

Evaluation of a new packing material for H₂S removed by biofiltration

Eric Dumont, Yves Andres, Pierre Le Cloirec, François Gaudin

► **To cite this version:**

Eric Dumont, Yves Andres, Pierre Le Cloirec, François Gaudin. Evaluation of a new packing material for H₂S removed by biofiltration. *Biochemical Engineering Journal*, Elsevier, 2008, 42 (2), pp.120-127. 10.1016/j.bej.2008.06.012 . hal-00877844

HAL Id: hal-00877844

<https://hal-mines-nantes.archives-ouvertes.fr/hal-00877844>

Submitted on 2 Jul 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Evaluation of a new packing material for H₂S removed by biofiltration

E. Dumont^{a,*}, Y. Andrès^a, P. Le Cloirec^b, F. Gaudin^a

^a Ecole des Mines de Nantes, UMR CNRS 6144 GEPEA, 4 Rue Alfred Kastler, BP 20722, 44307 Nantes cedex 3, France

^b Ecole de Chimie de Rennes (ENSCR), UMR CNRS 6226, Sciences Chimiques, Campus de Beaulieu, Avenue du Général Leclerc, 35700 Rennes, France

This study aims to evaluate the feasibility of using a new packing material (UP20) in treating H₂S. Three identical laboratory-scale biofilters, filled with, respectively, UP20 alone, pine bark, and a configuration made of two layers of pozzolan/UP20 (80/20, v/v), were used for critical comparison. Various concentrations of H₂S (up to 100 ppmv) were used to determine the optimum biofilter performances. The superficial velocity of the polluted gas on each biofilter was 65 m h⁻¹ (0.018 m s⁻¹; gas flow rate 0.5 N m³ h⁻¹) corresponding to an empty bed residence time of 57 s. Changes in elimination capacity, removal efficiency, moisture content, temperature and pH were tracked during 95 days. The pressure drops along each biofilter were also measured by varying the gas flow rate from 0.5 to 4 N m³ h⁻¹. After 63 days of operation, the loading rate was significantly increased to 10 g m⁻³ h⁻¹ and the UP20 biofilter retained a removal efficiency of more than 93%, indicating a strong ability to stimulate microbial activity (compared to 69% for the pine bark biofilter and 74% for the biofilter filled with a configuration of two layers of pozzolan/UP20). A Michaelis–Menten type equation was applied and the maximum removal rate (V_m) and saturation constant (K_s) were calculated. V_m was evaluated at 35 g H₂S m⁻³ biofilter h⁻¹ for UP20 (14 and 15 g H₂S m⁻³ biofilter h⁻¹ for pine bark and pozzolan/UP20, respectively). The saturation constant K_s was 70 ppmv for UP20 (18 ppmv for pine bark and 20 ppmv for pozzolan/UP20) indicating that the new packing material will be effective in treating large pollutant concentrations. At low concentrations of pollutant, the results suggest that a biofilter with a configuration of two layers of pozzolan/UP20 is the most suitable choice for treating H₂S.

1. Introduction

Biofiltration is currently the most used biological gas treatment technology. It involves microorganisms immobilized in the form of a biofilm on a porous carrier such as peat, soil, compost, synthetic substances or combinations of these. Biofiltration has gained worldwide acceptance as an economical air pollution control technology for the treatment of gas streams containing low concentrations of biodegradable volatile organic and inorganic compounds [1]. The pollutant substances are transferred from the air flow to the biofilm developing on the organic substrate where they are degraded by microorganisms. The treatment of H₂S in a biofilter leads to sulphate, thiosulphate or elemental sulphur production according to the operating conditions and to the microorganisms involved [2–4]. Although the microbiological aspects are of major importance in understanding the operating mode of microorganisms in biofiltration, the heart of the process

could be the packing material, which must provide a favourable environment in terms of moisture, temperature, pH, nutrients and oxygen supply [4–6]. An ideal packing material should have the following characteristics [7]: (i) suitable particle size, void fraction and specific surface area, which indicate the surface available for biomass attachment; (ii) high nutritive capacity; (iii) high moisture retention capacity; (iv) high buffering capacity avoiding large pH fluctuations and (v) mechanically resistant, chemically inert and stable.

The most common packing materials are peat, soil and compost followed by wood bark, sugarcane bagasse [8] and peanut shells [5]. However, these materials lead to bed compression causing pressure drops and thus decreasing biofilter efficiency. Organic media also need to be replaced after 3–5 years, and they are difficult to regenerate [9]. Inorganic materials have also been studied. Metal oxides like porous ceramics, calcinated cristobalite [10] or perlite [11] have been used. However, their cost remains high and they do not provide any nutrients to the biomass. As for the geometrical characteristics of the material, it has been demonstrated that the best carrier must have a cylindrical shape [12,13].

Consequently, a new packing material, a cylindrical-shaped extrudate called UP20 (containing mainly calcium carbonate and an organic binder), has been developed in our laboratory for the treat-

* Corresponding author. Tel.: +33 2 51 85 82 66; fax: +33 2 51 85 82 99.
E-mail addresses: eric.dumont@emn.fr (E. Dumont), yves.andres@emn.fr (Y. Andrès), Pierre.le-cloirec@ensc-rennes.fr (P. Le Cloirec), francois.gaudin@emn.fr (F. Gaudin).

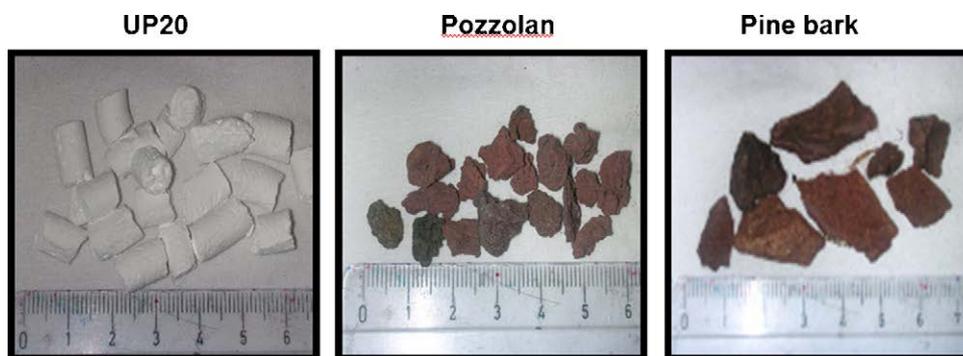


Fig. 1. Packing materials used.

ment of H_2S . The formulation of several new materials has been described in a previous work [7] and it has been demonstrated that the newly formulated UP20 offers a real advantage to the process at relatively high pollution concentration by providing both nutrients for the biomass and a buffering effect.

The main objective of this work is to investigate the removal of H_2S as a single pollutant in a biofilter packed with the new UP20 in terms of elimination capacity, removal efficiency, pH changes and pressure drops. The results are compared with two biofilters, one packed with pine bark and the other with a configuration made of pozzolan and UP20 stratified in two layers (80/20, v/v). Moreover, the kinetic constants are evaluated using a suitable mathematical model.

2. Materials and methods

2.1. Packing materials

UP20 material contains CH_4N_2O , H_3PO_4 , $CaCO_3$ (C/N/P molar ratio: 100/5/1) and an organic binder (20% in mass) from Elotex industry (it is a white powder commonly used in the building industry and mainly constituted of ethylene and vinyl acetate). UP20 has been extruded in a cylindrical shape according to the following procedure: first, the dry salt powders have been mixed in a container by shaking for 15 min; second, the organic binder has been introduced into water; third, the mixture of salt powders has been added to water. The amount of water was 66% of the dry salt mixture weight. Extrusion has been performed with a meat mincer and the granules have been dried at $50^\circ C$ for 20 h [7]. The dimensions of granules (Fig. 1) are 7 mm in diameter and 15 mm in length (average length calculated from a sample of 50 granules). Two others packing materials have been used for performance comparisons: pine bark and pozzolan (Fig. 1). Pine bark has been chosen for its good physical properties (low bed density) and very low price. It seemed interesting to compare the results obtained on the UP20 with those obtained on an organic material in operating conditions. Pozzolan is a volcanic siliceous rock, inert and relatively cheap. Its mechanical characteristics are very favourable for water filtration processes (low density, large porosity, large specific surface area and low ability to retain water). Pozzolan used in this study was mainly composed with SiO_2 (44%), Al_2O_3 (15%), Fe_2O_3 (15%) and CaO (10%) and appeared as irregular spherical beads with diameters ranging from 5 to 10 mm (Fig. 1). Pozzolan has been chosen in order to study a composite biofilter filled with an “ideal packing material”: an inert mineral material having good mechanical properties in association with a layer of UP20 providing the nutrients to the biomass.

Table 1 presents some characteristics of the three packing materials. The specific surface area (a_{vs}) and the density (ρ_{bulk}) were measured by mercury intrusion porosimetry (Micromeritics AutoPore IV 9500). It appears that the specific surface area of UP20 is the lowest: $705\text{ m}^2\text{ m}^{-3}$ against $1120\text{ m}^2\text{ m}^{-3}$ for pine bark and $1060\text{ m}^2\text{ m}^{-3}$ for pozzolan. Herrygers et al. [14] indicated that the specific surface area of filtering materials lies typically between 300 and $1000\text{ m}^2\text{ m}^{-3}$ indicating that UP20 has a sufficiently high specific surface area to be a medium for biofiltration. Table 1 also indicates the maximum H_2S sorption capacities for the three biofilter beds in dry conditions [7]. It is clear that UP20 and pozzolan have much lower H_2S sorption capacities than pine bark (110 mg kg^{-1}). In comparison, Barona et al. [15] obtained a value close to 370 mg kg^{-1} for activated carbon. Consequently, the non-biological removal of the pollutant will be very low and it is assumed that H_2S will be directly transferred from the gas phase to the water phase in order to be transformed by the microorganisms.

2.2. Experimental setup

The experimental equipment used in this work is shown in Fig. 2. Three biofilters were constructed with plastic cylinders (1.5 m in height and 0.1 m in diameter). The first biofilter was filled with 4.95 kg of UP20 ($H=1\text{ m}$; white material on the left column in Fig. 2a); the second biofilter was packed with 1.55 kg of pine bark (1 m) and the third biofilter was filled with 5.06 kg of pozzolan (0.8 m) topped with 1.02 kg of UP20 (0.2 m; Fig. 2a). 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_2S (99.7% purity from the gas cylinder) with the air stream (Fig. 2b). H_2S flow was controlled by a 5850S Brooks mass flow controller. The polluted air temperature in the biofilters ranged from 20 to $22^\circ C$. The superficial velocity of the polluted gas in the biofilter (empty bed) ranged from $U_0=0.018\text{--}0.142\text{ m s}^{-1}$ ($65\text{--}520\text{ m h}^{-1}$) corresponding to $Q=0.4\text{--}4\text{ N m}^3\text{ h}^{-1}$ in flow rate. Five sampling ports were located along the column, at 20 cm intervals from the bottom, for gas sampling and pressure measurements. The H_2S concentration was measured using an Onyx 5220 device (Cosma France). To maintain the bed humidity, tap water was sprayed for 1 h on the top of the column (corre-

Table 1
Some characteristics of the three packing materials

| | Specific surface area ($\text{m}^2\text{ m}^{-3}$) | Density (kg m^{-3}) | Maximal sorption capacity ($\text{mg H}_2\text{S kg}^{-1}$ dry support) |
|-----------|--|--------------------------------|--|
| UP20 | 705 | 920 | 5 |
| Pine bark | 1120 | 370 | 110 |
| Pozzolan | 1060 | 1500 | 7 |

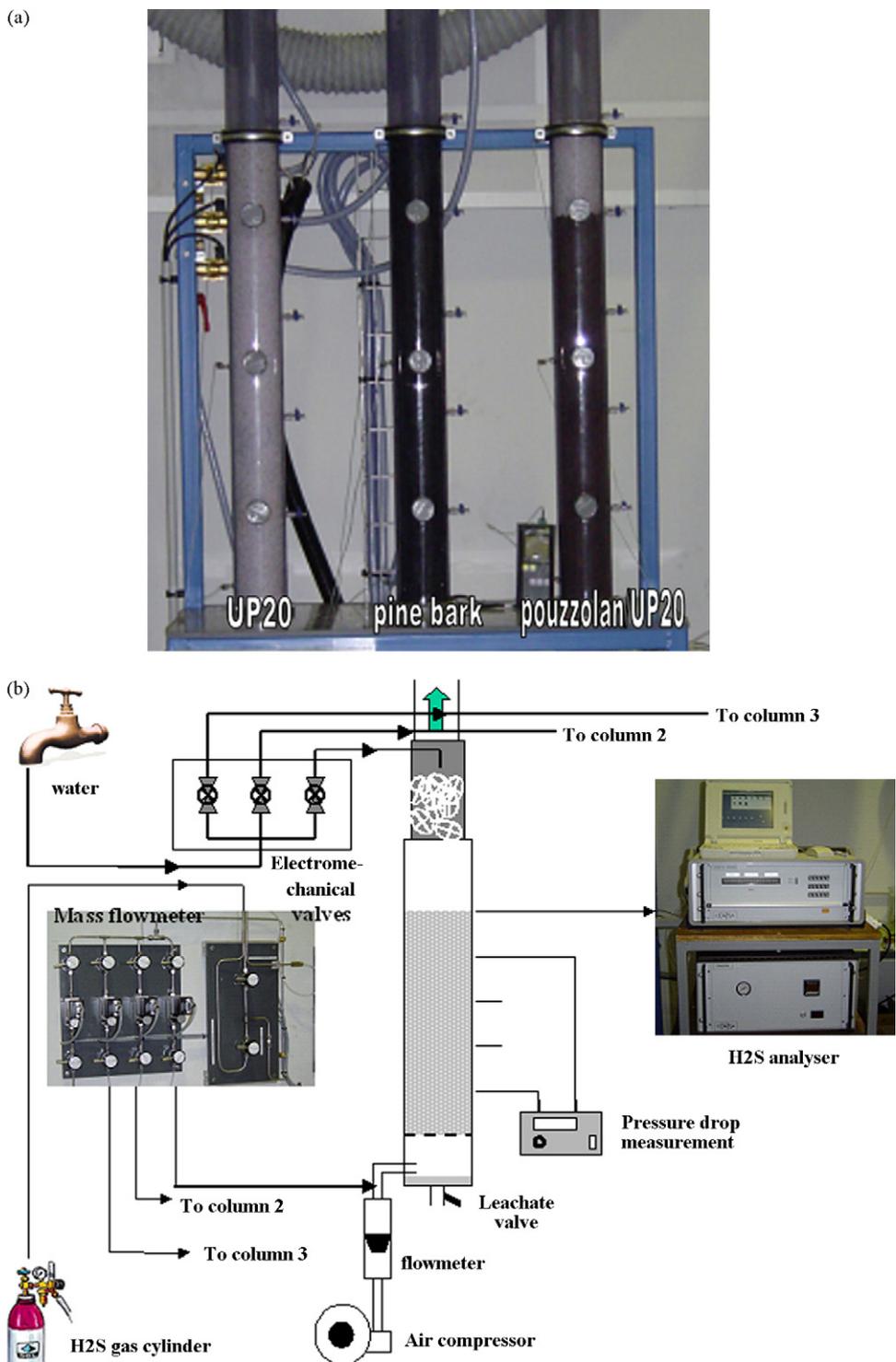


Fig. 2. (a) Experimental pilot-scale biofilters: from left to right; UP20 alone (white material), pine bark and pouzzolan/UP20. (b) Schematic diagram of biofilter system for H_2S treatment.

sponding to approximately 331), followed by 1 h stand-by. The packing materials were inoculated with washed activated sludge (1.35 g dry weight) per column twice in two weeks. The initial biomass came from the activated sludge of a wastewater treatment plant (city of Nantes, France) and was not acclimatized to treat H_2S . Apart from polluted air and UP20 material, no nutritive solution for feeding microorganisms was introduced into the biofilters.

3. Results and discussion

3.1. Effect of H_2S loading rate and pH change

The three biofilters were operated continuously for 95 days. Table 2 presents the removal capacities (RC; Eq. (1); $g\ m^{-3}\ h^{-1}$) and the removal efficiencies (RE; Eq. (2); %) for the three columns and according to the six loading rates (LR; Eq. (3); $g\ m^{-3}\ h^{-1}$) used

Table 2
Average performances of the three pilot-scale biofilters during the six running periods ($Q = 0.5 \text{ N m}^3 \text{ h}^{-1}$; $U_0 = 65 \text{ m h}^{-1}$; $\text{EBRT} = 57 \text{ s}$)

| LR ($\text{g m}^{-3} \text{ h}^{-1}$) | RC ($\text{g m}^{-3} \text{ h}^{-1}$) | RE (%) | pH | T (°C) | Pine bark | | | | | | Pozzolan/UP20 | | | | | |
|---|---|--------|-----|--------|-------------|-------------|-------------|-------------|-------------|-------------|---------------|-------------|-------------|-------------|-------------|-------------|
| | | | | | 1 (19 days) | 2 (14 days) | 3 (12 days) | 4 (18 days) | 5 (16 days) | 6 (14 days) | 1 (19 days) | 2 (14 days) | 3 (12 days) | 4 (18 days) | 5 (16 days) | 6 (14 days) |
| 0.45 | 0.86 | 0.81 | >95 | 7.7 | 0.45 | 0.88 | 1.87 | 3.29 | 4.85 | 9.13 | 0.46 | 1.21 | 2.20 | 3.29 | 5.13 | 9.24 |
| 0.41 | 8.32 | 8.32 | >93 | 6.5 | 0.41 | 0.84 | 1.83 | 3.11 | 4.11 | 6.35 | 0.39 | 1.17 | 2.14 | 3.18 | 4.50 | 6.85 |
| >90 | >95 | >95 | >95 | 7.1 | >90 | >95 | >94 | >94 | >86 | >69 | >82 | >96 | >97 | >97 | >88 | >74 |
| 7.0 | 7.0 | 7.0 | 6.1 | 2.4 | 6.1 | 3.2 | 3.1 | 3.1 | 3.2 | 2.7 | 5.5 | 3.3 | 3.4 | 3.9 | 3.3 | 2.9 |
| 23 | 23 | 23 | 24 | 24 | 24 | 23 | 24 | 24 | 25 | 24 | 24 | 23 | 25 | 24 | 25 | 25 |

in this study. The H_2S mass loading rate was increased period by period from 0.4 to roughly $10 \text{ g m}^{-3} \text{ h}^{-1}$. For each of the six periods (2–3 weeks per period) the loading rate was kept constant. Several measurements of gas concentration from sampling ports were carried out each day of each period in order to check the condition of “steady state”.

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

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

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

The change in RE versus time shows some similarity for the different packing materials and three different phases can be distinguished: (i) 30 days for the microorganisms to adapt to H_2S removal (periods 1 and 2); (ii) a maximal removal efficiency for the biofilters corresponding to periods 3 and 4 and (iii) a decrease in efficiency related to the increase in the loading rate concentration (periods 5 and 6).

After the period in which the microorganisms adapt, the three biofilters degrade more than 95% of the incoming H_2S when LR is less than $5 \text{ g m}^{-3} \text{ h}^{-1}$. The removal efficiencies obtained at the beginning of periods 2–4 are close to the values measured during all the duration of each period, which indicates the good ability of the immobilized biomass to oxidize H_2S . After 63 days of operation, LR was increased significantly to $10 \text{ g m}^{-3} \text{ h}^{-1}$ by varying the inlet concentration. It is found that there is a noticeable decrease in the RE values for the pine bark biofilter (69%) and for the biofilter filled with the pozzolan/UP20 configuration (74%). Kim et al. [16], treating H_2S loading rates up to $13 \text{ g m}^{-3} \text{ h}^{-1}$ by the use of biomedica (from wastewater treatment plant) encapsulated by sodium alginate and polyvinyl alcohol, has obtained similar results. It thus appears that the biomass is not able to sustain such loads. In contrast, the UP20 biofilter retains a removal efficiency of more than 93% indicating a strong ability to stimulate microbial activity. This result is consistent with the results of our previously published microbial studies [7].

The removal capacity plotted as a function of the H_2S loading rates (Fig. 3) shows a linear relation up to $5 \text{ g m}^{-3} \text{ h}^{-1}$ for all three biofilters. For higher LR, the removal capacity increases at a slower rate but is of the same order for the two biofilters filled with pine bark and with the pozzolan/UP20 configuration. However, in the specific case of the biofilter filled with pozzolan/UP20, it can be concluded that such a configuration presents a benefit in comparison with pine bark: (i) UP20 stimulates the growth of bacterial activity by dissolving nutrients that flow through the pozzolan bed and (ii) the mechanical properties of pozzolan reduce the settling of the bed, which consequently should reduce the pressure drops in the biofilter. Barona et al. [17], testing four organic packing materials for H_2S removal (horse manure, sludge, soil and algae; pig manure and sawdust) have demonstrated that only pig manure and sawdust material were able to reach high removal efficiency. They obtained $\text{RE} = 97\%$ for $\text{LR} = 5 \text{ g m}^{-3} \text{ h}^{-1}$ corresponding to our results. Malhautier et al. [18], using granulated sludge from sewage treatment plant for the simultaneous biofiltration of ammonia and hydrogen sulfide, proposed very high removal efficiencies: 100% for loading rates up to $20 \text{ g H}_2\text{S m}^{-3} \text{ h}^{-1}$.

Fig. 4 presents the evolution of the pH in the leachate versus time for the three columns. A major contrast is observed between the UP20 biofilter and the other two. The UP20 biofilter presents a slow decrease from pH 8 to 6 throughout the six operating periods, whereas both the other biofilters drop from pH 7 to 3 during period 1 (beginning on the fifth day of H_2S treatment). A stabiliza-

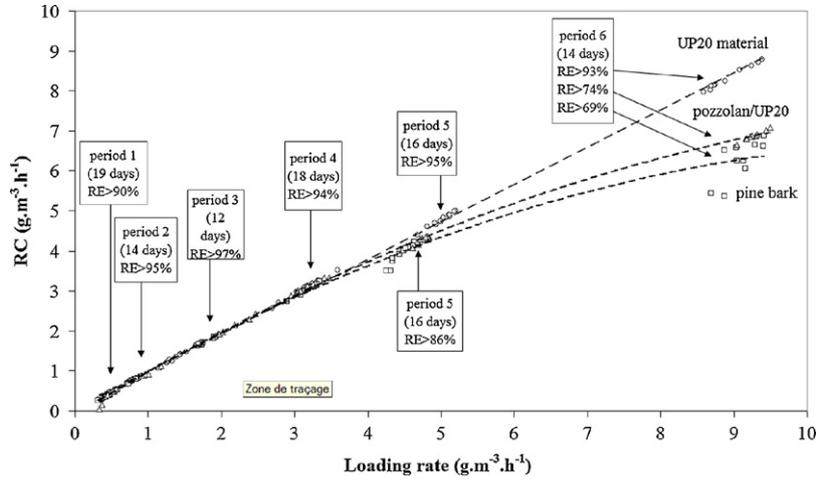


Fig. 3. Removal capacity versus H_2S loading rates for the three pilot-scale biofilters.

tion period of 40 days is then observed before a new fall to pH 2.5 until the end of the experiment. Brennan et al. [19] measured a pH drop from 7–6.5 to 4.8–3.6 after 3 weeks of H_2S and methylmercaptan treatment, and after 6 months the pH decreased to reach 2. The observed rapid fall in pH could be attributed to the bio-transformation of sulphite into sulphuric acid. Hence, Vincent and Hobson [20] measured a rapid acidification of the filtration material for an H_2S concentration up to 15 ppmv. In our case, the acidification occurs at a pollutant inflow concentration close to 7 ppmv. For UP20 material that has good buffering properties, the pH 8 value measured in the first days could be related to the dissolution of calcium carbonate and phosphates present in this material. This could also explain the small pH change to 6.5. Nevertheless, this acidification of the medium did not affect the removal efficiency. These results have already been observed by Yang and Allen [21], who noted that the biofiltration capacity is not affected until pH 3.2. In more acidic conditions, these authors measured a decrease in the pollutant treatment capacity.

3.2. Changes in packing material moisture content and pressure drops

The correct moisture content of a biofilter medium is also a key parameter to ensure a good performance. According to Herrygers et

al. [14], the moisture content usually ranges from 40 to 60% in the biofiltration of sulphured VOC. Fig. 5 summarizes the average values of the humidity of the three pilot-scale biofilters in relation to the height of sampling and the operation time. Similar results were obtained for the biofilters filled with UP20 and pine bark. Moisture content was around 50% for UP20 at the top of the biofilter during all the operation time (70% for pine bark) while lower values were measured at the bottom of the columns. Significant decreases in moisture content with time were then measured at sampling ports 0.2 and 0.5 m, mainly due to biomass accumulation, bed compaction, clogging or/and channelling effects. Such moisture content changes are typical of the up flow gas and down flow water column. For the biofilter filled with the configuration made of two layers of pozzolan/UP20, the moisture content was around 50% at the top of the column (corresponding to the UP20 layer) but the measured values dropped in the pozzolan layer to reach roughly 15–20%. Such values correspond to the water retention capacity of pozzolan (21%). However, pozzolan showed weak variations in moisture content in the lower part of the column with time, which could indicate that this material limits drying effects and consequently preferential pathways. This result was confirmed by the measurement of pressure drops. Pressure drops in biofilters depend on both the moisture content of the packing material and the hydrodynamic conditions (superficial velocity and particle size). The Ergun equa-

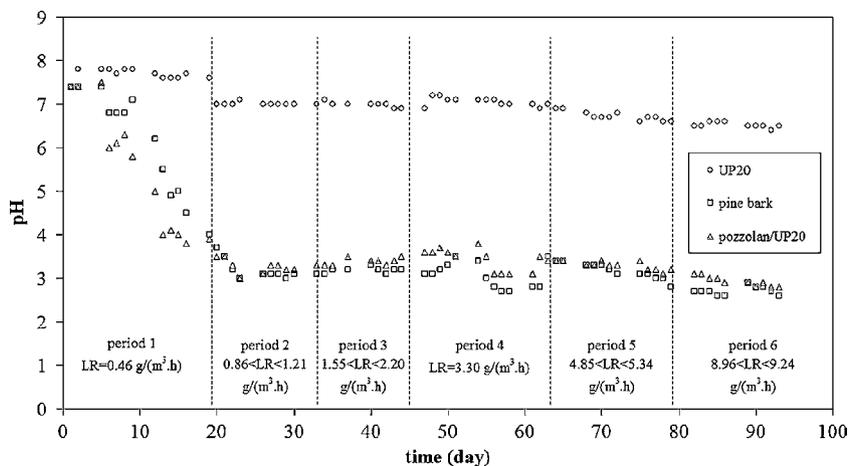


Fig. 4. pH evolution in leachate versus time for the three pilot-scale biofilters.

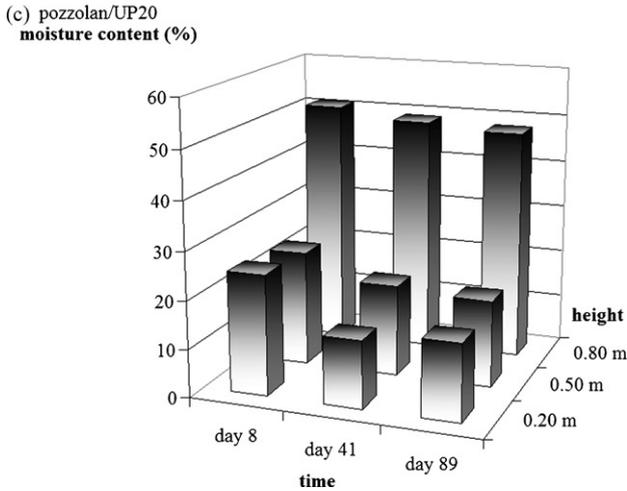
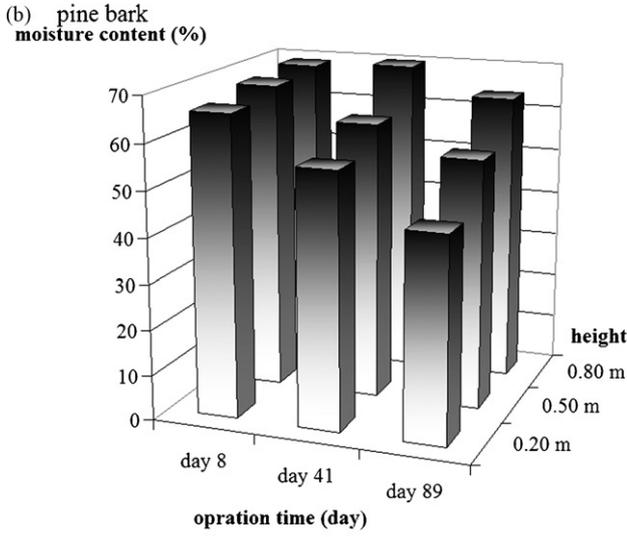
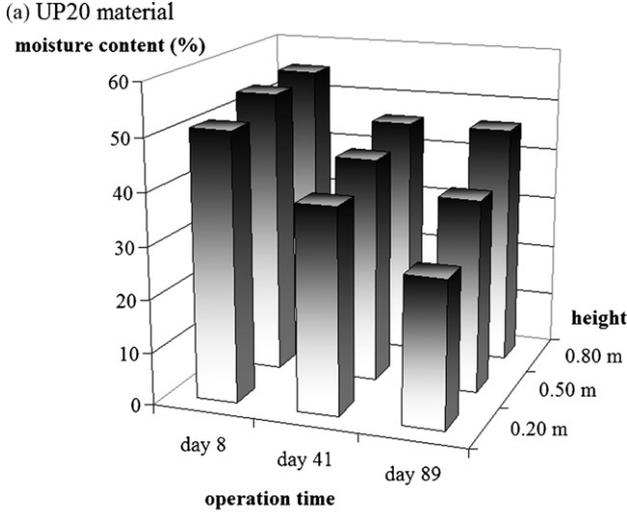


Fig. 5. Changes in the moisture content versus operation time and along the length of each pilot-scale biofilter (from the bottom): gas flow; $Q=0.5 \text{ N m}^3 \text{ h}^{-1}$, $U_0 = 64 \text{ m h}^{-1}$, EBRT=57 s, sequential irrigation; 1 h aspersion ((27–39) h^{-1}), 1 h stand-by).

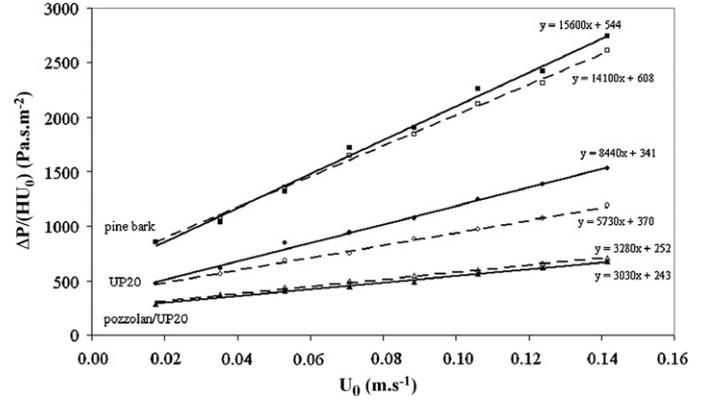


Fig. 6. Pressure drops for the three pilot-scale biofilters: (dashed line) at the beginning, i.e., materials saturated with water; (black line): after 60 days in operating conditions.

tion [22] describes the pressure drop behaviour for a packed bed of spheres:

$$\frac{\Delta P}{H} = AU_0 + BU_0^2 \quad (4)$$

where ΔP is the pressure drop along the bed length (H), U_0 is the superficial velocity, and A and B are constants. Comiti and Renaud [23] proposed a model applicable in both linear and non-linear laminar flow regimes taking into account bed tortuosity and overlap between particles:

$$\frac{\Delta P}{H} = A'a_{vd}^2\tau^2U_0 + B'a_{vd}\tau^3U_0^2 \quad (5)$$

where A' and B' are constants and a_{vd} is the dynamic surface area of particles, which can be different from the specific surface area (Table 1) if particles overlap mutually. The tortuosity (τ) is defined as:

$$\tau = \frac{L}{H} \quad (6)$$

where L is the length of the mean fluid path and H is the bed height. According to Mauret and Renaud [24], the model (Eq. (5)) provides a good description of pressure drops for various media such as non-consolidated beds of spheres, parallelepipedal particles, short cylinders, fibrous media and metallic foams. Eq. (5) can be rewritten as:

$$\frac{\Delta P}{HU_0} = \alpha + \beta U_0 \quad (7)$$

where α and β are the linear regression parameters allowing a_{vd} and τ to be calculated.

Fig. 6 shows examples of changes in pressure gradient for the three biofilters. For these measurements, the gas flow rate ranged from 0.5 to 4 $\text{N m}^3 \text{ h}^{-1}$ (65–520 m h^{-1}) and the pressure drops were measured between the sampling ports at 0.2 and 0.8 m. In this way, it is possible to compare the influence of the three packing materials (UP20, pine bark and pozzolan) on pressure drops and to take into account the presence of the 20 cm layer of UP20 topping the pozzolan bed. From the linear relation between $\Delta P/(HU_0)$ and U_0 , the hydrodynamic parameters a_{vd} and τ were assessed from the slope and the intercept for each packing material (Table 3). Basically, an increase of the tortuosity (τ) indicates that the contact time between the gas and the packing material increases that is favourable for the H_2S treatment. And a decrease of the dynamic surface area (a_{vd}) that could be due to the development of the biofilm should be also better for the H_2S treatment.

At the beginning of the experiment (Fig. 6), the pressure drops measured in pine bark were 2.5-fold higher than in UP20 and 3.7-

Table 3
Hydrodynamic characteristics of the three packing materials: (a) at the beginning, i.e., materials saturated with water and (b) after 60 days in operating conditions

| Support | α (Pa s m ⁻²) | | β (Pa s ² m ⁻³) | | τ | | a_{vd} (m ² m ⁻³) | |
|-----------|----------------------------------|---------|--|---------|-----------|-------------|--|------------|
| | Beginning | 60 days | Beginning | 60 days | Beginning | 60 days | Beginning | 60 days |
| UP20 | 370 | 342 | 5,730 | 8,440 | 1.78 | 2.26 (+27%) | 420 | 342 (-19%) |
| Pine bark | 608 | 544 | 14,100 | 15,600 | 3.29 | 3.58 (+9%) | 722 | 617 (-15%) |
| Pozzolan | 252 | 243 | 3,280 | 3,030 | 1.88 | 1.88 (-) | 730 | 730 (-) |

fold higher than in pozzolan. These results are consistent with the moisture content measurements mentioned above and can be related to the great tortuosity of the pine bark bed ($\tau = 3.29$; see Table 3). For each biofilter, the dynamic surface area decreased in comparison with the specific surface area initially measured in dry materials (-40% for UP20, -36% for pine bark and -32% for pozzolan). After 60 days of operation, the growth of microorganisms, the development of the biofilm, the sulphur precipitation, the moisture content and the attrition of the packing material all changed the hydrodynamic properties of the biofilters (Fig. 6 and Table 3). For UP20, the pressure drop changes were the greatest. Pressure drops ranged from 8 to 217 Pa m⁻¹ against 8 to 168 Pa m⁻¹ at the start of the experiment. Visual observations indicated a compaction of the bed, which was confirmed by the increase in tortuosity (+27%). The decrease in the dynamic surface area (-19%) is mainly due to both the development of the biofilm and the progressive dissolution of the UP20 material. For pine bark, pressure drops varied from 15 to 388 Pa m⁻¹ (from 15 to 370 Pa m⁻¹ at the start of the experiment), which are comparable to the values noted by Elias et al. [4] using pig manure and sawdust (15–460 Pa m⁻¹) but lower than those of Yang and Allen [21] using compost (0–3500 Pa m⁻¹). The development of the biofilm led to a decrease in the dynamic surface area (-15%) and an increase in tortuosity (+9%). For pozzolan topped with UP20, pressure drops did not change in comparison with those measured at the beginning of the experiment (from 5 to 100 Pa m⁻¹), which is comparatively lower than the pressure drops previously mentioned in conventional biofilters treating H₂S [1]. It is important to note that both τ and a_{vd} did not vary with time, which indicates that pozzolan is a good mechanical material for biofiltration. Moreover, the low moisture content in this part of the column filled with pozzolan seems to be sufficient to allow the development of a biofilm able to transform H₂S without increasing pressure drops. Consequently, pozzolan could represent the best material from a hydrodynamic point of view.

3.3. Biokinetic constants: the Michaelis–Menten type model

The removal rate of H₂S in the immobilized cell biofilter was modelled using a modified Michaelis–Menten type model [25] (with units proposed by [25] in order to compare the results with the literature data):

$$\frac{1}{R} = \frac{K_s}{V_m} \frac{1}{C_{in}} + \frac{1}{V_m} \quad (8)$$

R: apparent removal rate (g H₂S m⁻³ h⁻¹); K_s: apparent half-saturation constant (ppmv); V_m: maximum apparent removal rate (g H₂S day⁻¹ kg⁻¹ dry material); C_{in}: logarithmic mean concentration (ppmv)

$$C_{in} = \frac{C_{in} - C_{out}}{\ln(C_{in}/C_{out})} \quad (9)$$

$$R = \frac{Q(C_{in} - C_{out})}{698W[273 + T/273]} \quad (10)$$

where Q is the gas flow rate (m³ day⁻¹); W is the dry weight of packing material (kg) and T is the temperature (°C). The kinetic constants

obtained from Eq. (8) can be used to compare the characteristics and performance of various immobilized biological systems having different packing materials and configurations [26]. For H₂S treatment, the kinetic constants will depend on the microorganisms attached on the surface of packing material. Fig. 7 presents the linear relation of (1/R) versus (1/C_{in}) corresponding to Eq. (8). The values of V_m and K_s obtained from this experimental study are given in Table 4. The maximum apparent removal rate was obtained for the biofilter filled with UP20 (35 g m⁻³ h⁻¹) whereas the same results were obtained for the biofilters filled with pine bark and pozzolan/UP20 (14 and 15 g m⁻³ h⁻¹, respectively). However, the K_s value determined for UP20 material was the largest (70 ppmv). Consequently, it appears that UP20 would be particularly effective in treating high concentrations of pollutant. The physical meaning of K_s corresponds to the H₂S concentration that must be treated in order to reach V_m/2. In other words, a material having a large K_s value has a small affinity for H₂S and the removal rate will tend toward V_m for small inlet concentrations. Consequently, both parameters V_m and K_s should not be considered separately and it is useful to compare the ratio V_m/K_s, which can give a measure of the specific activity of the microorganisms attached on the packing material for H₂S treatment (Table 4; note that K_s has been converted from ppmv to g m⁻³ in order to obtain the ratio V_m/K_s in h⁻¹). The microorganisms attached on pine bark have the same specific affinity than the microorganisms developed in pozzolan/UP20 biofilter. This specific activity is greater than those measured on UP20 alone indicating that these microorganisms can be different from those developed on both other biofilters. In conclusion, it appears that (according to the Michaelis–Menten type model): (i) at low concentrations of the pollutant, UP20 is not the most efficient material of the three tested; (ii) the configuration of two layers of pozzolan/UP20 gives better results than UP20 alone; (iii) the biofilters filled with pine bark and pozzolan/UP20 have the same efficiency for H₂S treatment. In comparison with other studies, where the operating conditions were different, it appears that the configuration of the two layers of pozzolan/UP20 is better than alginate beads and not so far from peat [22,24].

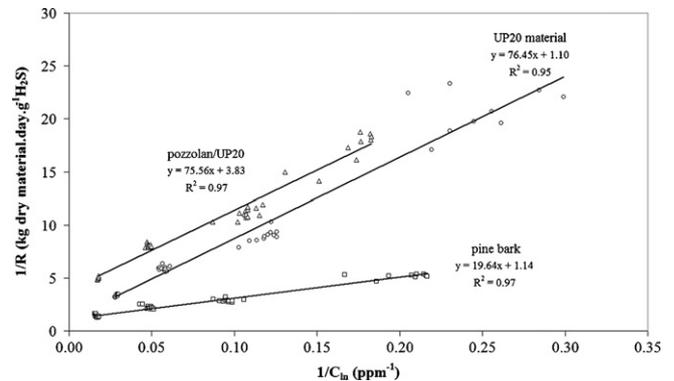


Fig. 7. 1/R versus 1/C_{in} according to the Michaelis–Menten type model.

Table 4
Kinetic constants according to the Michaelis–Menten type model

| Support | K_s (ppmv) | V_m ($\text{g H}_2\text{S kg}^{-1} \text{ day}^{-1}$) | $V_m / (K_s \text{ m}^{-3} \text{ h}^{-1})$ | V_m/K_s (calculated from SI units) (h^{-1}) |
|---------------------|--------------|---|---|--|
| UP20 | 70 | 0.91 | 35 | 357 |
| Pine bark | 18 | 0.88 | 14 | 556 |
| Pozzolan/UP20 | 20 | 0.26 | 15 | 536 |
| Peat [25] | 55 | 5.0 | 56 ^a | 727 |
| Alginate beads [27] | 47 | 1.34 | 22 ^b | 334 |

^a Estimated value from density of peat = 270 kg m^{-3} .

^b Estimated value from density of alginate beads = 400 kg m^{-3} .

4. Conclusion

The performance of three biofilters to treat H_2S at different loading rates was investigated in order to evaluate the new packing material UP20. The results from a biofilter completely filled with UP20 were critically compared with those obtained from two other biofilters, one filled with pine bark and the other with a configuration made of two layers of pozzolan/UP20. It appears that UP20 offers a real advantage for H_2S treatment at relatively high pollutant concentrations by providing both nutrients to the microbial biomass and a buffering effect. Hence, when the loading rate is significantly increased to $10 \text{ mg m}^{-3} \text{ h}^{-1}$, the UP20 biofilter retains a removal efficiency of more than 93% indicating a strong ability to stimulate microbial activity (compared to 69% for the pine bark biofilter and 74% for the biofilter filled with pozzolan/UP20). Nevertheless, at low concentrations of H_2S , UP20 is better used in combination with pozzolan as demonstrated by removal efficiency and pressure drop measurements and according to the Michaelis–Menten type model. The combined effects of pozzolan and UP20 present several advantages:

- (i) the biofilter filled with pozzolan/UP20 is able to treat the same H_2S loading rate as the biofilter filled with pine bark but with a pressure drop 3.5 times smaller;
- (ii) pozzolan is a good mechanical, chemical and physical material for biofiltration and has a long lifetime, but it is completely inert in terms of nutrient release;
- (iii) UP20 is an excellent support for biofilm development;
- (iv) UP20 provides nutrients for the development of a biofilm on pozzolan. Although the addition of nutrients would increase operating costs, it could also significantly reduce the size of the biofilter;
- (v) the UP20 layer, located on top of the pozzolan layer, could easily be replaced or fitted when required.

Acknowledgement

The authors would like to thank the French Environment and Energy Agency (ADEME) for partial financial support of this research programme.

References

- [1] C. Kennes, M.C. Veiga, *Bioreactors for Waste Gas Treatment*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.
- [2] 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.
- [3] Y.C. Chung, C. Huang, C.P. Tseng, Operation optimization of *Thiobacillus thioparus* CH11 biofilter for hydrogen sulphide removal, *J. Biotechnol.* 10 (1996) 1–6.
- [4] A. Elias, A. Barona, A. Arreguy, J. Rios, I. Aranguiz, J. Penas, Evaluation of a packing material for the biodegradation of H_2S and product analysis, *Process Biochem.* 37 (2002) 813–820.
- [5] E. Ramirez-Lopez, J. Corone-Hernandez, L. Dendooven, P. Range, F. Thalasso, Characterization of five agricultural by-products as potential biofilter carriers, *Bioresour. Technol.* 88 (2003) 259–263.
- [6] Y. Andrès, E. Dumont, P. Le Cloirec, E. Ramirez-Lopez, Wood bark as packing material in a biofilter used in air treatment, *Environ. Technol.* 27 (2006) 1297–1302.
- [7] F. Gaudin, Y. Andrès, P. Le Cloirec, Packing material formulation for odorous emission biofiltration, *Chemosphere* 70 (2008) 958–966.
- [8] 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.
- [9] D. Gabriel, M.A. Deshusses, Performance of a full scale biotrickling filter treating H_2S at a gas contact time of 1.6–2.2 s, *Environ. Prog.* 22 (2003) 111–118.
- [10] 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.
- [11] C. Kennes, H.H.J. Cox, H.J. Doddema, W. Harder, Design and performance of biofilters for the removal of alkylbenzene vapors, *J. Chem. Technol. Biotechnol.* 66 (1996) 300–304.
- [12] K. Shinabe, S. Oketani, S. Kanchanatawee, M. Matsumura, Characteristics of hydrogen sulphide removal in a carrier-packed biological deodorization system, *Biochem. Eng. J.* 5 (2000) 209–217.
- [13] A. Elias, A. Barona, J. Rios, A. Arreguy, M. Munguira, J. Penas, J.L. Sanz, Application of biofiltration to the degradation of hydrogen sulphide in gas effluents, *Biodegradation* 11 (2000) 423–427.
- [14] V. Herrygers, H. Van Langenhove, E. Smet, Biological treatment of gases polluted by volatile sulphur compounds, in: P.N.L. Lens, L. Hulshoff Pol (Eds.), *Environmental Technologies to Treat Sulfur Pollution: Principles and Engineering*, IWA Publishing, London, 2000, pp. 281–304.
- [15] A. Barona, A. Elias, R. Aris, I. Cano, R. Gonzalez, Biofilter response to gradual and sudden variations in operating conditions, *Biochem. Eng. J.* 22 (2004) 25–31.
- [16] J.H. Kim, E.R. Rene, H.S. Park, Biological oxidation of hydrogen sulphide under steady and transient state condition in an immobilized cell biofilter, *Bioresour. Technol.* 99 (2008) 583–588.
- [17] A. Barona, A. Elias, A. Amurrio, I. Cano, R. Arias, Hydrogen sulphide adsorption on a waste material used in bioreactors, *Biochem. Eng. J.* 24 (2005) 79–86.
- [18] L. Malhautier, C. Gracian, J.-C. Roux, J.-L. Fanlo, P. Le Cloirec, Biological treatment process of air loaded with an ammonia and hydrogen sulphide mixture, *Chemosphere* 50 (2003) 145–153.
- [19] B.M. Brennan, M. Donlon, E.B. Bolton, Peat biofiltration as an odour control technology for sulphur-based odours, *Water Environ. J.* 10 (1996) 190–198.
- [20] A. Vincent, J. Hobson, J. Odour Control, *CIWEM monographs on best practice* no. 2, vol. 31, London, UK: Chart. Inst. Water Environ. Manage., 1998.
- [21] Y. Yang, E.R. Allen, Biofiltration control of hydrogen sulphide. 1. Design and operational parameters, *J. Air Waste Manage. Assoc.* 44 (1994) 863–868.
- [22] S. Ergun, Fluid flow through packed columns, *Chem. Eng. Prog.* 48 (1952) 89–94.
- [23] J. Comiti, M. Renaud, A new model for determining mean structure parameters of fixed bed from pressure drop measurements: application to beds packed with parallelepipedal particles, *Chem. Eng. Sci.* 44 (1989) 1539–1545.
- [24] E. Mauret, M. Renaud, Transport phenomena in multi-particle systems. I. Limits of applicability of capillary model in high voidage beds: application to fixed beds of fibers and fluidized beds of spheres, *Chem. Eng. Sci.* 52 (1997) 1807–1817.
- [25] M. Hirai, M. Ohtake, M. Shoda, Removal kinetics of hydrogen sulfide, methanethiol and dimethyl sulfide by peat biofilters, *J. Fermentation Bioeng.* 70 (1990) 334–339.
- [26] Y.X. Chen, J. Yin, K.X. Wang, Long-term operation of biofilters for biological removal of ammonia, *Chemosphere* 58 (2005) 1023–1030.
- [27] 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.