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# Biofiltration using peat and a nutritional synthetic packing material: influence of the packing configuration on H<sub>2</sub>S removal

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This study aims to evaluate the feasibility of using a nutritional synthetic material (UP20) combined with fibrous peat as a packing material in treating H<sub>2</sub>S (up to 280 ppmv). Three identical laboratory-scale biofilters with different packing material configurations (peat only; peat + UP20 in a mixture; peat + UP20 in two layers) were used to determine the biofilter performances. The superficial velocity of the polluted gas on each biofilter was 65 m/h (gas flow rate 0.5 Nm<sup>3</sup>/h) corresponding to an empty bed residence time = 57 s. Variations in elimination capacity, removal efficiency, temperature and pH were tracked during 111 d. A removal efficiency of 100% was obtained for loading rates up to 6 g/m<sup>3</sup>/h for the biofilter filled with 100% peat, and up to 10 g/m<sup>3</sup>/h for both biofilters using peat complemented with UP20. For higher loading rates (up to 25.5 g/m<sup>3</sup>/h), the configuration of peat-UP20 in a mixture provided the best removal efficiencies (around 80% compared to 65% for the configuration of peat-UP20 in two layers and 60% for peat only). Microbial characterization highlighted that peat is able to provide sulfide-oxidizing bacteria. Through kinetic analysis (Ottengraf and Michaelis-Menten models were applied), it appeared that the configuration peat-UP20 in two layers (80/20 v/v) did not show significant improvement compared with peat alone. Although the configuration of peat-UP20 in a mixture (80/20 v/v) offered a real advantage in improving H<sub>2</sub>S treatment, it was shown that this benefit was related to the bed configuration rather than the nutritional properties of UP20.

**Keywords:** biofiltration; packing material; fibrous peat; H<sub>2</sub>S; nutrients

## Introduction

Industrial activities, wastewater treatment plants and agricultural waste disposal can generate malodorous effluents. In the case of low concentrations, and high flow rates, these can be treated by biological processes like biofiltration in which fibrous peat is usually used as the packing material [1–4]. Peat is composed of vegetable fibres, which have a high surface area allowing a good water retention capacity, sufficient nutrient release for microbial growth and acceptable hydrodynamic properties. However, some waste gas streams contain only some of the nutrients needed for microorganism growth (nitrogen, phosphorus, potassium) leading to inefficient biofiltration. With a view to optimizing the biofiltration process, a nutritional synthetic material (UP20) has been developed. Previous studies have demonstrated that this synthetic material could offer a real advantage in the treatment of H<sub>2</sub>S at relatively high pollutant concentrations by providing nutrients to the microbial biomass and a buffering effect [5–7]. Recently, other nutritional synthetic packing materials have been developed in order to improve biofiltration performances [8–10]. However, these were produced to replace completely the natural

filter materials traditionally used (peat, wood bark, compost, soil). As biofiltration must remain as cheap as possible, it seems more economical to supplement a peat biofilter, whose biofiltration performances are well known, with a small amount of a nutritional packing material. The addition of a solid nutritional packing material could also improve the mechanical behaviour over a long period (limiting the bed compaction and the pressure drops). In this way, the aim of the present work was to characterize the ability of UP20 to improve the performance of a biofilter using fibrous peat. First, the characterization of the materials (peat and UP20) in terms of bulk density, water retention capacity and elementary composition was carried out. Secondly, the combination of peat + UP20 was tested in three laboratory-scale biofilters (BF1–BF3) for H<sub>2</sub>S treatment. BF1 was filled with 100% peat (in order to have a reference). BF2 was filled with peat and UP20 stratified in two layers (80/20 v/v). This configuration was chosen because it could be easily adapted to a large scale. BF3 contained peat mixed with UP20 (80/20 v/v). In this configuration, the presence of the UP20 could limit the compaction of the peat bed during the running operation. The microbial characterization of the

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packing material was carried out and the removal capacity of H<sub>2</sub>S was determined in order to compare critically the results from the three biofilters.

## Materials and methods

### Packing materials

The fibrous peat used in this study was purchased from the company ‘La Florentaise’ (44850 Saint-Mars-du-Désert, France, www.florentaise.fr). Its chemical composition, determined using an elemental analyzer (Flash 1112 Series EA Thermofisher Scientific), was: C 50.2%, O 33%, H 6.0%, N 0.8% (organic content 90%).

UP20 is a synthetic material manufactured in our laboratory whose formulation was described in a previous paper [5]. The characteristics of this material are its buffering effect and its nutrient content, making the addition of extra buffer and nutrient solutions unnecessary. UP20 contains CH<sub>4</sub>N<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>, CaCO<sub>3</sub> (C/N/P molar ratio: 100/5/1) and an organic binder (20% in mass) from the Elotex company (this is a white powder commonly used in the building industry and mainly constituted of ethylene and vinyl acetate). The biodegradability of UP20 was evaluated for more than one year and no biodegradation was observed [5]. UP20 was extruded into a cylindrical shape according to the procedure described in [5]. The dimensions of the granules were 7 mm in diameter and 15 mm in length (average length calculated from a sample of 50 granules).

Table 1 presents some characteristics of the peat and UP20 materials. Specific surface area and density were measured by mercury intrusion porosimetry (Micromeritics AutoPore IV 9500). Table 1 indicates that both peat and UP20 have low H<sub>2</sub>S sorption capacities. In comparison, the sorption capacity of pine bark is 110 mg/kg [6] while Barona *et al.* obtained a value close to 370 mg/kg for activated carbon [11]. Consequently, the non-biological removal of the pollutant will be very low and it is assumed that H<sub>2</sub>S will be directly transferred from the gas phase to the water phase in order to be transformed by the microorganisms.

Table 1. Some characteristics of fibrous peat and UP20 material.

	Fibrous peat	UP20 [1]
Density (kg/m <sup>3</sup> )	270	920
Bulk density (kg/m <sup>3</sup> )	107	560
Water retention capacity (% by weight)	250	47
pH	4.5	8.1
Maximal sorption capacity (mg H <sub>2</sub> S/kg dry support)	2	5

### Experimental set-up

The experimental equipment used in this work is shown in Figure 1. Three biofilters were constructed with plastic cylinders (1.5 m in height and 0.1 m in diameter). Biofilter No. 1 (BF1) was packed with 100% fibrous peat (0.84 kg;  $H = 1\text{m}; V = 7.85\text{ L}$ ; left column in Figure 1(a)). Biofilter No. 2 (BF2) was filled with peat (0.67 kg) topped up with UP20 (0.88 kg) corresponding to an 80/20 volume ratio ( $H = 0.8 + 0.2\text{ m}; V = 7.85\text{ L}$ ; right column in Figure 1(a)). Biofilter No. 3 (BF3) was filled with fibrous peat (0.67 kg) mixed with UP20 (0.88 kg) corresponding to an 80/20 volume ratio ( $H = 1\text{ m}; V = 7.85\text{ L}$ ; middle column in Figure 1(a)). For each biofilter, the polluted air was introduced into the bottom of the column. The gas flow to be treated was obtained by mixing H<sub>2</sub>S (99.7% purity from the gas cylinder) with the air stream (Figure 1(b)). A 5850S Brooks mass flow controller controlled the H<sub>2</sub>S flow. The polluted air temperature in the biofilters ranged from 20 to 22°C. The superficial velocity of the polluted gas in the biofilters (empty bed) was 0.018 m/s (65 m/h) corresponding to  $Q = 0.5\text{ Nm}^3/\text{h}$  in flow rate (empty bed residence time =  $V/Q = 57\text{ s}$ ). Five sampling ports were located along the column, at 20 cm intervals from the bottom, for gas sampling and pressure measurements. The H<sub>2</sub>S concentration was measured using an Onyx 5220 device (Cosma France; accuracy 1%) whose calibration was performed daily from a gas standard. To maintain the bed humidity, tap water was sprayed for 5 min on the top of the column followed by a 20 min stand-by (corresponding to roughly 10 L/d). The packing materials were neither inoculated with washed activated sludge nor acclimatized to treat H<sub>2</sub>S in order to observe the ability of the UP20 to stimulate the biofilm development by providing nutrients on an excellent support. Apart from polluted air and UP20 material, no nutritive solution for feeding microorganisms was introduced into the biofilters.

### Microbiological identification

The sampling of packed material was done in duplicate on the raw material before use, and after 35 and 91 d. The sampling locations (BF1 and BF2) were at 30 cm from the bottom for the peat and at 80 cm from the bottom for UP20 (Figure 1). The microorganisms were collected by mixing and shaking a known mass of packing material in 100 mL of sterile NaCl solution (9 g/L) for 17 h. The microbial enumeration was carried out by the counting plate method using Nutrient agar (Biokar) for the bacterial population, dichloran rose bengal chlortetracycline agar (Biokar) for fungi and Starkey medium for sulfide-oxidizing bacteria (SOB). From the petri dish the most predominate colonies were isolate and sub cultivate in pure culture. The Microseq<sup>®</sup> analysis was used for microbial identification [12].

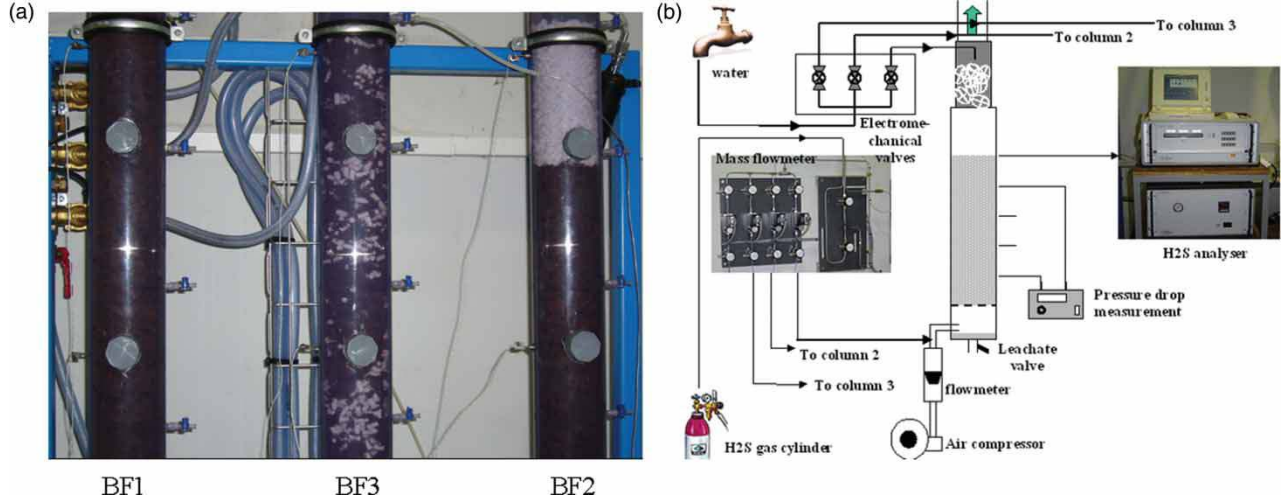


Figure 1. (a) Experimental pilot-scale biofilters. From left to right: BF1: peat alone; BF3: peat mixed with UP20 (80/20 v/v); BF2: peat and UP20 stratified in two layers (80/20 v/v). (b) Schematic diagram of the biofilter system for H<sub>2</sub>S treatment.

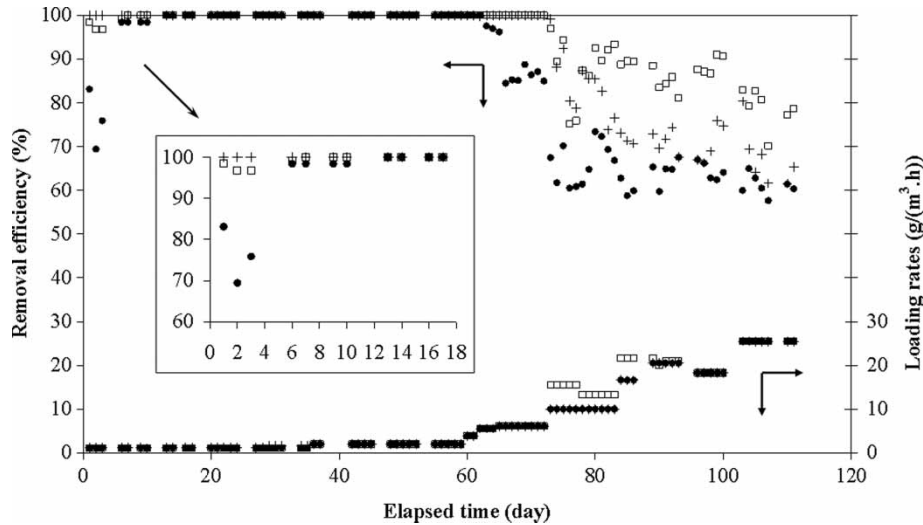


Figure 2. Removal efficiency and loading rates versus elapsed time for the three pilot-scale biofilters (●: BF1 (100% peat); □: BF2 (peat/UP20 stratified in two layers); +: BF3 (peat/UP20 mixed)).

## Results and discussion

### Effect of H<sub>2</sub>S loading rate

The three biofilters were operated continuously for 111 d. The removal capacities (RC; Equation (1); g/m<sup>3</sup>/h) and the removal efficiencies (RE; Equation (2); %) were calculated according to the loading rates (LR; Equation (3); g/m<sup>3</sup>/h) used in this study (increased from 1.1 to 25.5 g/m<sup>3</sup>/h).

$$RC = \frac{Q}{V}(C_{in} - C_{out}) \quad (1)$$

$$RE = 100 \frac{C_{in} - C_{out}}{C_{in}} \quad (2)$$

$$LR = \frac{Q}{V}C_{in} \quad (3)$$

Figure 2 presents the changes in RE and LR versus time for the three biofilters whereas Figure 3 summarizes the

changes in removal capacities versus LR. Both these figures are completed with Figure 4 presenting the change in the pH in the leachate versus time. Three main comments can be made from these figures: (I) the acclimation time of the microorganisms for H<sub>2</sub>S removal ranged from 2 d for the peat-UP20 in a mixture to 13 d for 100% peat (7 d for the peat-UP20 in two layers). As the 3 biofilters were identically fed with tap water, these different results can be attributed to the presence of UP20. As UP20 has to stimulate microbial activity by dissolving nutrients in the packed bed, the 100% removal during the first days was probably not due to biodegradation; physical interactions could take place between the gas and UP20 (such as (i): absorption into water film around packing materials, (ii): adsorption onto UP20 surface and (iii): acid-base reactions between H<sub>2</sub>S and UP20 reactive grains). (II) After the adaptation period of the microorganisms, the three biofilters

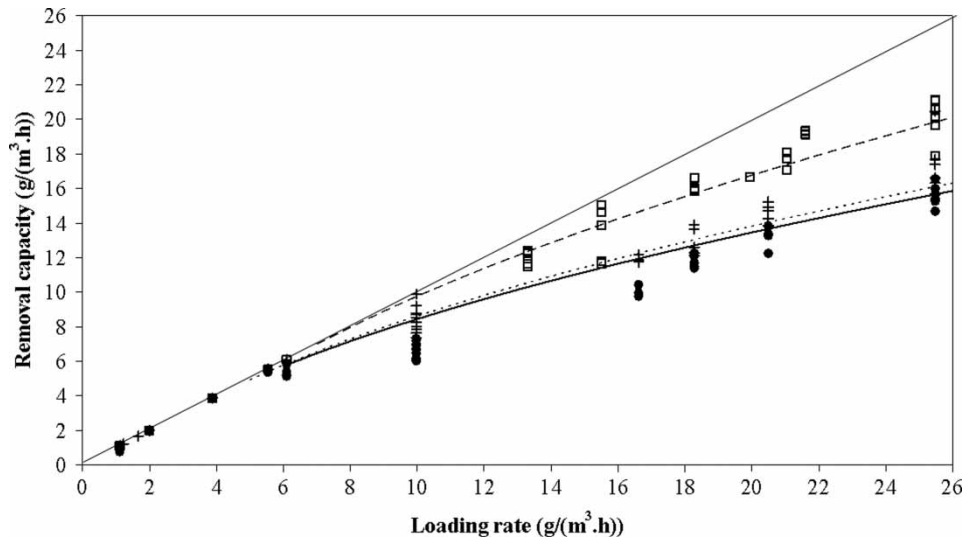


Figure 3. Removal capacity versus loading rate for the three pilot-scale biofilters (experimental points (●: BF1 (100% peat); □: BF2 (peat/UP20 stratified in two layers); +: BF3 (peat/UP20 mixed)) and Ottengraf model - dashed line).

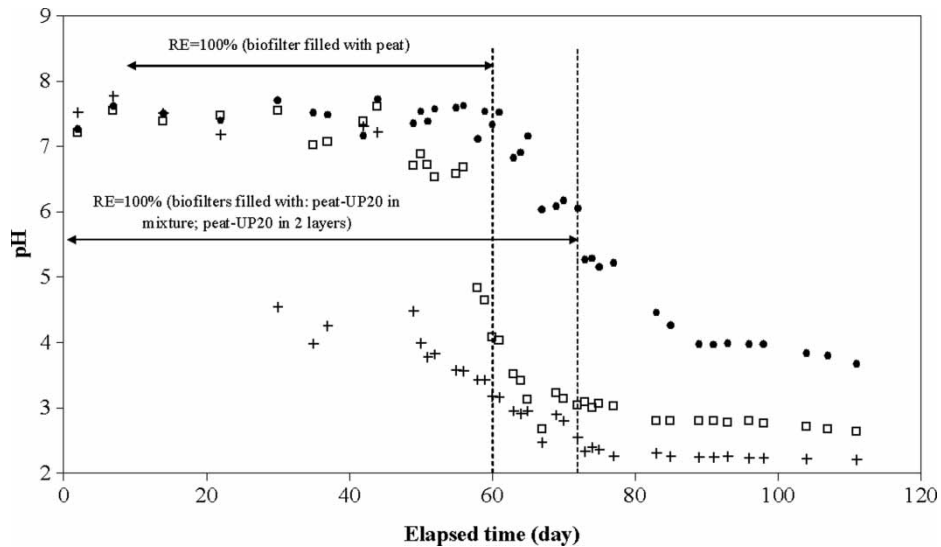


Figure 4. pH versus loading rate for the three pilot-scale biofilters (●: BF1 (100% peat); □: BF2 (peat/UP20 stratified in two layers); +: BF3 (peat/UP20 mixed)).

were able to degrade 100% of the incoming  $H_2S$  when the LR was less than  $5 \text{ g/m}^3/\text{h}$ . Considering the change in pH in the leachate versus time for the three biofilters, the curves show a similar trend but are out of phase. The drop in pH is due to the biodegradation of  $H_2S$ , which produces mainly  $H^+$ , elemental sulfur, sulfate and thiosulfate [13]. However, in biological process, there is a wide variety of SOB, each of the bacteria having its specific sulfide-oxidizing pathway [14]. Generally, sulfide is firstly converted into elemental sulfur particles as an intermediate in the oxidation of hydrogen sulfide to sulfate [14]. The presence of sulfur particles or sulfate (i.e. sulfur and sulfate selectivity) depends on the operating conditions, mainly sulfide load and dissolved oxygen. As observed on Figure 4, the presence of the UP20 material enhances the pH drop (the acidification

is faster for the mixing configuration), which indicates that UP20 improves the hydrogen sulfide oxidation to sulfate. The difference between both biofilters filled with UP20 can be explained by the bed configuration. As explained in the part 'biokinetic constants', the biofilm surface area is more developed in the mixing configuration, which enhances the sulfate production. (III) After 60 d of operation, the LR was progressively increased to  $25.5 \text{ g/m}^3/\text{h}$  by varying the inlet concentration. A noticeable decrease in the RE values was then observed for the biofilter filled with 100% peat for  $LR = 6 \text{ g/m}^3/\text{h}$  whereas both biofilters using peat-UP20 were able to retain a removal efficiency of 100% for LR up to  $10 \text{ g/m}^3/\text{h}$  confirming the ability of the UP20 to improve the biofilter performances (until the 72 d). The growth of microorganisms was confirmed by the change in

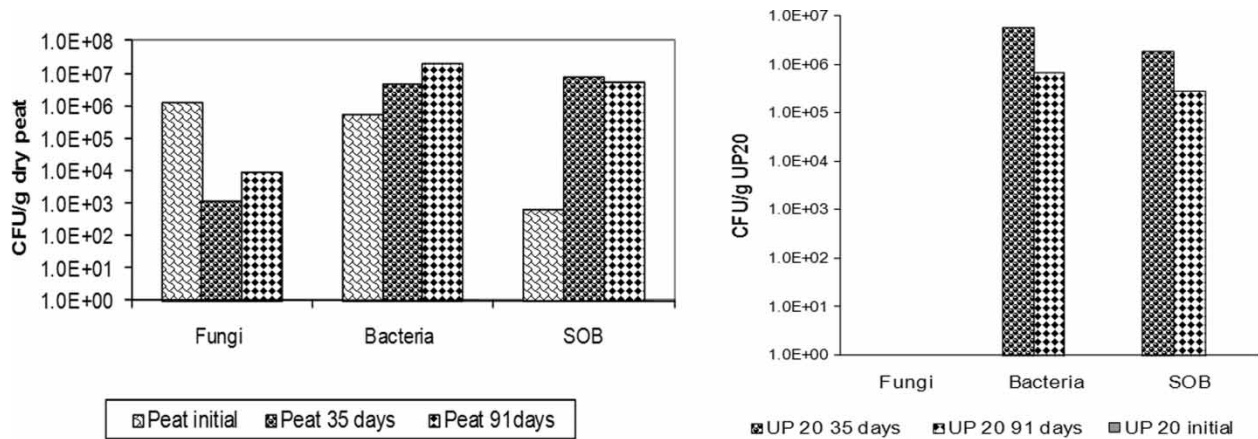


Figure 5. Changes in microorganism colonization in peat and in UP20 (the sampling locations were at 30 cm from the bottom for the peat and at 80 cm from the bottom for UP20)).

Table 2. Kinetic constants according to the Ottengraf model ( $K_1$ ) and the Michaelis-Menten model ( $V_m$ ;  $K_s$ ). (1) not calculated due to the difference in density of the two layers; (2) calculated using a pseudo-density of the mixture; (3) estimated value from peat density.

Packing material	$K_1$ ( $\text{g}_{\text{H}_2\text{S}}^{0.5}/\text{m}^{1.5}/\text{h}$ )	$K_s$ ( $\text{mg}/\text{m}^3$ )	$V_m$ ( $\text{g}_{\text{H}_2\text{S}}/\text{m}^3/\text{h}$ )
BF1: 100% peat	15.3	113.5	53.4
BF2: Peat-UP20; 2 layers	15.9	111.8	— <sup>(1)</sup>
BF3: Peat-UP20; mixture	21.3	89.2	55.3 <sup>(2)</sup>
Peat [20]	—	—	56 <sup>(3)</sup>
Peat [21]	—	—	55

the pH in the leachate, which dropped significantly with the LR increase (Figure 4). Using the synthetic inorganic media BIOSORBENS in similar operating conditions [8], Shareefdeen *et al.* observed the same pH drop. Similarly, Brennan *et al.* measured a pH drop from 7–6.5 to 4.8–3.6 after 3 weeks of  $\text{H}_2\text{S}$  and methylmercaptan treatment, while after 6 months the pH decreased to 2 [15]. The acidification of the medium could affect the removal efficiency but it was noted that biofiltration capacity was not affected until pH 3.2 [16].

As indicated in Figure 3, the configuration of peat-UP20 in a mixture presented the best removal efficiency for higher LR (around 80% for  $\text{LR} = 25.5 \text{ g}/\text{m}^3/\text{h}$ ). This result confirms that biofilters packed with peat are able to treat efficiently polluted gas loaded with high  $\text{H}_2\text{S}$  concentration. Equivalent performances are reported in the literature for peat [17] and for other organic media [8,18].

### Microbiological identification

Figure 5 shows the change in microorganisms (fungi, bacteria, SOB) present on the peat and on UP20 during  $\text{H}_2\text{S}$  biofiltration (BF1, BF2 and BF3). UP20 was initially measured but the found values were lower than the detection limits. This result highlights that peat is able to provide SOB. The main change on the peat corresponds to an increase in the number of SOB, which are bacteria directly involved in sulfide transformation. It is also

possible to follow a decrease in fungi. Moreover, bacteria, and more specifically the SOB, were able to colonize UP20 (it must be highlighted that the concentration of bacteria in UP20 is roughly 10 times lower than in the peat). Finally, the identification of the main bacterial species present on the packing material was not successful for the SOB colonies, but *Paenibacillus* sp., *Leifsonia* sp., *Aeromonas* sp., *Microbacterium* sp. and *Ochrobactrum* sp. were found.

### Biokinetic constants

The removal rate of  $\text{H}_2\text{S}$  in the immobilized cell biofilter was modelled using both an Ottengraf model [19] and a modified Michaelis-Menten model [20]. These kinetic constants, obtained from the experimental data, are a simple way to compare the behaviour of the three biofilter configurations. From the Ottengraf model, values of the overall parameter  $K_1$  ( $\text{g}_{\text{H}_2\text{S}}^{0.5}/\text{m}^{1.5}/\text{h}$ ), which gives a useful information about the biofilm surface area, can be obtained by linear regression of  $(C_{\text{out}}/C_{\text{in}})^{0.5}$  versus  $1/(C_{\text{in}})^{0.5}$  (Table 2). Using the modified Michaelis-Menten model, a maximum apparent removal rate ( $V_m$  in  $\text{mg}_{\text{H}_2\text{S}}/\text{kg}_{\text{dry material}}/\text{s}$ ) and a half-saturation constant ( $K_s$  in  $\text{mg}_{\text{H}_2\text{S}}/\text{m}^3$ ) can be obtained from a linear regression (Figure 6). The physical meaning of  $K_s$  corresponds to the  $\text{H}_2\text{S}$  concentration at which the reaction rate reaches half of its maximum value ( $V_m/2$ ). The values of  $V_m$  and  $K_s$ , determined from the experimental

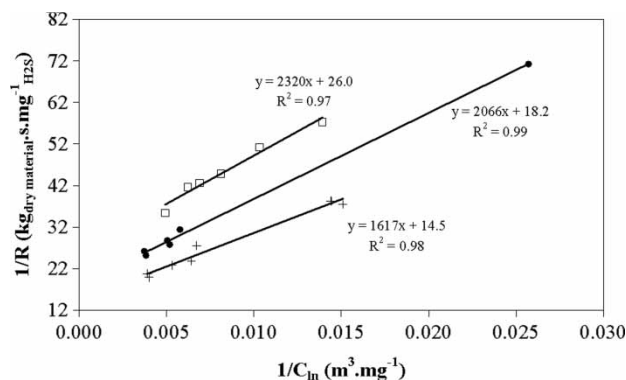


Figure 6.  $1/R$  versus  $1/C_{ln}$  according to the Michaelis-Menten model (●: BF1 (100% peat); □: BF2 (peat/UP20 stratified in two layers); +: BF3 (peat/UP20 mixed)).  $\frac{1}{R} = \frac{K_s}{V_m} \frac{1}{C_{ln}} + \frac{1}{V_m}$  and  $C_{ln} = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{in}}{C_{out}}\right)}$ .

data, are given in Table 2 (note that the same data were used for both models).

According to Table 2, it appears that the maximum apparent removal rate for 100% peat is around  $55 \text{ g/m}^3/\text{h}$ , which is in agreement with the literature data [20,21]. Moreover, Table 2 and Figure 3 show that both biofilters filled with 100% peat and peat-UP20 in two layers (BF1 and BF2) present a similar trend for  $\text{H}_2\text{S}$  degradation indicating that the configuration in layers is not the best choice to improve biofiltration performance (similar  $K_1$  values:  $15.9$  and  $15.3 \text{ g}_{\text{H}_2\text{S}}/\text{m}^{1.5}/\text{h}$ , which indicates that both biofilters have the same biofilm surface area). Conversely, the configuration of peat-UP20 in a mixture clearly demonstrates the advantage of using UP20. The  $K_1$  values ( $21.3$  against  $15.3 \text{ g}_{\text{H}_2\text{S}}/\text{m}^{1.5}/\text{h}$ ) reflect the increase in the removal capacity of BF3 (Figure 3) whereas the  $K_s$  values ( $89.2$  against  $113.5 \text{ mg/m}^3$ ) suggest that BF3 has a greater affinity for  $\text{H}_2\text{S}$  than both BF1 and BF2. However, it can be highlighted that this improvement cannot be attributed to the nutritional properties of UP20 since BF1 and BF2 presented similar performances. The difference observed between the two biofilters containing UP20 could be related to the increase of the biofilm surface area (+40% on the basis of  $K_1$  values). This increase can be related to the overall bed characteristics (change in tortuosity and porosity, for instance) because the presence of UP20 inside the fibrous peat bed limits the compaction effects. This explanation was confirmed with the help of pressure drop measurement. Whereas both biofilters presented the same pressure drop for a gas flow rate  $Q = 0.5 \text{ Nm}^3/\text{h}$  (around  $10 \text{ Pa/m}$ ), the difference between BF2 and BF3 appeared at a higher gas flow rate (for  $Q = 4 \text{ Nm}^3/\text{h}$ , the BF3 pressure drop was 30% higher than the BF2 pressure drop).

## Conclusion

The performance of three biofilters to treat  $\text{H}_2\text{S}$  at different LR was investigated in order to evaluate the capacity of a

synthetic packing material (UP20) to provide nutrients to the biofilm present in the biofilter. In comparison with peat alone, the configuration peat-UP20 in two layers (80/20 v/v) did not show significant improvement. Conversely, the configuration of peat-UP20 in a mixture (80/20 v/v) offered a real advantage in improving  $\text{H}_2\text{S}$  treatment. In this case, the RC were 100–80% at LR of 0–26  $\text{g}_{\text{H}_2\text{S}}/\text{m}^3/\text{h}$ . However, it was shown that the benefit of using a mixture of peat-UP20 was related to the bed configuration rather than the nutritional properties of UP20. Consequently, any other inert packing material could offer the same advantage in the same configuration. Clearly, the cheap and durable packing material, which can provide the nutrients required for biomass remains to be found or developed.

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