffering capacity, and elemental composition. A final factor affecting the practical application of biofilter media is cost; the less expensive the packing medium, the more desirable it is. For these reasons, the selection of an appropriate packing media is essential to the overall odour removal performance of a biofilter [10,11].

In previous reports, a variety of packing materials have been employed as carriers of microorganisms in biofilters, such as cell-laden Ca-alginate [2], mixtures of compost/perlite, hog fuel/perlite and compost/hog fuel/perlite [9,15], porous ceramics, calcinated cristobalite, calcinated and formed obsidian, granulated and calcinated soil [16], pig manure and sawdust [17], compost [18,19], peat [1], peat moss, wood chips, ceramic and granular activated carbon [8], pellet activated carbon [20], Na-alginate and polyvinyl alcohol [6], and synthetic media (UP20), pozzolan and pine bark [21].

Recently, there has been an increasing trend towards more efficient utilisation of agro-industrial residues, including sugarcane bagasse and coconut fibre, as packing materials [22–27]. Besides being inexpensive raw materials, the possibility of using a waste as a packing material in biofilters is particularly attractive from an environmental point of view [28].

Sugarcane bagasse is the main solid waste produced by the Brazilian agro-industry, which is the most extensive in the world, followed by India and Australia. Although utilised in sugar and ethanol factories as fuel for boilers, it is estimated that 8–10% of this waste is not reutilised, causing problems such as unpleasant smells and fermentation of the remaining sugar [29]. Additionally, Brazil is one of the ten largest coconut producers in the world, and its production of coconut fibre is greater than 7000 tons per year. It is estimated that 15–20% of the coconut fibre is not reutilised, but instead is deposited on the sides of roads or in open landfills [29].

Further, a literature survey revealed that only a few researchers have investigated sugarcane bagasse and coconut fibre as packing materials for the biofiltration of waste gas. Sugarcane bagasse was used as efficient packing material for biofilters in the treatment of ethanol [30], benzene [23], and benzene, toluene, ethyl benzene, and xylene [26]. Additionally, coconut fibre was used by Baquerizo et al. [25] and Gabriel et al. [27] in the biofiltration of ammonia. Encouraged by the good results obtained by the aforementioned authors with these materials in the treatment of other gaseous pollutants, we decided to test them in biofilters treating hydrogen sulphide.

Polyurethane foam, in turn, is a synthetic macroporous material, known to be an efficient carrier in biofiltration of toluene [31,32], paint spray vapors [33], and benzene, toluene, and xylene and methyl tert-butyl ether [34]. This synthetic material has been used as packing material in biotrickling filters treating reduced sulphur composts [35,36]. However, there are no studies in the literature in which these materials have been specifically employed to treat hydrogen sulphide in biofilters.

Finally, the objective of this work was to evaluate the performance of three packing materials (polyurethane foam, sugarcane bagasse, and coconut fibre) for the oxidation of high levels of hydrogen sulphide and for their ability to maintain constant removal efficiency in a long-term operation.

2. Materials and methods

2.1. Organisms and culture medium

The mixed culture was obtained from two sources: (a) a biofilter-aerated submerged unit (post-treatment of an up-flow anaerobic sludge blanket)—Wastewater Treatment Plant, Água Vermelha, São Carlos, São Paulo, Brazil, and (b) an activated sludge unit (secondary treatment)—Wastewater Treatment Plant, São Carlos Paper Industry, São Carlos, São Paulo, Brazil. Both cultures were acclimated to ATCC 290-S6 for about one week. The composition of the medium is as follows: $MnSO_4$, 0.02 g L^{-1}; KH_2PO_4, 1.2 g L^{-1}; $MgSO_4{\cdot}7H_2O$, 1.8 g L^{-1}; $(NH_4)_2SO_4$, 0.1 g L^{-1}; $CaCl_2$, 0.1 g L^{-1}; $FeCl_3$, 0.02 g L^{-1}; $Na_2S_2O_3$, 10 g L^{-1}.

After this preliminary acclimatization period, both cultures – which had been previously adapted to thiosulphate – were placed a single flask. Therefore, ATCC 290-S6 medium addition was maintained, but thiosulphate was replaced by hydrogen sulphide. This procedure, lasting a week, was aimed at promoting microorganism adaptation to the sulphur source to which it would be subsequently submitted in the biofilters.

The microorganism seeds were ready for inoculating into the biofilters. During the 15 days, morphologies such as coccus and rod shape bacteria were observed (with rod shape bacteria dominating—data not shown), which are the most common morphologies among the species of microorganisms used for the degradation of H_2S or other sulphur compounds [5]. For all continuous experiments, the same mineral medium was used. In general, the optimum pH for the growth of the mixed culture is 6–8 [10,11]. For this reason, the final pH was adjusted to approximately 7 by using 50 mg L^{-1} Na_2CO_3 in the thiosulphate media.

2.2. Packing material preparation

At the start of the procedure, the organic packing materials (sugarcane bagasse and coconut fibre) were collected, dried, and ground. After the grinding process, sugarcane bagasse and coconut fibre were washed with warm water (40 °C), rushing water, and deionised water. After the washing step, the organic media was dried again prior to the sieving process to obtain adequate particles for granulometry. Finally, sugarcane bagasse and coconut fibre were sterilised in an autoclave (temperature of 121 °C and pressure of 1 atm).

The polyurethane foam cubes were washed with warm water (40 °C) and rushing water. Shown in Fig. 1 is the support media at the end of the packing material preparation steps. In order to establish initial reference values for the packing materials, their pH was measured in water at a dry material weight/water volume ratio of 1:9 [37].

Table 1 presents some characteristics of the three packing materials.

2.3. Experimental set-up

The experimental equipment used in this work is shown in Fig. 2. Three biofilters were constructed with acrylic tubing of 0.052 m diameter (D) and 1.0 m length (L) (working volume of 1.8 L). The

Table 1
Characteristics of the three packing materials.

	Size (mm)	Density (kg m^{-3})	Porosity	pH
Polyurethane foam	5.0 × 5.0	23	0.85	7.0
Sugarcane bagasse	2.5–5.6	45	0.64	6.0
Coconut fibre	2.5–5.6	67	0.84	6.5

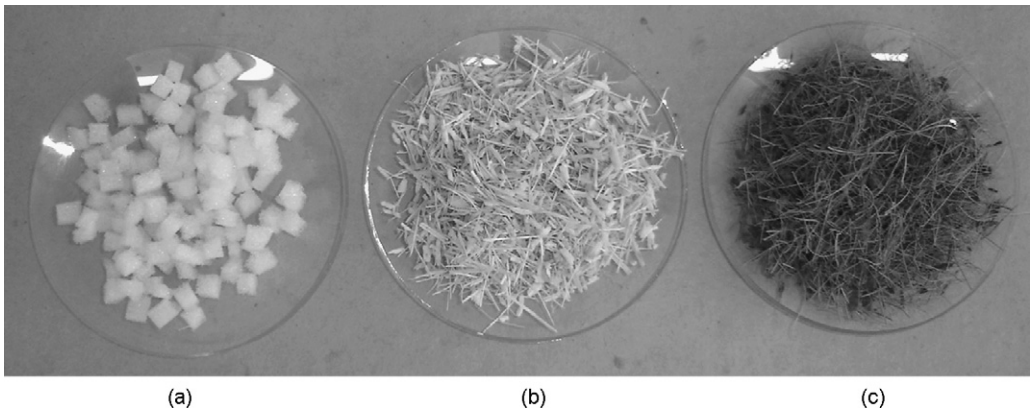

Fig. 1. Packing materials before the beginning of the operating period: (a) polyurethane foam; (b) sugarcane bagasse, and (c) coconut fibre.

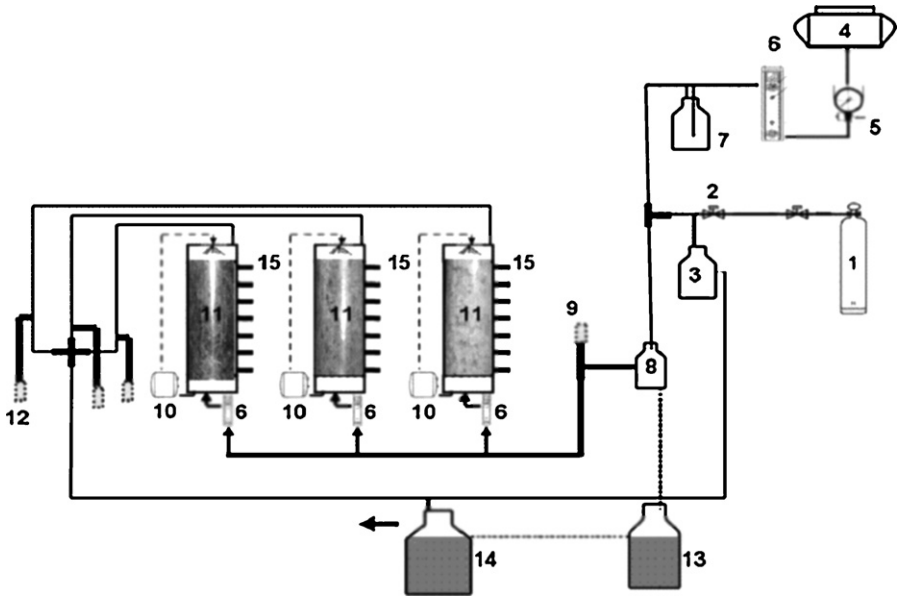

Fig. 2. Experimental set-up. (1) H_2S cylinder, (2) needle valve, (3) bubble counter, (4) air compressor, (5) manometer, (6) air flow meter, (7) humidifier, (8) mixing chamber, (9) inlet sampling port, (10) recirculation pumps, (11) biofilters, (12) outlet sampling port, (13) microorganism tank, (14) NaOH tank, and (15) sampling ports.

masses of each packing material used in the biofilters were defined according to their density.

The first biofilter was filled with 37.1 g of polyurethane foam (L = 0.88 m), the second biofilter was packed with 72.6 g of sugarcane bagasse (L = 0.84 m), and the third biofilter was filled with 108.1 g of coconut fibre (L = 0.84 m). First, the packing materials were saturated with previously enriched sludge, and then, the biofilters were carefully packed to avoid air channelling that results from variations in permeability due to spatial variations in the moisture content and medium characteristics. A sieve plate was located at the bottom and the top of the columns to support the packing materials and to ensure homogeneous distribution of the inlet gas across the face of the bed. Seven sampling ports were installed every 12 cm in the columns in the wall of biofilter (L/D of 3, 5, 7, 9, 11, 13, and 15) to allow for the verification of the H_2S removal along the length. The operating conditions of the biofilters are summarised in Table 2.

Pure H_2S gas was supplied from a gas cylinder, and fresh air was supplied by a compressor. The flow rates of each stream were measured by calibrated flowmeters. Prior to mixing with H_2S, the air was bubbled through distilled water to humidify the inlet stream. This was done because a humidity of less than 90–95% can result in a rapid loss of biodegradation activity in the biofilter [24]. The relative humidity of the inlet air was maintained

Table 2
Operating conditions of the biofilters.

Parameter	Polyurethane foam	Sugarcane bagasse	Coconut fibre
Bulk density (kg m^{-3})	19	40	60
Flow rate (m^3 h^{-1})	0.13	0.13	0.13
Bed porosity	0.31	0.21	0.27
Empty bed retention time (s)	49	49	49
Superficial loading rate (m^3 m^{-2} h^{-1})	61	61	61
Volumetric loading rate (h^{-1})	74	73	74
Air/dilution flow rate (m^3 h^{-1})	0.45	0.45	0.45
Superficial velocity (m s^{-1})	0,017	0.017	0.017

at a constant level of 97–100% throughout the experiments. The humidified air and the H_2S gas were blended in a mixing chamber before being fed to the biofilters. A fraction of the gas mixture influent was fed into a tank containing the mixed culture used for inoculation of the biofilter. The flow rates were controlled by stainless steel needle valves and measured by previously calibrated flowmeters to obtain the desired H_2S inlet concentrations in the biofilters. The biofilters were continuously operated at room temperature ($28 \pm 2\,^{\circ}C$). Finally, the long-term operation was divided into four stages, according to the average hydrogen sulphide inlet concentration, as follows: 185, 328, 519, and 646 ppmv, in that order.

2.4. Moisture content, nutrient, and pH control

The moisture content of the three biofilters was maintained at the desired level (60–70%) by distributing the nutrient solution, ATCC 290-S6 (without thiosulphate), by means of a spray nozzle at the top of the packing material. The leachate (volume ~5 mL) was collected at the bottom of the biofilters, recirculated to the top by peristaltic pumps operating in a closed circuit and periodically switched on by a timer, and supplemented with fresh nutrient solution once a day. If the pH was out of the range of 6–8, a bicarbonate solution was also added once a day to keep the pH in a proper range for the microorganisms.

2.5. Pressure drop

The pressure drop and superficial gas velocity are important parameters in determining the operating costs of biofilters. Tests were carried out on these parameters under abiotic conditions. The pressure drop tests were conducted using the same configuration shown in Fig. 2. The pressure points were installed at the bottom and top of the columns to allow the effective packing length to be utilised for pressure drop measurements. A water differential manometer was used to measure the pressure drop across the packing materials at various air flow rates.

To this end the Ergum equation [38], which describes load loss behavior in a bed with irregular-shaped particles (besides being easily found in studies about biofilters), was chosen:

$$\frac{\Delta P}{Lv} = \alpha + \beta v \tag{1}$$

where ΔP is the pressure drop along the bed length (Pa), L is the working length (m), v is the superficial gas velocity ($m\,s^{-1}$), and α ($Pa\,s^{-1}\,m^{-2}$) and β ($Pa\,s^{-2}\,m^{-3}$) the linear regression parameters.

2.6. Adsorption tests

Adsorption can be defined as a process by which molecules diffuse from the bulk of a fluid (gas) to the surface of a solid adsorbent and form a distinct adsorbed phase [39]. The average concentration of H_2S in the influent in the adsorption tests was 230 ppmv, which is in the range (50–330 ppmv) studied by Barona et al. [12]. Additionally, the average concentration in the influent used in this test was similar to the average concentration in the influent applied during the first stage of the biofilter continuous operating period.

The H_2S adsorption tests were conducted using the same configuration shown in Fig. 2, as well as the same biofilter configuration and operating conditions shown in Table 1. The adsorption tests were carried out under abiotic conditions at 25–30 °C, and the columns were packed with dried packing materials, polyurethane foam (37.1 g), sugarcane bagasse (72.6 g), and coconut fibre (108.1 g).

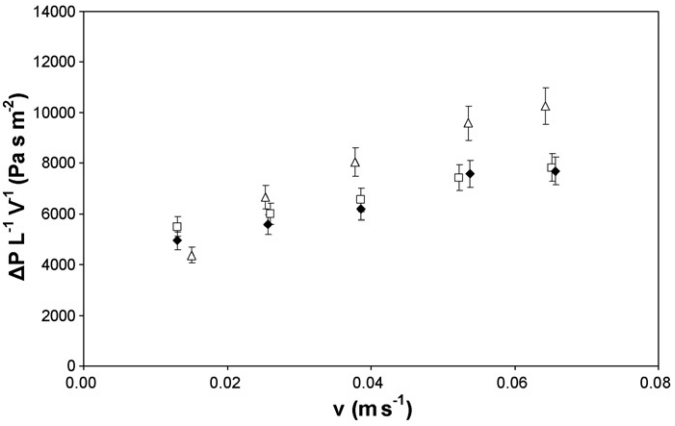

Fig. 3. Average pressure drop values for polyurethane foam (♦), sugarcane bagasse (□), and coconut fibre (Δ).

2.7. Analytical methods

Hydrogen sulphide was analysed using a method based on the methylene blue method [40]. An alteration was made that consists of bubbling H_2S in a flask containing 50 mL of sodium hydroxide (pH approximately equals to 13) because the gas is very stable in this solution. The pH of each biofilter medium was measured using the potentiometer method [40]. Microscope analyses were carried out using a scanning electron microscope (SEM) (Digital Scanning Microscope DSM 960, ZEISS) at the end of the long-term operating period to observe the presence of morphologies that oxidise hydrogen sulphide, such as the rod and coccus shaped bacteria. Elemental analysis was conducted using energy dispersive X-ray analysis (EDX) after the support medium was dried at 105 °C for 12 h.

2.8. Definitions

The performance of biofilters will be reported in this paper as the loading rate (LR) ($g\,m^{-3}\,h$), and the removal of a certain mass of pollutant will be represented by the elimination capacity (EC) ($g\,m^{-3}\,h$), which is usually normalised by the volume of the biofilters. The efficiencies of the reactors are commonly expressed in terms of the removal efficiency (RE) (%). These terms are defined in Eqs. (2)–(4), as follows:

$$\mathrm{LR} = \frac{C_{in}Q}{V} \tag{2}$$

$$\mathrm{EC} = \frac{(C_{in} - C_{out})Q}{V} \tag{3}$$

$$\mathrm{RE} = \frac{(C_{in} - C_{out})}{C_{in}}100 \tag{4}$$

where C_{in} is the influent concentration ($g\,m^{-3}$), C_{out} is the effluent concentration ($g\,m^{-3}$), Q is the flow rate ($m^3\,h^{-1}$), and V is the volume of the filter bed (m^3).

3. Results and discussion

3.1. Pressure drop

The pressure drop caused by the system was directly proportional to the increase in the superficial velocity of gas, and the results reveal that pressure data fit Ergunís equation fairly well. The linear correlations were 0.983, 0.994, and 0.979 for the biofilters filled with polyurethane foam, sugarcane bagasse, and coconut fibre, respectively (Fig. 3). Different degrees of increases in the pressure drop were observed for the different packing materials.

Table 3
A comparison of pressure drop results obtained from the literature to those obtained in this work.

Author	Packing material	$\Delta P/L$ (Pa m^{-1})	v (m s^{-1})
Yang and Allen [41]	Compost: <1.2 mm, 1.2–2.4 mm, 2.4–3.4 mm, 3.4–12 mm, >12 mm	0–3500	0.02–0.28
Wu et al. [42]	Peat: <10 mm, >10 mm	98	0.02
Chung et al. [43]	Cell-laden Ca-alginate beads: 3 mm	74–177	0.004–0.018
Elias et al. [17]	Pig manure + sawdust: 6.5 mm × 10.0 mm	15–460	0.028–0.056
Ramírez-López et al. [24]	Sugarcane bagasse	91–2200	0.004–0.039
	Coconut shells	175–620	0.017–0.039
Dumont et al. [21]	Synthetic media (UP20): 7 mm × 15 mm	8–168	0.02–0.14
	Pozzolan: 5–10 mm	5–100	
	Pine bark	15–370	
This work	Polyurethane foam: 5.0 mm × 5.0 mm	40–504	0.006–0.064
	Sugarcane bagasse: 2.5–5.6 mm	40–510	
	Coconut fibre: 2.5–5.6 mm	20–550	

The values found for the β constant were 55, 813, 46,708 and 114,775 Pa s^{-2} m^{-3} (0.0043, 0.0036 and 0.0089 Pa h^{-2} m^{-3}) for biofilters packed with polyurethane foam, sugarcane bagasse, and coconut fibre, respectively. The β constant values obtained are comparatively much lower than those than obtained for peanut shells, bagasse, maize stubble, rice husk and coconut husk: 0.055, 0.077, 0.057, 0.054 and 0.020 Pa h^{-2} m^{-3}, respectively (values obtained from Fig. 1 of Ramírez-López et al. [24]).

According to Fig. 3, the biofilter packed with coconut fibre provided the greatest pressure drop, with an average value of 550 Pa m^{-1} for a velocity of 0.064 m s^{-1}. For this velocity, the average pressure drop for the biofilters filled with sugarcane bagasse and polyurethane foam reached 510 Pa m^{-1}.

According to Yang and Allen [41], the pressure drop depends on the biofilter packing procedure. If the packing density is high, the pressure drop is also high for the same gas superficial velocity. The density of the packing of coconut fibre (60 kg m^{-3}) is the largest of the three materials tested, which may explain the higher values of load loss occurring with this material.

Ramírez-López et al. [24] studied the pressure drop of five agricultural packing materials—peanut shells, rice husks, coconut shells, maize stubble, and sugarcane bagasse. The authors showed that, for all velocities studied, the coconut shell presented a lower pressure drop than sugarcane bagasse. For a superficial velocity of 0.017 m s^{-1}, the sugarcane bagasse pressure drop was 587 Pa m^{-1}. On the other hand, for the same velocity, the coconut shells presented a pressure drop of 175 Pa m^{-1}.

The pressure drop values shown in Fig. 3 are not consistent with those presented by Ramírez-López et al. [24] because, for our experiments, the coconut fibre showed pressure drop values that were higher than those for sugarcane bagasse. This can be explained by the fact that we observed fibres of several sizes in the coconut fibre packings, despite the screening process. These, in turn, tended to fill the voids between the fibres, which would have provided this increase in the loss of the fibre load. After packing of beds, test results indicated bed porosities of 0.31, 0.21, and 0.27 for polyurethane foam, coconut fibre, and sugarcane bagasse, respectively (Table 2). The lowest bed porosity – observed in the bed packed with coconut fibre – may explain the highest values of load loss it provided as a function of the experimental procedures.

For the superficial velocities applied during the operating period (0.017 m s^{-1}), the $\Delta P/L$ values were around 94, 97, and 98 Pa m^{-1} for the beds of polyurethane foam, sugarcane bagasse, and coconut fibre, respectively. The pressure drop after long-term operation increased 40%, 20% and 20% for an empty bed residence time of 49 s for the biofilter packed with coconut fibre, sugarcane bagasse and polyurethane foam, respectively.

For the sake of comparison, a summary of pressure drop values obtained in the literature is shown in Table 3.

3.2. Adsorption

According to Fig. 4, the saturation achievement time for the packing materials is very short, with one hour for polyurethane foam and coconut fibre and two hours for sugarcane bagasse. This result means that the adsorption effects are quite irrelevant in long-term operation.

Fig. 4 shows that both the organic and synthetic materials used in our tests have a poor adsorption potential, as compared to the activated carbon studied by Barona et al. [12], if we consider long-term operation. Thus, this test was important to prove that the adsorption interference was quite irrelevant and that the biochemical reactions were effective in long-term operation.

3.3. Performance of the biofilters during long-term operation

As can been seen in Fig. 5, during the long-term continuous operation of the biofilters, the inlet concentrations of H_2S varied in four stages according to the average sulphide inlet concentration, as follows: 185, 328, 519, and 646 ppmv.

A start-up period of only two days was used in all biofilters, even for the applied average initial concentrations of 150 ppmv. On the third operating day, the biofilters removed 100% of the applied influent concentration. In view of the fact that the biomass had been previously adapted to hydrogen sulphide (Section 2.1) before being inoculated in the biofilters, we believe that the obtained stability

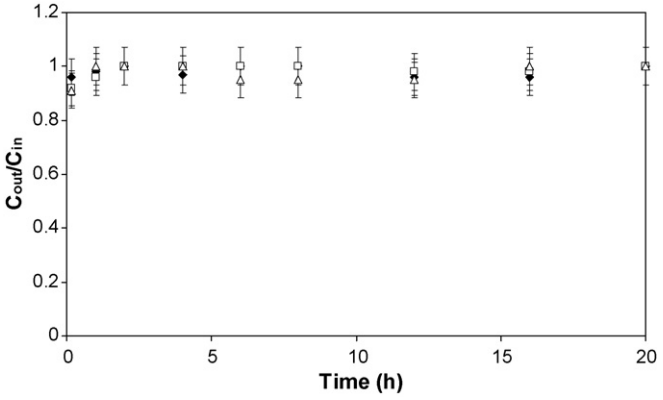

Fig. 4. Adsorption test data for polyurethane foam (♦), sugarcane bagasse (□), and coconut fibre (Δ).

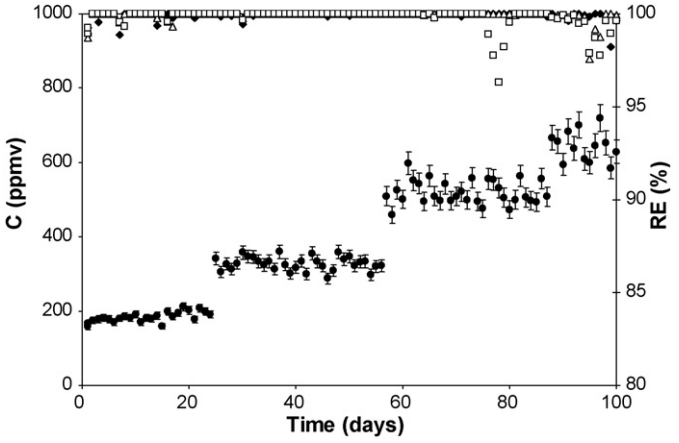

Fig. 5. General view of the long-term operating period in terms of influent H_2S concentrations (●) and removal efficiencies: polyurethane foam (♦), sugarcane bagasse (□), and coconut fibre (Δ) effluent concentrations.

(100% removal efficiency) derives from biological activity alone. Hartikainen et al. [44,45] observed similar results utilising pure culture immobilised on peat, and Shojaosadati and Elyasi [46] also observed efficiencies above 99%, although these were observed a few hours after the start-up of the system (Fig. 6).

Both the average concentration and the removal efficiencies of the operating stage I were close to those verified by Duan et al. [20] and Dumont et al. [21], who applied concentrations in the range of 10–125 ppmv and obtained removal efficiencies of 94%. Kim et al. [6] observed that, for a range of 10–130 ppmv, the removal efficiencies varied between 45 and 100% during the different operating stages.

In operating stage II, the same performance was observed in the biofilters. The work by Oyarzún et al. [1], which used peat inoculated with *Thiobacillus thioparus* (ATCC 23645) as a solid support, also achieved removal efficiencies of 100% when the biofilters were under concentrations of 335 ppmv for a considerably high empty bed retention time of 2 min.

During the operating stage III, the biofilter filled with sugarcane bagasse presented a decrease in efficiency, especially on the 78th day. However, on the 81st day, an efficiency of 100% was observed. No abrupt oscillations concerning the inlet concentration, the flow rate, or the pH were verified in that biofilter. On the contrary, the biofilters filled with polyurethane foam and coconut fibre were able to maintain the performance verified for stages I and II with an efficiency close to 100%.

In operating stage IV, H_2S removal rates for all of the biofilters were similar to those provided in the previous phases, even for peaks higher than 700 ppmv. On the 99th day of operation the biofilter packed with polyurethane foam performed at its lowest efficiency level (98.2% removal); on the 95th day the biofilter packed with coconut fibre performed at 97.6%; and the biofilter packed with sugarcane bagasse removed 97.7% of sulphide on the 97th day. The work by Park et al. [47], which used pure culture immobilised on calcium alginate, noted that, when the concentration increased from 520 to 680 ppmv, the removal efficiency decreased from 100% to 68%.

In conclusion, the most commonly noted practical problems associated with this method of waste gas treatment are sudden fluctuations in inlet concentration and flow rate [17]. The fact is that a low fluctuating inlet concentration was repeatedly observed during the 100 days of running time, and the biofilters were robust enough to consistently remove incoming H_2S with increasing average concentrations of 185–646 ppmv.

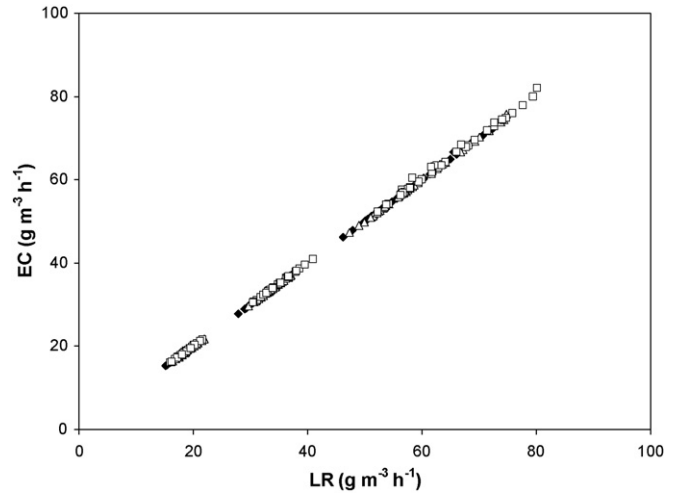

Fig. 6. Elimination capacity as a function of the loading rate for polyurethane foam (♦), sugarcane bagasse (□), and coconut fibre (Δ).

3.4. Loading rate and elimination capacity

The pollutant loading rate is an important variable in a biofilter design [10,11]. In this study, the loading rate changes were the result of fluctuations in the H_2S inlet concentration. The empty bed retention time did not vary.

During the research, the maximum elimination capacities obtained were 74, 79, and 75 g m^{-3} h^{-1} and averages of 66, 73, and 68 g m^{-3} h^{-1} for the biofilters packed with polyurethane foam, sugarcane bagasse, and coconut fibre, respectively. These differences in elimination capacity, both in terms of maximum values and averages, derive mainly from different effective bed heights verified in all of the three systems due to decreasing effective bed height, especially in the sugarcane bagasse biofilter (7 cm). The decrease in the coconut-fibre and polyurethane foam biofilters was 3 cm. Hence, because sugarcane bagasse biofilter displayed the greatest decrease in effective height and, consequently, the volume available in it for gas flowing decreased, which, in turn, caused the applied loading rates to increase, and, because it performed well, caused its elimination capacity to increase as these parameters are normalised by biofilter volume.

According to Elias et al. [17], values of 45 g m^{-3} h^{-1} are the rates of many industrial emissions. Since the biofilters could eliminate all loading rates applied, the resulting elimination capacities were the same regardless of the loading applied (maximum of 80 g m^{-3} h^{-1}). These capacities are higher than those obtained in some studies that used peat as a packing material, which is the most traditional material used in biofilter systems. The capacities found in various studies are as follows: Hirai et al. [48] obtained 25 g m^{-3} h^{-1}, Zhang et al. [49] obtained 15–30 g m^{-3} h^{-1} using different inoculums, Cho et al. [50] obtained 50 g m^{-3} h^{-1}, and Oyarzún et al. [1] obtained a maximum EC of 55 g m^{-3} h^{-1}.),

It is important to note that that the level indicating maximum elimination capacity was not achieved by the systems in our study. In other words, no applied loading rates (approximately 80 g m^{-3} h^{-1}) led to the breakthrough of the biofilters.

Christen et al. [30], using *C. utilis* and sugarcane bagasse, observed that the removal efficiency was greatly influenced by the pollutant load (ethanol). They observed a removal efficiency of 100% with a load of 93.7 g m^{-3} h^{-1}, but the elimination of higher loads was not sustained. Our results, however, showed sugarcane bagasse to be an excellent packing medium for hydrogen sulphide biofiltration, providing high removal efficiencies during long-term operation of biofilters, even under high loads.

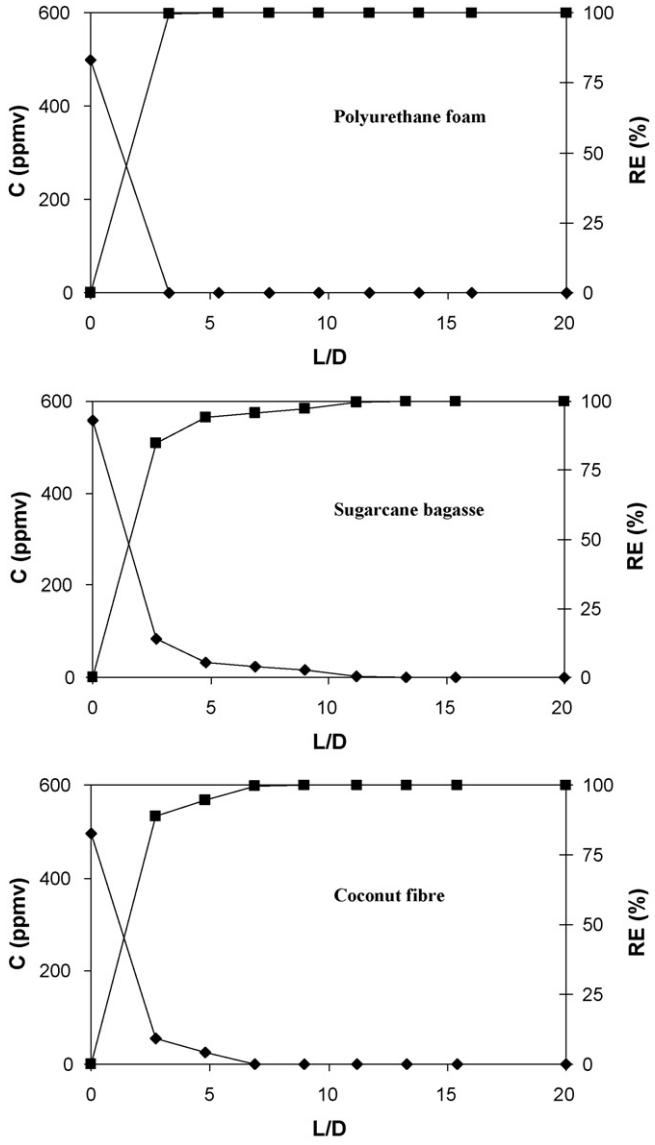

Fig. 7. Spatial degradation profile in the biofilters filled with polyurethane foam (C_{in} = 499 ppmv), sugarcane bagasse (C_{in} = 559 ppmv), and coconut fibre (C_{in} = 496 ppmv).

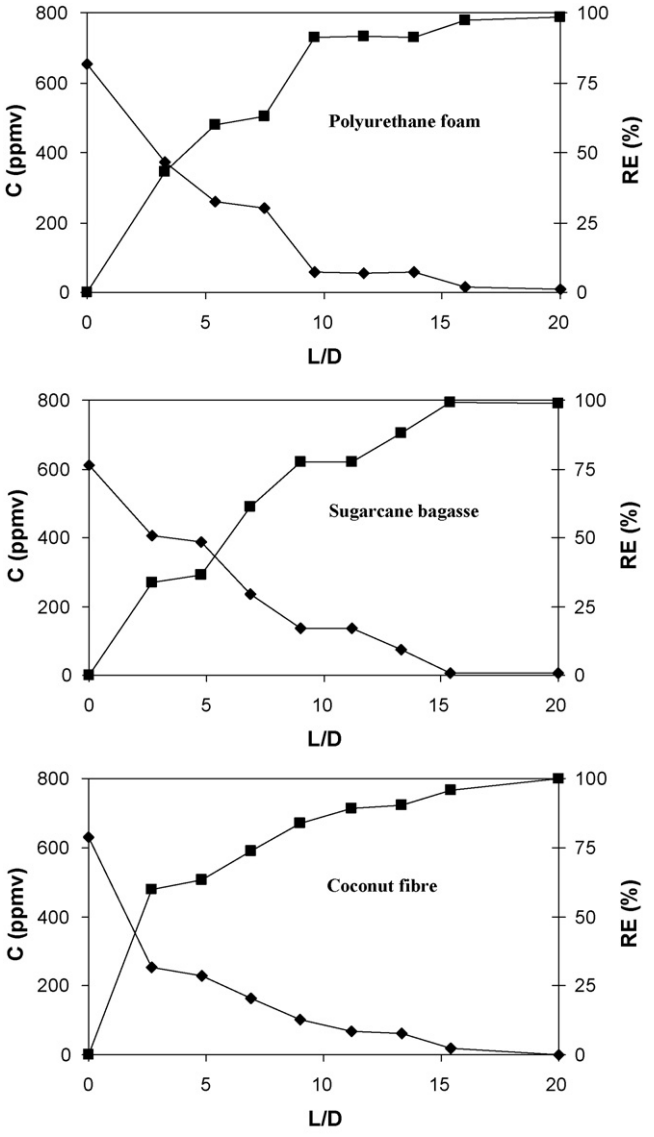

Fig. 8. Spatial degradation profile in the biofilters filled with polyurethane foam (C_{in} = 653 ppmv), sugarcane bagasse (C_{in} = 610 ppmv), and coconut fibre (C_{in} = 629 ppmv).

This performance may be due to the fact that practically all of the relevant biofiltration parameters were controlled so as not to have a significant impact on hydrogen sulphide removal capacity. For instance, many microorganism species capable of promoting H_2S oxidation do so within the pH range maintained during most of the operation (6–8). The temperature to which they were submitted during the long-term operation (28 °C) is deemed as optimum for at least four species of the genus *Thiobacillus*. Reactor-top nutrient aspersion and upstream humidification contributed to maintaining biofilter humidity within an adequate range.

3.5. Spatial profiles

According to the results of the tests carried out for concentrations of approximately 180 ppmv for the first stage and 350 ppmv or 40 g m^{-3} h^{-1} for the second stage, we verified that H_2S was removed before an *L*/*D* of approximately 3. Elias et al. [17] showed that the microorganism population grew quickly in the region close to the inlet point of the biofilters. This implies that, in this region, most of the contaminant was effectively removed.

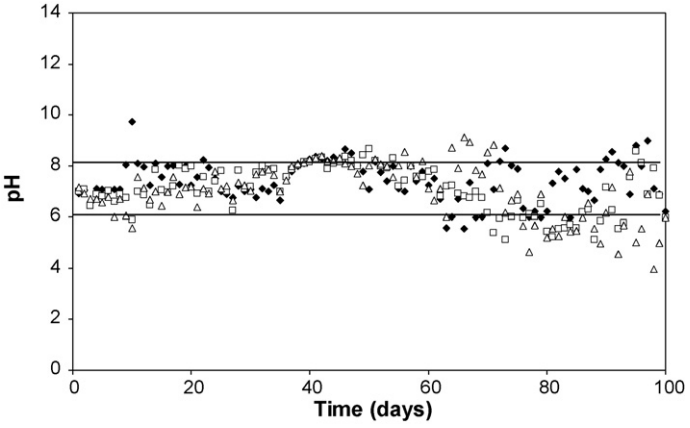

Fig. 9. pH during the operating period for polyurethane foam (♦), sugarcane bagasse (□), and coconut fibre (Δ).

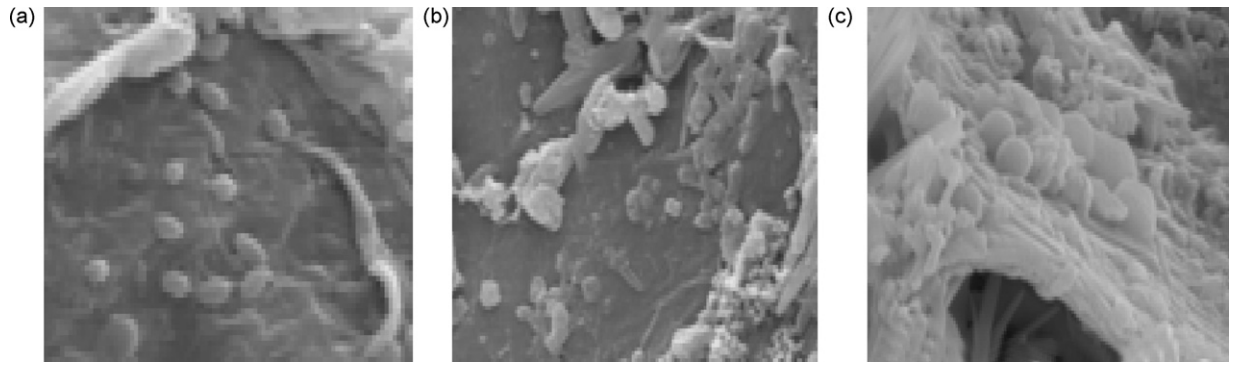

Fig. 10. SEM results of the biofilters filled with polyurethane foam, sugarcane bagasse, and coconut fibre after long-term operation. Samples were taken from the bottom of the bed. Polyurethane foam (a), sugarcane bagasse (b), and coconut fibre (c).

In Fig. 7, which shows the spatial profiles for operating stage III, we can observe that the biofilter packed with polyurethane foam removed all of the inlet sulphide before the first sampling point (L/D of approximately 3). Furthermore, the biofilter packed with sugarcane bagasse removed all of the sulphide at an L/D of approximately 11, and the biofilter packed with coconut fibre eliminated H_2S at an L/D of approximately 7. Nevertheless, it is important to observe that the inlet concentration applied to the biofilter with sugarcane bagasse was higher (559 ppmv) than that applied to the biofilters with polyurethane foam (499 ppmv) and coconut fibre (496 ppmv).

This performance indicates that, if we take into consideration the L/D portion in which H_2S was completely removed, the real elimination capacities of the biofilters are much higher than those that were calculated (approximately 80 g m^{-3} h^{-1}).

During the operating stage IV (Fig. 8 it was possible to verify removal efficiencies of 100%, 100%, and 97% in an L/D of approximately 16 for the biofilters packed with polyurethane foam, sugarcane bagasse, and coconut fibre. Although a high concentration was applied (more than 600 ppmv), the biofilters filled with polyurethane foam and sugarcane bagasse removed more than 40%, and the biofilter filled with coconut fibre removed more than 60% of the inlet H_2S at an L/D of approximately 3.

These facts suggest intense biological activity occurring in the initial length of the beds, which was reported by Elias et al. [17] and Morgan-Sagastume and Noyola [19], and it also indicates the occurrence of biological activity all along the bed, even with lower intensity. In operating stages I and II, each biofilter removed all of the inlet sulphide at $L/D = 3$. The inlet sulphide was also completely removed in stage III at $L/D = 3$, 5, and 7 and in the final stage at an L/D of approximately 16 for all of the biofilters. This shows that the biological removal moved from the bottom to the top of each biofilter.

During biofilter operation, white sediment was observed on the surface of packing materials, especially in more active areas, located around the gas mixture inlet. This sediment was equally observed in other areas of the biofilters, although in less quantity. This may be a limitation of the system since the occurrence of byproducts and excess biomass in the bed may lead to its clogging. However, no significant efficiency decrease or load loss was observed. Consonant with Duan et al. [20], the sediment color gradually changed from white to dark yellow. Also, the rate of material sedimentation seemed to be proportional to the increase in applied loading rates.

3.6. pH

Acidification has often been an obstacle to using traditional methods for acid gas treatment. Hence, pH control at a constant level in the system is very important for bioreactor function [8]. The pH of the liquid phase did not present abrupt oscillations (Fig. 9). In general, during almost the entire operating period, the pH of the packing materials was kept in the range of 6–8 using a sodium carbonate solution (50 mg L^{-1}), which provided good buffer capacity for the systems. For a few days during the operation, a pH lower than 6 or higher than 8 was observed, but the stability of the biofilters was not influenced by the pH conditions outside of the range, as is shown by the elimination capacity results.

3.7. Morphology visualisation and element content of the different packing materials

At the end of the operating period, samples were taken from the biofilters and analysed using SEM. In Fig. 10, the surface of the three packing materials after use is shown. While the morphologies are difficult to see, both the rounded bacillus and coccus are present.

Any difficulties in visualising the organisms were due to the presence of many sulphur particles. Elemental sulphur accumulation throughout the operating time was visually observed and detected by energy dispersive X-ray analysis—EDX (Table 4). Sulphur deposition did not clog the bed, as is evident by the fact that the pressure drop did not reach high values during the operating period. The same phenomenon was observed by Elias et al. [17].

According to Buisman et al. [51], the chemical oxidation equations for metabolising H_2S are as follows:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad (5)$$

$$\Delta G^0 = -169.35\ \text{kJ mol}^{-1}$$

$$2S^0 + 3O_2 + 2OH^- \rightarrow 2SO_4{}^{2-} + 2H^+ \quad (6)$$

$$\Delta G^0 = -563.23\ \text{kJ mol}^{-1}$$

The SEM (visual observation) and EDX (physical and chemical detection) results allow us to suggest that partial oxidation of hydrogen sulphide to elemental sulphur occurred in the three

Table 4
Element content on the surface of the packing materials.

Element	Polyurethane foam		Sugarcane bagasse		Coconut fibre	
	Before	After	Before	After	Before	After
Si	14.7	9.3	2.2	–	2.2	–
K	–	11.8	9.9	1.7	7.0	3.2
Na	1.1	–	37.7	35.1	25.4	10.6
Al	76.9	37.5	–	–	–	–
Mg	–	–	–	4.3	–	1.9
P	5.0	–	20.0	15.8	23.2	4.0
S	2.3	41.4	12.3	43.1	20.4	79.3
Ca	–	–	6.8	–	10.4	0.26
Fe	–	–	11.1	–	11.4	0.71

Note: Unit is percentage.

biofilters, even for high concentrations of both hydrogen sulphide (electron donor) and oxygen (electron acceptor). This partial oxidation (recovery of sulphur) is extremely important from both environmental and economical points of view because, for example, sulphur is the main element used by chemical industries in the production of sulphuric acid.

4. Conclusions

In general, the results obtained lead to the conclusion that the systems were able to treat H_2S for the experimental conditions evaluated. For the high loading rates applied (about $80\,g\,m^{-3}\,h^{-1}$), elimination capacities of about $80\,g\,m^{-3}\,h^{-1}$ were achieved by the biofilters. The use of a mixture of activated sludge unit and biofilter-aerated submerged unit as biofilter inoculum (in association with the adopted culture protocol) was shown to be totally viable given the high efficiencies achieved (100%) in removing sulphide after just two operation days. The pressure drop tests carried out for each packing material suited quite well to the Ergun equation, and the results showed that all of them provided low drop pressures (approximately $98\,Pa\,m^{-1}$). In addition, adsorption was found to be irrelevant if we take into account long-term operation. Spatial degradation profiles showed the points of degradation along the beds. No significant acidification phenomenon occurred in the biofilters during H_2S treatment. The decrease in effective bed height, probably because of H_2S oxidation side-effects, did not have an impact on the system efficiency. A partial oxidation of H_2S to elemental sulphur was detected by EDX tests, even for a high inlet concentration of oxygen.

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References

[1] P. Oyarzún, F. Arancibia, C. Canales, G.E. Aroca, Biofiltration of high concentration of hydrogen sulphide using *Thiobacillus thioparus*, Process Biochem. 39 (2003) 165–170.
[2] Y.C. Chung, C. Huang, C.P. Tseng, Operation optimization of *Thiobacillus thioparus* CH11 biofilter for hydrogen sulfide removal, J. Biotechnol. 52 (1996) 31–38.
[3] Y.L. Ma, J.L. Zhao, B.L. Yang, Removal of H_2S in waste gases by an activated carbon bioreactor, Int. Biodeter. Biodegr. 57 (2006) 93–98.
[4] H.H.J. Cox, M.A. Deshusses, Co-treatment of H_2S and toluene in a biotrickling filter, Chem. Eng. J. 87 (2002) 101–110.
[5] M. Syed, G. Soreanu, P. Falleta, M. Béland, Removal of hydrogen sulfide from gas streams using biological processes–a review, Can. Biosyst. Eng. 48 (2006), 2.1–2.14.
[6] J.H. Kim, E.R. Rene, H.S. Park, Biological oxidation of hydrogen sulfide under steady and transient conditions in an immobilized cell biofilter, Bioresour. Technol. 99 (2008) 583–588.
[7] A. Fernández-Vergara, L.L. Molina, N.A. Pulido, G. Aroca, Effects of gas flow rate, inlet concentrations and temperature on the biofiltration of toluene vapors, J. Environ. Manag. 84 (2006) 115–122.
[8] Y.L. Ma, B.L. Yang, J.L. Zhao, Removal of H_2S by *Thiobacillus denitrificans* immobilized on different matrices, Bioresour. Technol. 97 (2006) 2041–2046.
[9] A.H. Wani, R.M.R. Branion, A.K. Lau, Effects of periods of starvation and fluctuating hydrogen sulfide concentration on biofilter dynamics and performance, J. Hazard. Mater. 60 (1998) 287–303.
[10] J.S. Devinny, M.A. Deshusses, T.S. Webster, Biofiltration for Air Pollution Control, Boca Raton, Lewis Publishers, Boca Raton, 1999.
[11] C. Kennes, M.C. Veiga, Bioreactors for Waste Gas Treatment, Kluwer Academic Publishers, Dortrecht, 2001.
[12] A. Barona, A. Elías, A. Amurrion, I. Cano, R. Arias, Hydrogen sulphide adsorption on a waste material used in bioreactors, Biochem. Eng. J. 24 (2005) 79–86.
[13] J.P. Maestre, X. Gamisans, D. Gabriel, J. Lafuente, Fungal biofilters for toluene biofiltration: evaluation of the performance with four packing materials under different operating conditions, Chemosphere 67 (2007) 684–692.
[14] F. Gaudin, Y. Andres, P. Le Cloirec, Packing material formulation for odorous emission biofiltration, Chemosphere 70 (2008) 958–966.
[15] A.H. Wani, A.K. Lau, M.R. Branion, Biofiltration control of pulping odors–hydrogen sulphide: performance, macrokinetics and coexistence effects of organo-sulfur species, J. Chem. Technol. Biotechnol. 74 (1999) 9–16.
[16] M. Hirai, M. Kamamoto, M. Yani, M. Shoda, Comparison of the biological H_2S removal characteristics among four inorganic packing materials, J. Biosci. Bioeng. 91 (2001) 396–402.
[17] A. Elias, A. Barona, A. Arreguy, J. Rios, I. Aranguiz, J. Peñas, Evaluation of a packing material for the biodegradation of H_2S and product analysis, Process Biochem. 37 (2002) 813–820.
[18] J.M. Morgan-Sagastume, A. Noyola, S. Revah, S.J. Ergas, Changes in physical properties of a compost biofilters treating hydrogen sulfide, J. Air Waste Manag. Assoc. 53 (2003) 1011–1021.
[19] J.M. Morgan-Sagastume, A. Noyola, Hydrogen sulfide removal by compost biofiltration: effect of mixing of the filter media on operational factors, Bioresour. Technol. 97 (2006) 1546–1553.
[20] H. Duan, L.C.C. Koe, R. Yang, X. Cheng, Biological treatment of H_2S using pellet activated carbon as a carrier of microorganisms in a biofilter, Water Res. 40 (2006) 2629–2636.
[21] E. Dumont, Y. Andrès, P. Le Cloirec, F. Gaudin, Evaluation of a new packing material for H_2S removed by biofiltration, Biochem. Eng. J. 42 (2008) 120–127.
[22] A. Pandey, C.R. Soccol, P. Nigam, V.T. Soccol, Biotechnological potential of agro-industrial residues. I: sugarcane bagasse, Bioresour. Technol. 74 (2000) 69–80.
[23] L. Sene, A. Converti, M.G.A. Felipe, M. Zilli, Sugarcane bagasse as alternative packing material for biofiltration of benzene polluted gaseous streams: a preliminary study, Bioresour. Technol. 83 (2002) 153–157.
[24] E. Ramírez-López, J. Corona-Hernández, L. Dendooven, P. Rangel, F. Thalaso, Characterization of five agricultural by-products as potential biofilter carriers, Bioresour. Technol. 88 (2003) 259–263.
[25] G. Baquerizo, J.P. Maestre, T. Sakuma, M.A. Deshusses, X. Gamisans, D. Gabriel, J. Lafuente, A detailed model of a biofilter for ammonia removal: model parameters analysis and model validation, Chem. Eng. J. 113 (2005) 205–214.
[26] A.K. Mathur, C.B. Majumder, S. Chatterjee, Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC as biofilter media, J. Hazard. Mater. 148 (2007) 64–74.
[27] D. Gabriel, J.P. Maestre, L. Martín, X. Gamisans, J. Lafuente, Characterization and performance of coconut fibre as packing material in the removal of ammonia in gas-phase biofilters, Biosyst. Eng. 97 (2007) 481–490.
[28] M. Zilli, D. Daffonchio, R. Di Felice, M. Giordani, A. Converti, Treatment of benzene-contaminated airstreams in laboratory-scale biofilters packed with raw and sieved sugarcane bagasse and with peat, Biodegradation 15 (2004) 87–96.
[29] J.L.R. Pantoja Filho, Utilization of different packing materials in the hydrogen sulfide biofiltration, Department of Hydraulics and Sanitation, Dissertation, University of São Paulo, Brazil, 2008, "In Portuguese".
[30] P. Christen, F. Domenech, G. Michelena, R. Auria, S. Revah, Biofiltration of volatile ethanol using sugar cane bagasse inoculated with *Candida utilis*, J. Hazard. Mater. 89 (2002) 253–265.
[31] W.M. Moe, R.L. Irvine, Polyurethane foam medium for biofiltration. I: characterization, J. Environ. Eng. 126 (2000) 815–825.
[32] W.M. Moe, R.L. Irvine, Polyurethane foam medium for biofiltration. II: operation and performance, J. Environ. Eng. 126 (2000) 826–835.
[33] B. Qi, W.M. Moe, K.A. Kinney, Treatment of paint spray booth off-gases in a fungal biofilter, J. Environ. Eng. 131 (2005) 180–189.
[34] E.H. Shim, J. Kim, K.S. Cho, H.W. Ryu, Biofiltration and inhibitory interactions of gaseous benzene, toluene, xylene, and methyl *tert*-butyl ether, Environ. Sci. Technol. 40 (2006) 3089–3094.
[35] D. Gabriel, M.A. Deshusses, Retrofitting existing chemical scrubbers to biotrickling filters for H_2S emission control, Proc. Natl. Acad. Sci. U.S.A. 100 (2003) 6308–6312.
[36] M. Ramirez, J.M. Gómez, G. Aroca, D. Cantero, Removal of hydrogen sulfide and ammonia from gas mixtures by co-immobilized cells using a new configuration of two biotrickling filters, Water Sci. Technol. 59 (2009) 1353–1359.
[37] A. Barona, A. Elias, R. Arias, I. Cano, R. Gonzáles, Biofilter response to gradual and sudden variations in operating conditions, Biochem. Eng. J. 22 (2004) 25–31.
[38] S. Ergun, Fluid flow through packed columns, Chem. Eng. Prog. 48 (1952) 89–94.
[39] W.L. McCabe, J.C. Smith, P. Harriott, Unit Operations of Chemical Engineering, fifth ed., McGraw-Hill, New York, 1993.
[40] A.P.H.A., A.W.W.A., W.P.C.P., Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, Washington, DC, 1999.
[41] Y. Yang, E.R. Allen, Biofiltration control of hydrogen sulfide: 1. Design and operational parameters, J. Air Waste Manag. Assoc. 44 (1994) 863–868.
[42] G. Wu, B. Conti, A. Leroux, R. Brzezinski, G. Viel, M. Heitz, A high performace biofilter for VOC emission control, J. Air Waste Manag. Assoc. 49 (1999) 185–192.
[43] Y.C. Chung, C. Huang, C.P. Tseng, Biological elimination of H_2S and NH_3 from waste gases by biofilter packed with immobilized heterotrophic bacteria, Chemosphere 43 (2001) 1043–1050.
[44] T. Hartikainen, J. Ruuskanen, P.J. Martikainen, Carbon disulfide and hydrogen sulfide removal with a peat biofilter, J. Air Waste Manag. Assoc. 51 (2001) 387–392.
[45] T. Hartikainen, P.J. Martikainen, M. Olkonnen, J. Ruuskanen, Peat biofilters in long-term experiment for removing odorous sulphur compounds, Water Air Soil Pollut. 133 (2002) 335–348.
[46] S.A. Shojaosadati, S. Elyasi, Removal of hydrogen sulfide by the compost biofilter with sludge of leather industry, Resour. Conserv. Recycl. 27 (1999) 139–144.
[47] D.H. Park, J.M. Cha, H.W. Ryu, G.W. Lee, E.Y. Yu, J.I. Rhee, J.J. Park, S.W. Kim, I.W. Lee, Y.I. Joe, Y.W. Ryu, B.K. Hur, J.K. Park, K. Park, Hydrogen sulfide removal

utilizing immobilized *Thiobacillus* sp. IW with Ca-alginate bead, Biochem. Eng. J. 11 (2002) 167–173.
[48] M. Hirai, M. Ohtake, M. Shoda, Removal kinetics of hydrogen sulfide, methanethiol and dimethyl sulfide by peat biofilters, J. Ferment. Bioeng. 70 (1990) 334–339.
[49] L. Zhang, M. Hirai, M. Shoda, Removal characteristics of dimethyl sulfide, methanethiol and hydrogen sulfide by *Hyphomicrobium* sp. I55 isolated from peat biofilter, J. Ferment. Bioeng. 72 (1991) 392–396.
[50] K.S. Cho, M. Hirai, M. Shoda, Degradation characteristics of hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl disulfide by *Thiobacillus thioparus* DW44 isolated from peat biofilter, J. Ferment. Bioeng. 71 (1991) 384–389.
[51] C.J.N. Buisman, B.G. Geraats, P. Ijspeert, G. Lettinga, Optimization of sulphur production in a biotechnological sulphide-removing reactor, Biotechnol. Bioeng. 35 (1990) 50–56.