Biofiltration of H2S in air-experimental comparisons of original packing materials and modeling

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Abstract

The treatment of hydrogen sulfide using a biofilter packed with expanded schist and topped with a layer of a synthetic nutritional material (UP20) was examined at a constant H_2S concentration (100 ppmv). The impact of the empty bed residence time (EBRT) on process performances was clearly underlined by varying the polluted air flow from 4 to 20 $m^3\ h^{-1}$ corresponding to a variation in the EBRT from 63 to 13 s. Complete H_2S degradation was observed when the EBRT was higher than 51 s. Experimental data collected at various EBRTs (13 – 63 s) were fitted using the Ottengraf model equations. The α_{lump} parameter value was found to be 26.4 $g^{1/2}\ m^{-3/2}\ h^{-1}$. This single parameter, which enables the performance of the biofilter as a whole to be characterized whatever its composition (mixture or layers of different packing materials) and whatever the EBRT, is a powerful tool to compare packing materials and to design such bioreactors. The α_{lump} value characterizing the performances of expanded schist coupled with a thin layer of UP20 was higher than the α_{lump} values obtained for other packing materials (natural or synthetic) reported in previous studies.

Key words: Biofilters; Modeling; Diffusion-Reaction; Waste Treatment; Hydrogen sulfide; Odors.

Nomenclature

A: Specific area ($m^2_{biofilm}$ $m^{-3}_{packing\ material}$)
C: Gas concentration (g m^{-3}_{gas})
C_L: Pollutant concentration in the biofilm (g $m^{-3}_{biofilm}$)
d: Diameter (m)
D: Diffusion coefficient ($m^2_{biofilm}$ s^{-1})
EBRT: Empty Bed Residence Time (s); EBRT = V / Q_v
EC: Elimination Capacity (g_{H_2S} $m^{-3}_{packing\ material}$ s^{-1}); EC = (Q_v / V) (C_{in} – C_{out})
H: Height (m)
k: Zero order reaction rate constant (g $m^{-3}_{biofilm}$ s^{-1})
LR: Loading Rate (g_{H_2S} $m^{-3}_{packing\ material}$ s^{-1}); LR = (Q_v C_{in} / V)
m: Partition coefficient (-)
Q_v: Gas flow rate (m^3_{gas} s^{-1})
R: Reaction rate constant (g $m^{-3}_{packing\ material}$ s^{-1}); R = k A δ
RE: Removal Efficiency (%); RE = 100 (C_{in} – C_{out}) / C_{in}
U: Superficial gas velocity (m_{gas} s^{-1})
V: Bed volume of packing material ($m^3_{packing\ material}$)
x: Length coordinate (m)

Greek letters
α_{lump}: Lump parameter ($g^{1/2}$ $m^{-3/2}_{packing\ material}$ s^{-1}) (Ottengraf's equations)
δ: Total biofilm thickness (m)
ε: Porosity of the packing material (-)
ϕ: Thiele modulus (-)
λ: Effective biofilm thickness (m)
σ: Dimensionless length coordinate in the biofilm (= x/δ)

Subscripts
Crit: Critical
in: Inlet
out: Outlet

1. Introduction

Hydrogen sulfide (H_2S) is a hazardous, toxic air pollutant. It is a colorless, corrosive and flammable gas. H_2S can be problematic due to its unpleasant smell and low odor threshold. It is emitted from many industrial activities such as petroleum refining, leather, waste or wastewater treatments, food processing, anaerobic treatment of paper and pulp manufacturing. Conventionally, different processes have been used to remove H_2S from waste gas streams involving chemical and physical methods. For some years, the focus has shifted toward using biofiltration. This process presents an attractive technology for treating pollutants from air due to its effectiveness, low energy consumption and minimal by-product generation. The gas stream flows through the filter bed. Pollutants are then transferred from the gas phase to the biofilm, where they are metabolized by microorganisms. The by-products of the complete biodegradation of air pollutants are CO_2, water, and microbial biomass. In the case of H_2S biodegradation, sulfur oxidizing bacteria (SOB) are responsible for removing H_2S in aerobic conditions. For their maintenance and growth, SOB use H_2S as a source of energy and CO_2 as the main source of carbon [1,2]. Bacteria from the genus *Thiobacillus* are responsible for the oxidation of H_2S to sulfate and/or elemental sulfur according to the operating conditions [3,4]. The biofiltration of H_2S is well documented (Table 1). As this table shows, a variety of packing materials are used and biofiltration performances are disparate. These packing materials include: (i) organic materials such as soil, peat, compost and pine bark [3,5–10] and different forms of activated carbons [11,12]; (ii) inorganic materials like pozzolan, expanded schist and lava rock [13–15]; (iii) synthetic media such as a patented biofilter medium (Biosorbens™) developed by Shareefdeen [16,17]. Nonetheless, recent studies highlighted that biofilters filled with expanded schist topped with a layer of synthetic nutritional material (UP20) were very efficient for removing high loading rates of H_2S [15,18,19]. The good mechanical behavior of the expanded schist (low pressure drop) and the ability of biofilters to oxidize H_2S under extreme acidic conditions for a long period confirmed the advantage of using expanded schist coupled with UP20 for industrial applications [14,15,18,20]. In biofiltration, the empty bed residence time (EBRT) is the key parameter influencing biofilter performances. Usually, EBRTs from 20 to 60 s are applied to remove H_2S from air [6,16,21] but higher and lower values are reported in the literature. As illustrated in Table 1, the EBRT may be significantly different from one study to another (from 2 to 120 s, i.e. almost two orders of magnitude). Consequently, it is very difficult to compare the performance of different packing materials on the basis of the Elimination Capacity (EC in g m^{-3} h^{-1}) measured at different EBRTs and the Removal Efficiency (RE), which can be other than 100%. The literature results presented in Table 1 clearly illustrate that the comparison of biofilter performances is difficult. For instance, is it possible to compare the performance of peat reported by Oyarzun *et al*. [3] (EC = 14.8 g m^{-3} h^{-1} at EBRT = 120 s and RE = 100%) with that of the biofilter medium Biosorbens™ reported by Shareefdeen [16] (EC = 6 g m^{-3} h^{-1} at EBRT = 30 s and RE = 99%)? To overcome this problem, it would be better to base the comparison of the performances of packing materials on mathematical models. Several models have been proposed to predict the performances of biofilters and to improve biofilter design [22,23]. One of the earliest steady-state biofiltration models was developed by Ottengraf and Van den Oever [24]. Because of its mathematical simplicity, this model has been widely used for biofiltration [3,25,26]. Therefore, the objective of this work was to show

that a single parameter (called α_{lump}) derived from the Ottengraf model equations can be used as a simple tool to compare the performances of different carrier materials used in H_2S biofiltration whatever the configuration of the biofilter and whatever the EBRT. The Ottengraf model was therefore applied (i) to determine the α_{lump} parameter experimentally in order to evaluate the performance of a biofilter filled with expanded schist topped with a layer of synthetic nutritional material (UP20) and (ii) to compare this latter with the performance of packing materials reported in the literature. To achieve these objectives, the ability of the biofilter to oxidize H_2S at different EBRTs should be determined beforehand. Therefore, this paper presents a brief description of the mathematical model used and details the experimental study carried out.

Table 1. Examples of recent biofiltration results reported in the literature on the treatment of gas polluted by H_2S.

Packing material	**EBRT (s)**	**Elimination Capacity EC (g m^{-3} h^{-1})**	**Removal Efficiency RE (%)**	**Reference**
Compost	45	64	100	[27]
Peat	120	14.8	100	[3]
Peat	60	65.9	90	[28]
Peat	57	25.5	50	[21]
Fibrous peat	29	5.7	90	[29]
Peat moss	20 40		85 90	[30]
Pig manure + sawdust	24	5 46	97 83	[31]
Pig manure + sawdust (ABONLIR)	13.5 27	20 45	90 90	[32]
Sugarcane bagasse	49	73		[7]
Coconut fiber	49	68		[7]
Pine bark	57	10	69	[19]
Sapwood	57	8	50	[21]
Woodchips	20 40		90 95	[30]
Activated carbon	2 - 21	181	94	[33]
Granular activated carbon	20 40		96 100	[30]
Granular activated carbon	240	125	98	[34]
Pellet activated carbon	2	181	94	[12]
Exhausted carbon	4 - 25	Up to ≈ 40	94 - 99	[35]
Synthetic medium (UP20)	57	10	93	[19]
Synthetic medium	20		99	[36]
Synthetic medium (BIOSORBENS™)	30	6	99	[16]
Peat + UP20 (mixed)	57	25.5	80	[21]
Expanded schist	16	30	100	[14]
Expanded schist + UP20	16 24 35	20 25 36	90 90 100	[15]
Pozzolan + UP20 (layers)	57	10	74	[19]
Porous ceramic	6	160	96	[37]
Ceramic	20 40		80 83	[30]

Dried activated sludge	30	44.3	82	[38]
Mixed dried activated sludge with rice husk silica	30	52.3	97	[38]
Polyurethane foam	80	56.6	95	[39]
Polyurethane foam	49	66		[7]
Biomedium encapsulated by Na-alginate and polyvinyl alcohol	51	6	99	[40]

2. Ottengraf model equations

In order to describe the mechanisms of transfer and biodegradation in the biofilter (Fig. 1), Ottengraf and Van den Oever [24] proposed a simple model based on the theoretical model built by Jennings *et al.* [41]. The hypotheses are as follows:

- Biodegradation occurs in a biofilm considered to be water.
- Biofilm thickness is small compared to the packing material diameter.
- Biomass concentration is homogeneous in the reactor.
- Gas phase is ideal.
- Gas phase is a plug flow.
- Mass transfer resistance in the gas phase is negligible.
- Regime is at steady-state.
- Equilibrium occurs at the gas-biofilm interface.

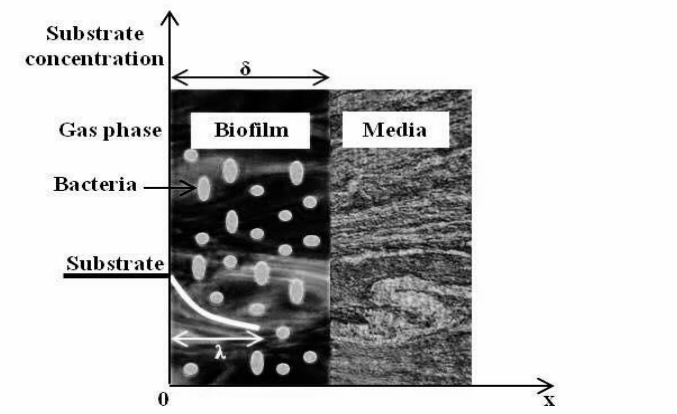

Fig. 1. Substrate concentration profile in the biofilm: diffusional regime.

Moreover, Ottengraf and Van den Oever considered that the reaction rate constant of the substrate elimination in the biofilm is of zero-order in the pollutant concentration, which assumes a very low value of the Michaelis-Menten constant in the Monod equation [24]. Zero-order kinetics are encountered at high concentrations of H_2S, which is generally the case in laboratory experiments. With these assumptions, the concentration of a nutrient component inside the biofilm (C_L) is described using the differential equation:

$$D\frac{d^2C_L}{dx^2} - k = 0 \quad (1)$$

with the boundary conditions:

$$x = 0; \quad C_L = \frac{C}{m} \tag{2}$$

$$x = \delta; \quad \frac{dC_L}{dx} = 0 \tag{3}$$

The solution of the differential equation is:

$$\frac{C_L}{C/m} = 1 + \frac{1}{2}\frac{\phi^2}{C/C_{in}}(\sigma^2 - 2\sigma) \tag{4}$$

with:

$$\phi = \delta\sqrt{\frac{m\,k}{D\,C_{in}}} \tag{5}$$

where ϕ is the Thiele modulus, $\sigma = x/\delta$ is the dimensionless length coordinate in the biofilm, and $m = (C/C_L)$ is the gas-liquid partition coefficient obtained from Henry's law. Two situations expected to be common in biofilters were then considered by Ottengraf and Van den Oever [24]: zero-order kinetics with biological limitation and zero-order kinetics with diffusional limitation.

Considering the reaction-limited regime, the conversion rate of the pollutant is controlled by the reaction rate and Ottengraf and Van den Oever [24] calculated that the pollutant conversion is:

$$\frac{C_{out}}{C_{in}} = 1 - \frac{A\ k\ \delta}{C_{in}}\ \frac{H}{U} \tag{6}$$

Considering the diffusion-limited regime, the substrate concentration in the biofilm is high and the diffusion into the biofilm is a limiting factor. Hence, the substrate cannot reach the bacteria, which leads to the presence of some inactive biofilm zones. An active biofilm thickness λ is defined, less than the biofilm thickness δ (Figure 1). In this case, the concentration profile provided by the Ottengraf model is given by the following equation:

$$\frac{C_{out}}{C_{in}} = \left(1 - \frac{A\ H}{U}\sqrt{\frac{k{\cdot}D}{2{\cdot}m}}\sqrt{\frac{1}{C_{in}}}\right)^2 \tag{7}$$

Taking into account that H/U = EBRT, Eq. (7) can be rewritten as:

$$\frac{C_{out}}{C_{in}} = \left(1 - A\sqrt{\frac{k{\cdot}D}{2{\cdot}m}}\sqrt{\frac{1}{C_{in}}}\ EBRT\right)^2 \tag{8}$$

From Eq. (8), Deshusses and Shareefdeen [23] included a parameter in this model (called α_{lump}) that can be expressed as follows:

$$\alpha_{\text{lump}} = A\sqrt{\frac{k \cdot D}{2 \cdot m}} \quad (9)$$

Subsequently, the concentration profile given by Eq. (7) can be written as:

$$\sqrt{\frac{C_{out}}{C_{in}}} = 1 - \text{EBRT}\,\alpha_{\text{lump}}\sqrt{\frac{1}{C_{in}}} \quad (10)$$

It should be kept in mind that in Eq. (9), k represents the reaction rate per unit of volume of the biofilm [24], while A is the surface area of the biofilm developed on the volume of packing material. As a result, the unit of the parameter α_{lump} ($g^{1/2}$ $m^{3/2}_{biofilm}$ $m^{-3}_{packing\ material}$ s^{-1}) is difficult to understand from a physical point view. Moreover, it should be noted that this unit of the parameter α_{lump} is not expressed in [23]. Shareefdeen suggested expressing it in (s^{-1}). In this case, the pollutant gas concentration and the EBRT can be expressed in (ppmv) and (s), respectively [17,36]. In another publication [42], this author suggested expressing the pollutant gas concentration in (kg m^{-3}), the EBRT in (s) and α_{lump} in (s^{-1}). However, in the latter case, the unit of the parameter α_{lump} should be ($kg^{1/2}$ $m^{-3/2}$ s^{-1}). Consequently, although the parameter α_{lump} could be a suitable tool to compare the performance of the packing materials used in biofiltration, the units used in Eq. (10) to calculate this parameter should be considered with caution.

Using the definitions of the Loading Rate (LR) and the Elimination Capacity (EC) usually employed in studies devoted to biofiltration, Eq. (10) can be easily written as follows:

$$EC = LR\left(1 - \left(1 - \alpha_{lump}\sqrt{\frac{EBRT}{LR}}\right)^2\right) \quad (11)$$

In Eq. (11), the unit of the parameter α_{lump} is ($kg^{1/2}$ $m^{-3/2}_{packing\ material}$ h^{-1}) and thus, by determining EC and LR, α_{lump} can be calculated in order to compare different packing materials for H_2S biofiltration as shown in [21,43]. In other words, by using EC and LR in (g $m^{-3}_{packing\ material}$ h^{-1}) and EBRT in (h), the determination of α_{lump} from Eq. (11) is unambiguous. Although some assumptions of the Ottengraf model are questionable, it has been validated by different authors in various conditions with good agreement between experimental data and calculated values [22]. Moreover, an analytical solution such as Eq. (11) is more suitable than a numerical solution for data analysis and biofilter design.

3. Materials and methods

3.1. Packing material

Expanded schist, a natural inorganic support (Granulex Company; France; www.granulex.fr) was used as packing material (Figure 2). Several studies carried out in laboratory-scale biofilters showed that this material is efficient for removing H_2S [14,15,18]. Moreover, its excellent mechanical behavior, which results in low pressure drops over a long period, is suitable for long-term industrial applications. The composition of this medium was determined using an Energy Dispersive X-ray Fluorescence Spectrometer (EDX-800HS,

Shimadzu Company). Its composition is as follows: SiO_2 (55.3%), Al_2O_3 (20.2%), Fe_2O_3 (13.3%) and K_2O (5.1%). The characteristics of the pieces of expanded schist used in this study are given in Table 2. The specific surface area was measured by a Micromeritics AutoPore IV 9500 mercury porosimeter.

In order to provide nutrients for the expanded schist, a synthetic nutritional material (UP20) was manufactured in our laboratory. This is a cylindrical-shaped extruded material (7 mm in diameter and 15 mm in length) whose formulation has been described previously [44]. UP20 contains urea phosphate (CH_4N_2O, H_3PO_4), calcium carbonate ($CaCO_3$) (C/N/P molar ratio: 100/10/5) and an organic binder (20% in mass) from the Elotex company. The Elotex binder contains ethylene and vinyl acetate. It has been shown that the combination of expanded schist and UP20 can be successfully used to remove high concentrations of H_2S, up to 360 ppmv [20].

Table 2. Characteristics of (i) expanded schist used in this study; (ii) patented medium (Biosorbens™) developed by Shareefdeen *et al.* [16].

	Expanded schist	**(Biosorbens™)**
Bulk density (kg m^{-3})	667	650
Particle size (mm)	8 - 14	5 - 25
Specific surface area (m^2 g^{-1})	50.1	40.9
pH	≈ 8	≈ 8

3.2. Experimental set-up

The laboratory-scale system used for the biofiltration of air loaded with H_2S is shown in Figure 2. It consisted of a PVC column with an internal diameter of 300 mm. The biofilter was filled with 70 L of expanded schist (1 m height) topped with a layer of UP20 (2 cm thickness). The bed of packing material was inoculated with 5 L of a diluted solution of activated sludge (about 50 mg of dry sewage sludge per liter) from a domestic wastewater treatment plant (Tougas, Nantes, France). The initial biomass came from this activated sludge and was not previously acclimatized to H_2S treatment.

As observed in Figure 2, a clean airflow was first humidified through a column (internal diameter 200 mm) packed with Hiflow rings (packing height = 1.50 m). Then, a stream of H_2S (99.7% purity) controlled by a mass flow controller (Model 5850S, Brooks Instrument, Hatfield, USA) was diluted in the atmospheric air at the outlet of the humidification column. The polluted air was then introduced at the bottom of the biofilter (upward load flow mode). To maintain optimal bed humidity, a watering system was implemented at the top of the biofilter. Tap water was sprayed once a day at a constant flow of 0.8 L min^{-1} for 15 minutes, which corresponds to a water flow rate of 12 L day^{-1}. To measure H_2S concentrations along the column, the biofilter was equipped with sampling ports located at the inlet and outlet of the biofilter, and at 10, 30, 50, 70, 90 and 100 cm from the biofilter bottom (Figure 2). The H_2S concentration was measured with an Onyx 5220 device (measurement accuracy ± 1%) from the Cosma Environment SA Company (Passy, France).

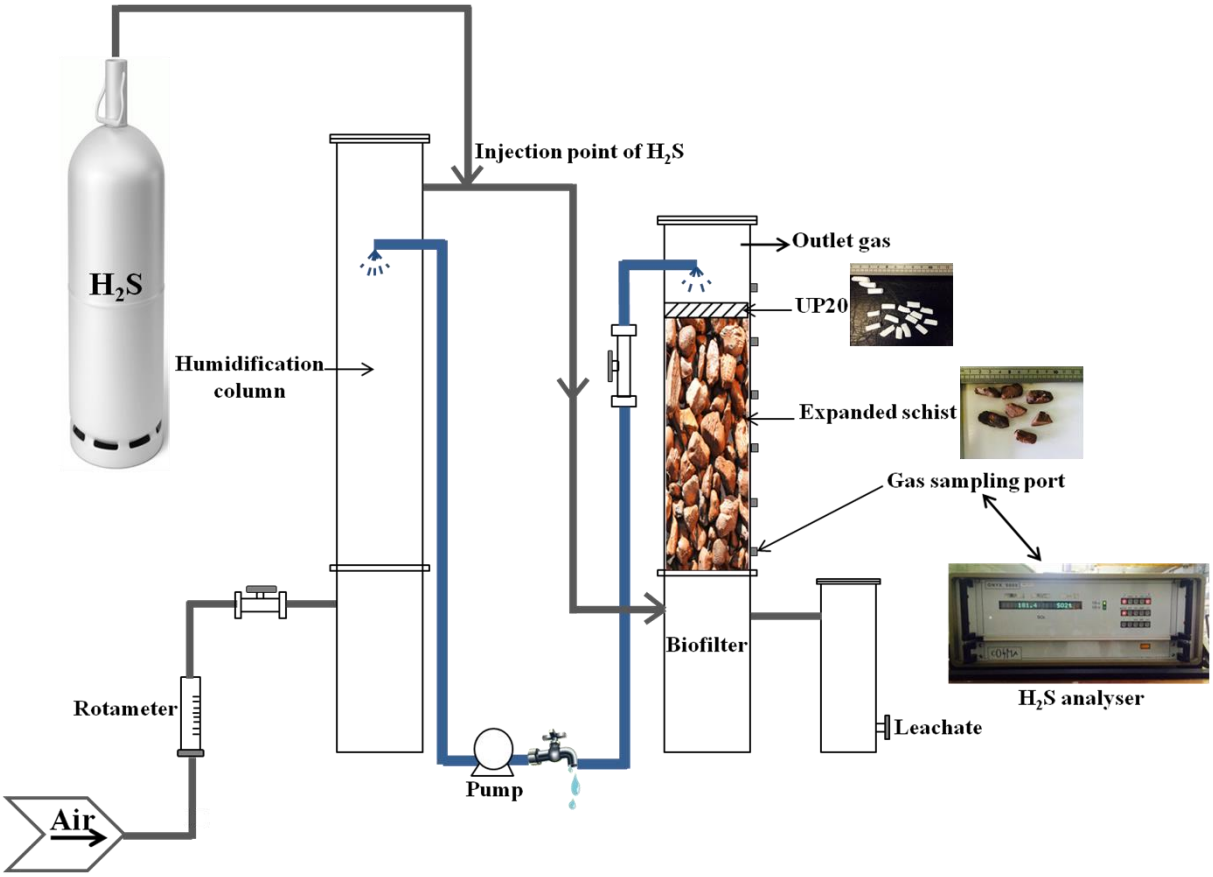

Fig. 2. Schematic diagram of the experimental pilot-scale biofilter.

3.3. Operating conditions

At the beginning of the experiment, the biofilter was fed continuously with 40 ppmv of H_2S for three weeks. The polluted air flow rate was 4 m^3 h^{-1} corresponding to an EBRT of 63 s (LR = 3.2 g m^{-3} h^{-1}). This period represented the acclimatization of the microbial communities to the biofilter environment. Nutrients were supplied by the layer of UP20 placed on top of the expanded schist. At the end of the acclimatization period, the H_2S concentration was increased from 40 ppmv to 100 ppmv. The impact of EBRT on the degradation of H_2S was then studied by varying the polluted air flow from 4 to 20 m^3 h^{-1} corresponding to an EBRT range of 63 to 13 s (Table 3). The concentration of H_2S was maintained at a constant value (100 ppmv) throughout the duration of the study.

Table 3. Operating conditions (H_2S concentration was maintained at a constant value of 100 ppmv).

Phase	Duration (days)	Q_v ($m^3 h^{-1}$)	EBRT (s)	LR ($g\ m^{-3} h^{-1}$)
1	11	4	63	7.9
2	10	5	51	9.9
3	6	7.5	34	14.8
4	7	10	25	19.8
5	8	12.5	20	24.7
6	6	15	17	29.7
7	5	20	13	39.6

4. Results and discussion

4.1. Effect of Empty Bed Residence Time (EBRT) on biofilter performances

Empty bed residence time (EBRT) is one of the most important operating factors that affect the performances of the biofilter. As shown in Figure 3, H_2S was totally removed with an EBRT greater than 51 s. By decreasing the EBRT, the removal efficiency decreased; the lowest RE value (47%) was obtained for an EBRT of 13 s. This result, widely reported in the literature devoted to biofiltration [8,15,45], is due to the increase in the gas superficial velocity in the bed material leading to a mass transfer limitation between the gas phase and the liquid phase. Using expanded schist coupled with UP20 to remove H_2S from waste air, Romero Hernandez *et al.* [15] showed that by increasing the EBRT from 16 to 35 s, the performances improved by about 35% in terms of elimination capacity. For a constant H_2S concentration of 100 ppmv, the elimination capacity is also defined as a function of the loading rate in Figure 3. At EBRT = 63 s, the elimination capacity (EC) was 7.9 $g\ m^{-3} h^{-1}$ (equivalent to RE = 100%). The biofilter achieved an RE higher than 80% up to LR = 14.8 $g\ m^{-3} h^{-1}$ (EBRT = 34 s), whereas at EBRT = 13 s, the EC value was 19 $g\ m^{-3} h^{-1}$ at an LR of 39.6 $g\ m^{-3} h^{-1}$ but the RE was only close to 45%.

These elimination capacity values are of the same order of magnitude as results reported in recent publications (Table 1). However, it should be noted that these results cannot be directly compared because the inlet concentrations and EBRTs are different. Moreover, no relationship between the properties of the packing materials and biofilter performances can be proposed. As can be observed in Table 1, H_2S elimination capacities can usually reach 60 - 70 $g\ m^{-3}\ h^{-1}$, but higher EC values can be obtained for materials based on activated carbon. However, such material is too expensive to be retained for full-scale applications [46].

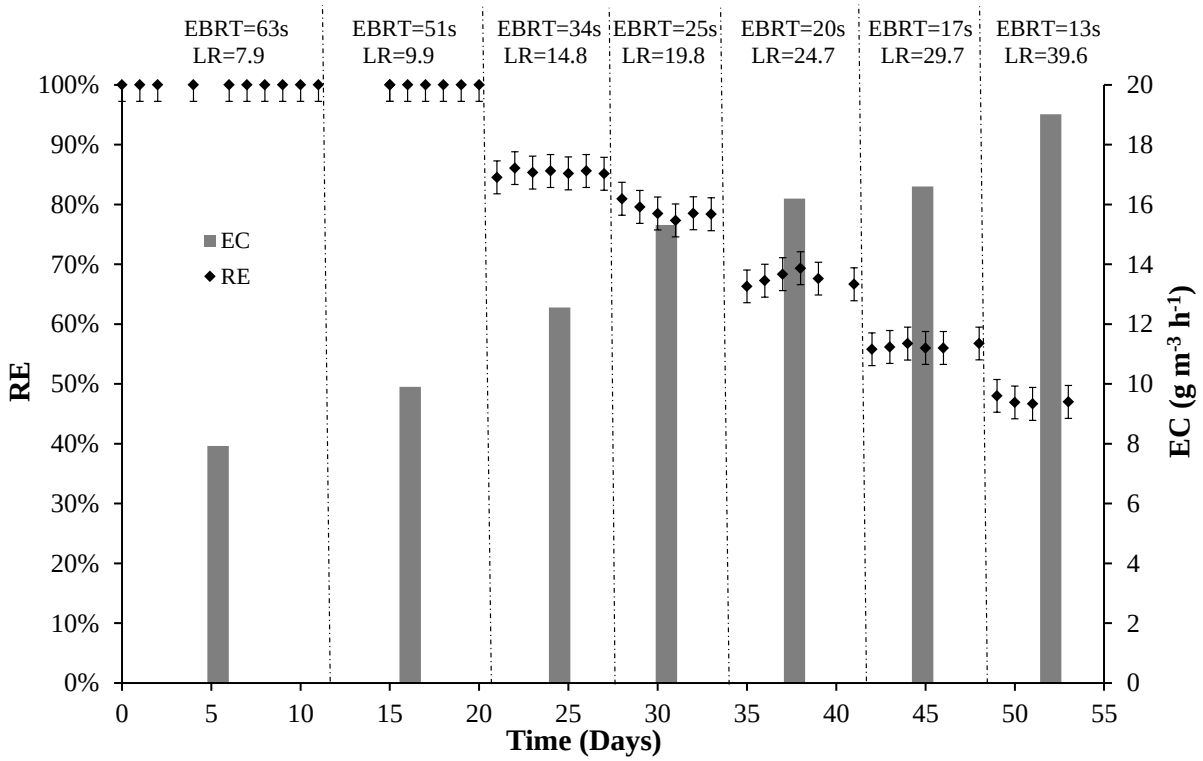

Fig. 3. EBRT influence on biofilter performance (inlet H_2S concentration = 100 ppmv). LR unit: g m^{-3} h^{-1}.

4.2. Determination of the α_{lump} parameter

In order to compare the performance of expanded schist coupled with UP20 with that of other materials reported in the literature, the units used to determine α_{lump} have to be selected carefully. Two cases are now considered.

Firstly, the experimental results can be directly compared with the values reported by Shareefdeen for two patented media [36,42]. From Eq. (10), the parameter α_{lump} was deduced from the curve $(C_{out}/C_{in})^{1/2}$ versus EBRT (Figure 4) in which the pollutant gas concentration and the EBRT were expressed in (ppmv) and (s), respectively. The value of α_{lump} calculated from the slope of the curve was 0.20 ± 0.02 s^{-1} according to the units used. This value is of the order of magnitude as the value reported for the patented medium (Biosorbens™) used by Shareefdeen [17] ($\alpha_{lump} = 0.18$ s^{-1}). This medium, whose properties given in Table 2 are close to those of expanded schist, was demonstrated as efficient for removing H_2S concentrations up to 40 ppmv (LR = 6.7 g m^{-3} h^{-1}) at an EBRT of 30 s [16]. Using another synthetic medium (consisting of a hydrophilic nucleus, hydrophobic coatings, metallic powder, micro-organisms, nutrients and acid; US Patent Pub. No. 2205/0084949 A1), Shareefdeen reported $\alpha_{lump} = 0.204$ s^{-1}. This medium gave complete H_2S removal (RE > 99%) at an EBRT of 20 s for H_2S concentrations of 50 ppmv [36]. By comparing α_{lump} values, these results highlight that a natural material, such as expanded schist coupled with a small amount of synthetic nutritional material UP20, is equivalent to synthetic media specifically developed for H_2S biofiltration. Moreover, due to its ability to treat high H_2S loading rates and its good mechanical behavior over a long period (no attrition, no bed compaction and low pressure

drops), expanded schist should be preferred for industrial applications. According to the definition given in Eq. (9), the parameter α_{lump} depends on: (i) A: the specific surface area of biofilm covering the packing material; (ii) k: the reaction rate constant; (iii) D: the diffusion coefficient of H_2S in the biofilm; and (iv) m: the partition coefficient of H_2S between the gas and liquid phases. Since the studies of Shareefdeen [17,36] and the present work are based on the biofiltration of H_2S in air, it can legitimately be assumed that they involve the same values of the diffusion coefficient and the partition coefficient. In other words, the α_{lump} values differ only on account of the values of A and k ($\alpha_{lump} \sim A\ k^{1/2}$). As the characteristics of the expanded schist used in this study are roughly similar to those of the patented medium (Biosorbens™) used in [17] in terms of specific surface area (Table 2), it can be concluded that the biofilms developed on both materials should present similarities in terms of microbial ecosystems and biodegradation kinetics. The results of the present study and those of Shareefdeen can be compared with the data reported in Oyarzun *et al*. [3]. Using a biofiltration system filled with peat as a solid support inoculated with *Thiobacillus thioparus*, these authors studied the performance of a biofilter treating H_2S at an inlet concentration of 257 ppmv for three different EBRTs (26, 52 and 120 s). From their data, it is possible to calculate that the value of the α_{lump} parameter for peat was 0.12 s^{-1}. This is 40% lower than the value obtained for the expanded schist coupled with UP20. As $\alpha_{lump} \sim A\ k^{1/2}$, this result may seem surprising at first sight. However, it should be noted that the intrinsic value of the specific surface area must be considered cautiously because the whole surface developed by the solid is not necessarily available for the development of the biofilm. Thus, whereas the specific surface area of peat is 705 $m^2\ g^{-1}$ [21], i.e. 14 times higher than that of schist (Table 2), the value of the α_{lump} parameter is lower for peat than for schist, which cannot be solely due to different values of k. Although the physical properties of the packing material are important, this result highlights that the overall properties of the packed bed have to be taken into account. The calculation of the specific surface area of biofilm covering the packing material is given below.

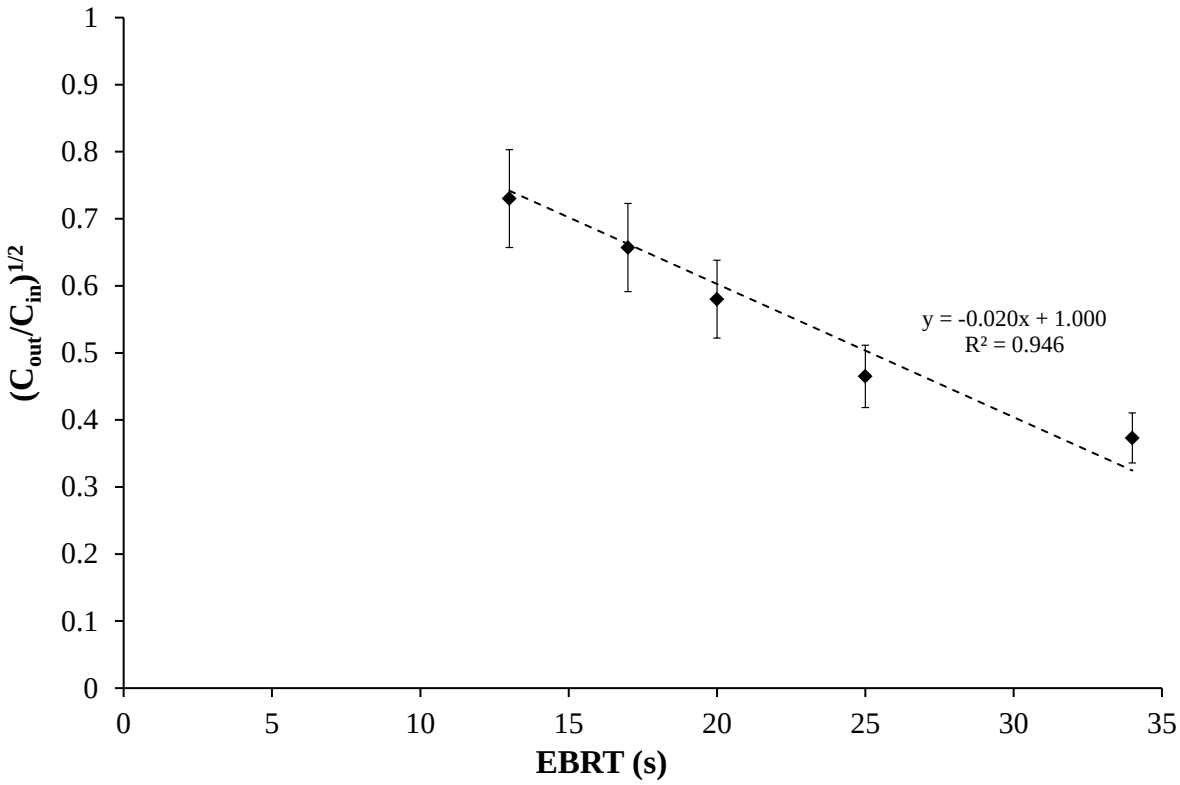

Fig. 4. Predicting the biofiltration process according to the Ottengraf model (Eq. 10).

Secondly, the parameter α_{lump} can be calculated from Eq. (11) by drawing the graph $(1-EC/LR)^{1/2}$ versus $(EBRT/LR)^{1/2}$. The line is similar to that reported in Figure 4, but the value of α_{lump} corresponding to the slope of the line was 26.4 ± 2.6 $g^{1/2}$ $m^{-3/2}$ h^{-1} according to the units used in this case (EC and LR in (g $m^{-3}_{packing\ material}$ h^{-1}) and EBRT in (h)). This method is useful because the α_{lump} value determined in this case enables the performances of the biofilter as a whole to be characterized whatever its composition (mixture or layers of different packing materials) and whatever the EBRT. Consequently, the value of α_{lump} can be compared with data reported in the literature (Table 4). It appears that the result obtained for the biofilter filled with expanded schist topped with a thin layer of UP20 is significantly higher than the results obtained for other packing materials, even those recorded with peat, considered the reference for H_2S biofiltration.

Table 4. Values of the α_{lump} parameter reported in [21]

Packing material	**α_{lump} ($g^{1/2}$ $m^{-3/2}$ h^{-1})**
Sapwood	7.9
Sapwood-UP20 (2 layers)	8.4
Pine bark	11.4
Pozzolan-UP20	11.9
Peat	15.3
Peat-UP20 (2 layers)	15.9
Peat-UP20 (mixed)	21.3
Expanded schist-UP20 (2 layers) *This study*	26.4 ± 2.6

The physical properties of the expanded schist, i.e. suitable particle size, void fraction and surface available for biomass attachment, largely explain this result. The specific surface area of biofilm covering the packing material can be estimated from Eq. (9). From the literature data, the diffusion coefficient of H_2S in the biofilm is D = 5.796 10^{-6} m^2 h^{-1} and the partition coefficient of H_2S between the gas and the liquid phase is m = 0.387 [47]. Based on the experimental EC values given in Figure 3 (from 10 to 20 g $m^{-3}_{packing\ material}$ h^{-1}), the reaction rate per unit of volume of the biofilm k can be calculated using the relationship given in Ottengraf and Van Den Oever [24]:

$$k = \frac{EC}{(1-\varepsilon)\left[1-\left(1-\frac{2\,\delta}{d}\right)^3\right]} \quad (12)$$

The porosity ε of the packed bed composed of pieces of expanded schist with an average particle diameter of 10 mm was determined to be 0.41 during the biofiltration of H_2S [14]. Assuming a biofilm thickness of around 100 μm, which seems very reasonable, the k values range from 300 to 580 g $m^{-3}_{biofilm}$ h^{-1} and hence the values of the specific surface area of the biofilm are from 600 to 400 $m^2_{biofilm}$ $m^{-3}_{packing\ material}$, respectively. These results are consistent with the estimated specific surface area of round particles, 10 mm in diameter [48]. However, although such values are of the order of magnitude of the expected results, the Ottengraf model is not adapted to obtain accurate values of biofilm specific surface area. Other models based on pressure drop measurements could be used to refine the results [14,48,49]. Nonetheless, it can be concluded that the Ottengraf model, through the determination of α_{lump}, is a powerful tool to describe simply the operation of a highly complex system such as a biofilter. Moreover, it can be used to design such bioreactors. For instance, from the α_{lump} value, the critical value of the elimination capacity (EC_{crit}) can be determined using Eq. (13) deduced from Eq. (11). This parameter corresponds to the value at which the loading rates exceed the elimination capacities of the biofilter, generating removal efficiencies less than 100%.

$$EC_{crit} = \alpha_{lump}^2 \; EBRT \quad (13)$$

The determination of the inlet concentration corresponding to EC_{crit} is obtained using Eq. (14) deduced from Eq. (10):

$$C_{in} = \alpha_{lump}^2 \; EBRT^2 \quad (14)$$

Figure 5 gives an overview of the ability of a biofilter filled with expanded schist completed with a thin layer of UP20 to treat efficiently (RE = 100%) a waste gas loaded with H_2S. As can be observed, for an EBRT higher than 30 s, the biofilter can treat inlet gas concentrations higher than 50 mg m^{-3}, which are higher than those encountered in many industrial applications. Consequently, this result usefully completes the data previously reported about biofiltration using expanded schist as the packing material [15,18,20].

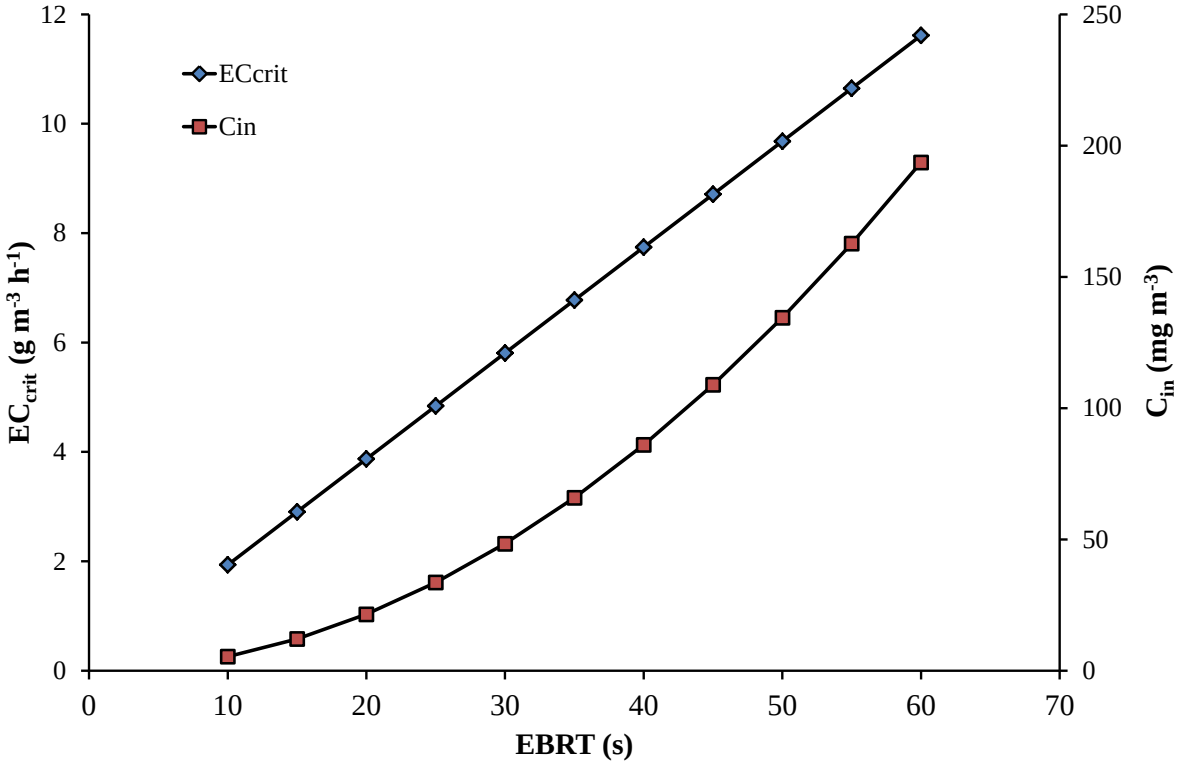

Fig. 5. Determination of the critical value of the elimination capacity (EC_{crit}) according to EBRT for a biofilter filled with expanded schist completed with a thin layer of UP20. Determination of the corresponding inlet gas concentration (H_2S).

5. Conclusion

The biological removal of H_2S in waste gas at a constant concentration (100 ppmv) was carried out using a biofilter packed with expanded schist and topped with a layer of a synthetic nutritional material (UP20). The effect of EBRT on the removal efficiencies of hydrogen sulfide was underlined. At EBRT > 51 s, H_2S was totally removed, whereas when the EBRT decreased, the removal efficiency decreased. From the EBRT results, the Ottengraf model equations were used to evaluate the performance of a biofilter. The parameter α_{lump} deduced from the Ottengraf model was used to compare the performance of expanded schist coupled with UP20 with that of other materials reported in the literature. In this study, the value of α_{lump} for expanded schist coupled with UP20 was found to be 26.4 $g^{1/2}$ $m^{-3/2}$ h^{-1}. This value, which enables the performance of the biofilter as a whole to be characterized whatever its composition (mixture or layers of different packing materials) and whatever the EBRT, is higher than those obtained for other packing materials (natural or synthetic) reported in the literature. Finally, the α_{lump} parameter, determined from Eq. (11) using EC and LR in (g $m^{-3}_{packing\ material}$ h^{-1}) and EBRT in (h), appears to be a powerful tool to compare unambiguously the packing materials used in biofiltration.

References

[1] R. Asano, K. Hirooka, Y. Nakai, Middle-thermophilic sulfur-oxidizing bacteria Thiomonas sp. RAN5 strain for hydrogen sulfide removal, J Air Waste Manag Assoc. 62 (2012) 38–43.

[2] E.Y. Lee, K.-S. Cho, H.W. Ryu, Characterization of sulfur oxidation by an autotrophic sulfur oxidizer, Thiobacillus sp. ASWW-2, Biotechnol. Bioprocess Eng. 5 (2000) 48–52. doi:10.1007/BF02932353.

[3] P. Oyarzún, F. Arancibia, C. Canales, G.E. Aroca, Biofiltration of high concentration of hydrogen sulphide using Thiobacillus thioparus, Process Biochemistry. 39 (2003) 165–170. doi:10.1016/S0032-9592(03)00050-5.

[4] M. Syed, G. Soreanu, P. Falletta, P. Béland, Removal of Hydrogen sulfide from gas streams using biological processes – A review, in: Canadian Biosystems Engineering, 2006: pp. 2.1–2.14.

[5] Y. Andres, E. Dumont, C. Gerente, Characterization techniques of packing material colonization in gas biofiltration processes, Can. J. Civ. Eng. 36 (2009) 1895–1902. doi:10.1139/L09-143.

[6] M. Ben Jaber, B. Anet, A. Amrane, C. Couriol, T. Lendormi, P.L. Cloirec, et al., Impact of nutrients supply and pH changes on the elimination of hydrogen sulfide, dimethyl disulfide and ethanethiol by biofiltration, Chemical Engineering Journal. 258 (2014) 420–426. doi:10.1016/j.cej.2014.07.085.

[7] J.L.R.P. Filho, L.T. Sader, M.H.R.Z. Damianovic, E. Foresti, E.L. Silva, Performance evaluation of packing materials in the removal of hydrogen sulphide in gas-phase biofilters: Polyurethane foam, sugarcane bagasse, and coconut fibre, Chemical Engineering Journal. 158 (2010) 441–450. doi:10.1016/j.cej.2010.01.014.

[8] Y. Yang, E.R. Allen, Biofiltration Control of Hydrogen Sulfide 1. Design and Operational Parameters, Air & Waste. 44 (1994) 863–868. doi:10.1080/1073161X.1994.10467287.

[9] Y. Yang, E.R. Allen, Biofiltration Control of Hydrogen Sulfide 2. Kinetics, Biofilter Performance, and Maintenance, Air & Waste. 44 (1994) 1315–1321. doi:10.1080/10473289.1994.10467328.

[10] Y. Andres, E. Dumont, P.L. Cloirec, E. Ramirez-Lopez, Wood Bark as Packing Material in a Biofilter used for Air Treatment, Environmental Technology. 27 (2006) 1297–1301. doi:10.1080/09593332708618747.

[11] C. Rattanapan, D. Kantachote, R. Yan, P. Boonsawang, Hydrogen sulfide removal using granular activated carbon biofiltration inoculated with Alcaligenes faecalis T307 isolated from concentrated latex wastewater, International Biodeterioration & Biodegradation. 64 (2010) 383–387. doi:10.1016/j.ibiod.2010.04.005.

[12] H. Duan, L.C.C. Koe, R. Yan, X. Chen, Biological treatment of H2S using pellet activated carbon as a carrier of microorganisms in a biofilter, Water Research. 40 (2006) 2629–2636. doi:10.1016/j.watres.2006.05.021.

[13] M. Ramírez, F. Almenglo, J.M. Gómez, D. Cantero, Pilot-scale biotrickling filter for hydrogen sulfide removal from biogas under continuous discharge flow, New Biotechnology. 31, Supplement (2014) S118–S119. doi:10.1016/j.nbt.2014.05.1900.

[14] E. Dumont, L.M. Ayala Guzman, M.S. Rodríguez Susa, Y. Andrès, H2S biofiltration using expanded schist as packing material: performance evaluation and packed-bed tortuosity assessment, J. Chem. Technol. Biotechnol. 87 (2012) 725–731. doi:10.1002/jctb.3713.

[15] A.C. Romero Hernandez, M.S. Rodríguez Susa, Y. Andrès, E. Dumont, Steady- and transient-state H2S biofiltration using expanded schist as packing material, New Biotechnology. 30 (2013) 210–218. doi:10.1016/j.nbt.2012.07.003.
[16] Z. Shareefdeen, B. Herner, D. Webb, S. Wilson, Hydrogen sulfide (H2S) removal in synthetic media biofilters, Environ. Prog. 22 (2003) 207–213. doi:10.1002/ep.670220319.
[17] Z. Shareefdeen, Hydrogen sulfide (H2S) removal using schist packings in industrial biofilter applications, Korean J. Chem. Eng. 32 (2015) 15–19. doi:10.1007/s11814-014-0349-z.
[18] A. Courtois, Y. Andrès, É. Dumont, H2S biofiltration using expanded schist as packing material: influence of packed bed configurations at constant EBRT, J. Chem. Technol. Biotechnol. 90 (2015) 50–56. doi:10.1002/jctb.4456.
[19] E. Dumont, Y. Andrès, P. Le Cloirec, F. Gaudin, Evaluation of a new packing material for H2S removed by biofiltration, Biochemical Engineering Journal. 42 (2008) 120–127. doi:10.1016/j.bej.2008.06.012.
[20] M. Ben Jaber, A. Couvert, A. Amrane, F. Rouxel, P. Le Cloirec, E. Dumont, Biofiltration of high concentration of H2S in waste air under extreme acidic conditions, New Biotechnology. 33 (2016) 136–143. doi:10.1016/j.nbt.2015.09.008.
[21] E. Dumont, Y. Andrès, Evaluation of innovative packing materials for the biodegradation of H2S: a comparative study, J. Chem. Technol. Biotechnol. 85 (2010) 429–434. doi:10.1002/jctb.2334.
[22] J.S. Devinny, M.A. Deshusses, T.S. Webster, Biofiltration for Air Pollution Control, CRC Press, 1999.
[23] M.A. Deshusses, Z. Shareefdeen, Modeling of biofilters and biotrickling filters for odor and VOC control applications, in: Biotechnology for Odor and Air Pollution Control, Shareefdeen/Singh (Eds.), Springer Science & Business Media, 2005: pp. 213–231.
[24] S.P.P. Ottengraf, A.H.C. Van Den Oever, Kinetics of organic compound removal from waste gases with a biological filter, Biotechnol. Bioeng. 25 (1983) 3089–3102. doi:10.1002/bit.260251222.
[25] M.A. Deshusses, P.D.G. Hamer, The removal of volatile ketone mixtures from air in biofilters, Bioprocess Engineering. 9 (1993) 141–146. doi:10.1007/BF00389921.
[26] G. Leson, A.M. Winer, Biofiltration: An Innovative Air Pollution Control Technology For VOC Emissions, Journal of the Air & Waste Management Association. 41 (1991) 1045–1054. doi:10.1080/10473289.1991.10466898.
[27] W. Limpaseni, N. Rattanamuk, Removal of hydrogen sulfide using upflow and downflow biofilters, Universidade da Coruña, 2007. http://ruc.udc.es/dspace/handle/2183/12819 (accessed January 10, 2016).
[28] I. Omri, H. Bouallagui, F. Aouidi, J.-J. Godon, M. Hamdi, H2S gas biological removal efficiency and bacterial community diversity in biofilter treating wastewater odor, Bioresource Technology. 102 (2011) 10202–10209. doi:10.1016/j.biortech.2011.05.094.
[29] T. Hartikainen, P.J. Martikainen, M. Olkkonen, J. Ruuskanen, Peat Biofilters in Long-Term Experiments for Removing Odorous Sulphur Compounds, Water, Air, & Soil Pollution. 133 (2002) 335–348. doi:10.1023/A:1012966705004.
[30] Y.-L. Ma, B.-L. Yang, J.-L. Zhao, Removal of H2S by Thiobacillus denitrificans immobilized on different matrices, Bioresource Technology. 97 (2006) 2041–2046. doi:10.1016/j.biortech.2005.09.023.
[31] A. Barona, A. Elías, R. Arias, I. Cano, R. González, Biofilter response to gradual and sudden variations in operating conditions, Biochemical Engineering Journal. 22 (2004) 25–31. doi:10.1016/j.bej.2004.07.006.

[32] A. Elias, A. Barona, A. Arreguy, J. Rios, I. Aranguiz, J. Peñas, Evaluation of a packing material for the biodegradation of H2S and product analysis, Process Biochemistry. 37 (2002) 813–820. doi:10.1016/S0032-9592(01)00287-4.
[33] H. Duan, L.C.C. Koe, R. Yan, X. Chen, Biological treatment of H2S using pellet activated carbon as a carrier of microorganisms in a biofilter, Water Research. 40 (2006) 2629–2636. doi:10.1016/j.watres.2006.05.021.
[34] C. Rattanapan, P. Boonsawang, D. Kantachote, Removal of H2S in down-flow GAC biofiltration using sulfide oxidizing bacteria from concentrated latex wastewater, Bioresource Technology. 100 (2009) 125–130. doi:10.1016/j.biortech.2008.05.049.
[35] X. Jiang, R. Yan, J.H. Tay, Reusing H2S-exhausted carbon as packing material for odor biofiltration, Chemosphere. 73 (2008) 698–704. doi:10.1016/j.chemosphere.2008.07.004.
[36] Z.M. Shareefdeen, Development of a biofilter media for removal of hydrogen sulphide, Global Nest Journal. 11 (2009) 218–222.
[37] E.Y. Lee, N.Y. Lee, K.-S. Cho, H.W. Ryu, Removal of hydrogen sulfide by sulfate-resistant Acidithiobacillus thiooxidans AZ11, Journal of Bioscience and Bioengineering. 101 (2006) 309–314. doi:10.1263/jbb.101.309.
[38] S.M. Mehdinia, P.A. Latif, H. Taghipour, A comparative evaluation of dried activated sludge and mixed dried activated sludge with rice husk silica to remove hydrogen sulfide, Iranian J Environ Health Sci Eng. 10 (2013) 22. doi:10.1186/1735-2746-10-22.
[39] H.-W. Ryu, S.-K. Yoo, J.M. Choi, K.-S. Cho, D.K. Cha, Thermophilic biofiltration of H2S and isolation of a thermophilic and heterotrophic H2S-degrading bacterium, Bacillus sp. TSO3, Journal of Hazardous Materials. 168 (2009) 501–506. doi:10.1016/j.jhazmat.2009.02.046.
[40] J.H. Kim, E.R. Rene, H.S. Park, Biological oxidation of hydrogen sulfide under steady and transient state conditions in an immobilized cell biofilter, Bioresource Technology. 99 (2008) 583–588. doi:10.1016/j.biortech.2006.12.028.
[41] P.A. Jennings, V.L. Snoeyink, E.S.K. Chian, Theoretical model for a submerged biological filter, Biotechnol. Bioeng. 18 (1976) 1249–1273. doi:10.1002/bit.260180906.
[42] Z.M. Shareefdeen, A biofilter design tool for hydrogen sulfide removal calculations, Clean Techn Environ Policy. 14 (2012) 543–549. doi:10.1007/s10098-011-0414-9.
[43] E. Dumont, F.D.S. Cabral, P. Le Cloirec, Y. Andrès, Biofiltration using peat and a nutritional synthetic packing material: influence of the packing configuration on H2S removal, Environmental Technology. 34 (2013) 1123–1129. doi:10.1080/09593330.2012.736691.
[44] F. Gaudin, Y. Andres, P. Le Cloirec, Packing material formulation for odorous emission biofiltration, Chemosphere. 70 (2008) 958–966. doi:10.1016/j.chemosphere.2007.08.014.
[45] Y.-C. Chung, C. Huang, Operation optimization of Thiobacillus thioparus CH11 biofilter for hydrogen sulfide removal, Journal of Biotechnology. 52 (1996) 31–38. doi:10.1016/S0168-1656(96)01622-7.
[46] B. Anet, C. Couriol, T. Lendormi, A. Amrane, P.L. Cloirec, G. Cogny, et al., Characterization and Selection of Packing Materials for Biofiltration of Rendering Odorous Emissions, Water Air Soil Pollut. 224 (2013) 1–13. doi:10.1007/s11270-013-1622-1.
[47] S. Kim, M.A. Deshusses, Development and experimental validation of a conceptual model for biotrickling filtration of H2S, Environ. Prog. 22 (2003) 119–128. doi:10.1002/ep.670220214.
[48] C. Alonso, M.T. Suidan, G.A. Sorial, F.L. Smith, P. Biswas, P.J. Smith, et al., Gas treatment in trickle-bed biofilters: Biomass, how much is enough?, Biotechnol. Bioeng.

54 (1997) 583–594. doi:10.1002/(SICI)1097-0290(19970620)54:6<583::AID-BIT9>3.0.CO;2-F.
[49] F. Morgan-Sagastume, B.E. Sleep, D.G. Allen, Effects of Biomass Growth on Gas Pressure Drop in Biofilters, Journal of Environmental Engineering. 127 (2001). doi:10.1061/(ASCE)0733-9372(2001)127:5(388).