



**HAL**  
open science

## **H<sub>2</sub>S removal using cellular concrete waste as filtering material Reactions identification and performance assessment**

Gaëlle Lebrun, Annabelle Couvert, Eric Dumont

► **To cite this version:**

Gaëlle Lebrun, Annabelle Couvert, Eric Dumont. H<sub>2</sub>S removal using cellular concrete waste as filtering material Reactions identification and performance assessment. *Journal of Environmental Chemical Engineering*, 2019, 7 (2), pp.102967. 10.1016/j.jece.2019.102967 . hal-02090012

**HAL Id: hal-02090012**

**<https://univ-rennes.hal.science/hal-02090012>**

Submitted on 16 Apr 2019

**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.

## **H<sub>2</sub>S removal using cellular concrete waste as filtering material Reaction identification and performance assessment**

Gaëlle LEBRUN<sup>a</sup>, Annabelle COUVERT<sup>a</sup>, Éric DUMONT<sup>b\*</sup>

<sup>a</sup>Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000, Rennes, France

<sup>b</sup>UMR CNRS 6144 GEPEA, IMT Atlantique, Campus de Nantes, La Chantrerie, 4 rue Alfred Kastler, CS 20722, 44307 Nantes Cedex 3, France

\* Corresponding author: eric.dumont@imt-atlantique.fr

### **Highlights**

- H<sub>2</sub>S removal using cellular concrete waste was investigated
- Cellular concrete is efficient for removing H<sub>2</sub>S in abiotic conditions
- H<sub>2</sub>S reacts with CaCO<sub>3</sub> in wet conditions to form gypsum
- At EBRT = 56 s, a maximum elimination capacity of 7.8 g m<sup>-3</sup> h<sup>-1</sup> was calculated

### **Abstract**

The removal of hydrogen sulfide (H<sub>2</sub>S) in air using cellular concrete waste as packing material was investigated and compared to results obtained with expanded schist. Air filtration was performed under abiotic conditions. Experiments were carried out in 3 laboratory-scale PVC columns (internal diameter of 100 mm) filled with a volume of 7.8 L of material (1 m height). Filter “BF1” was filled with a mixture of cellular concrete waste and expanded schist (65%/35% volume, respectively). Filters “BF2” and “BF3” were filled with 100% expanded schist and 100% cellular concrete waste, respectively. The difference in composition between cellular concrete and expanded schist allowed the identification of major components involved in H<sub>2</sub>S removal. It was demonstrated that wet conditions are required to obtain H<sub>2</sub>S removal. For a H<sub>2</sub>S concentration of 50 ppm, removal efficiency around 40-45% was obtained at an EBRT of 56 s (whereas 28% and 4% were measured for filters filled with the mixture of packing materials and expanded schist, respectively). It was

identified that the ability of cellular concrete waste to remove  $\text{H}_2\text{S}$  was mainly due to reactions occurring between  $\text{H}_2\text{S}$  and calcium carbonate leading to gypsum formation. A maximum elimination capacity of  $7.8 \text{ g m}^{-3} \text{ h}^{-1}$  was calculated. Considering that pressure drops were low for this material (around  $12 \text{ Pa m}^{-1}$ ),  $\text{H}_2\text{S}$  filtration using cellular concrete waste could be carried out beneficially as the humidification step of biofiltration systems.

## Keywords

Cellular concrete; Packing material;  $\text{H}_2\text{S}$ ,  $\text{CaCO}_3$ ; Iron oxide

## 1 Introduction

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a toxic, flammable and hazardous pollutant. Its rotten eggs smell is noticeable at very low concentrations, between 0.02 and 0.1 ppm depending on the individual. At higher concentrations, between 10 and 500 ppm, it may cause disorders in respiratory, nervous, cardiovascular and hematological systems, and immediate death above 500 ppm [1]. Sources of  $\text{H}_2\text{S}$  can be anthropogenic since it is discharged by many industries using chemical reaction with sulfur such as paper manufacturing, wastewater treatment and petroleum. It also occurs naturally in carbon and volcanic gases. Nowadays, gaseous  $\text{H}_2\text{S}$  in air or biogas can be treated in several ways such as absorption or adsorption processes, and biological processes. The interest for biotechniques is increasing because of their high removal efficiency and low running cost [1]. Incidentally, recent study has highlighted that cellular concrete waste, which can be used as packing material for biofiltration [2–4], could also be an effective medium for the treatment of  $\text{H}_2\text{S}$  in air without any microbial population [5] (i.e in abiotic conditions). For an  $\text{H}_2\text{S}$  concentration of 100 ppmv, a removal efficiency around 70% was reported. Therefore, such a waste material could appear as a cheap and eco friendly solution for  $\text{H}_2\text{S}$  treatment in

air or biogas at industrial scale. Cellular concrete is a building material mainly made up of calcium oxide (CaO), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), silicon dioxide (SiO<sub>2</sub>) and sulfur trioxide (SO<sub>3</sub>). However, interactions between cellular concrete components and H<sub>2</sub>S are not yet fully understood, nor are the operating conditions to reach the optimum recovery. The aim of this study is therefore to determine the physical reactions that occur between H<sub>2</sub>S and the main components of cellular concrete. For this purpose, the removal of H<sub>2</sub>S in air was experimentally study in three abiotic filters filled with: (i) waste of cellular concrete, (ii) expanded schist, and (iii) a mixture of expanded schist and cellular concrete waste. Thereby, the difference in composition between cellular concrete and expanded schist could allow the identification of major components involved in H<sub>2</sub>S removal.

## **2 Characterization and composition of materials**

The cellular concrete waste used in this study is a mineral material provided by the Florentaise company based in Nantes, France, and sold as “copolight” (<https://www.florentaise.com/fr>), whereas expanded schist is an inorganic material provided by the Granulex company based in Mayenne, France (<https://www.granulex.fr/>). Properties of both materials are reported in Table 1. Analytical materials used to determine these properties are described by Ben Jaber et al. [5]. Table 2 shows that both materials exhibit close chemical compositions determined by using an Energy Dispersive X-ray Fluorescence Spectrometer (EDX-800HS, Shimadzu Company). As a result, comparing performances of filters filled with cellular concrete waste and expanded schist, respectively, could ultimately highlight which compounds are mainly involved in H<sub>2</sub>S removal in abiotic conditions.

Table 1: Physico-chemical properties of material used in the study

Properties	Cellular concrete	Expanded schist
Density (kg m <sup>-3</sup> )	547 ± 5	1248 ± 12
Specific area BET (m <sup>2</sup> g <sup>-1</sup> )	44 ± 0.8	-
Porosity (%)	64	47
pH of surface	9.0 ± 0.1	7.0 ± 0.1
Water retention capacity (%)	56 ± 2	-

Table 2: Composition of cellular concrete and expanded schist (weight)

Elemental composition			Components		
Element	Cellular concrete (%)	Expanded schist (%)	Oxide	Cellular concrete (%)	Expanded schist (%)
Si	25	40	SiO <sub>2</sub>	50.5	56.4
Fe	5	25	Fe <sub>2</sub> O <sub>3</sub>	1.3	12.4
Al	(nd)	15	Al <sub>2</sub> O <sub>3</sub>	2.2	20.5
Ca	51	2	CaO	24.6	0.9
K	0.6	10	K <sub>2</sub> O	0.2	5
S	7	2	SO <sub>3</sub>	19.7	1.6
Ti	(nd)	2	TiO <sub>2</sub>	(nd)	(nd)
P	12	3	P <sub>2</sub> O <sub>5</sub>	1.4	12.4

nd: not determined

### 3 Possible mechanisms involved in H<sub>2</sub>S removal

Literature data are used to investigate possible mechanisms that occur between H<sub>2</sub>S and the components of materials. Findings are displayed in Figure 1. Sorption mechanisms and chemical reactions between H<sub>2</sub>S and the cellular concrete components can be considered. Cellular concrete may be used as adsorbent for heavy metals or halogens [6–8]. However, due to its specific surface area (44 m<sup>2</sup> g<sup>-1</sup>), adsorption tests carried out at laboratory scale indicated that cellular concrete waste used in this study is not a good adsorbent for H<sub>2</sub>S removal [5]. Chemical reactions between H<sub>2</sub>S and the cellular concrete components are consequently more probable. Nonetheless, there are no data suggesting a single-step reaction between H<sub>2</sub>S and cellular concrete. Considering the composition of cellular concrete waste (Table 2), the

thermodynamically favorable reactions for H<sub>2</sub>S removal involve iron oxides, calcium oxides, and potassium oxides (Table 3). However, it has to be noted that the role of potassium oxides in H<sub>2</sub>S removal in gases is not specifically described in the literature.

Table 3: Possible reactions between H<sub>2</sub>S and cellular concrete components ( $\Delta_r G^\circ$  is the Gibbs free energy of reaction):

$\text{SiO}_2 + 2\text{H}_2\text{S} \rightarrow \text{SiS}_2 + 2\text{H}_2\text{O}$	$\Delta_r G^\circ = + 262.7 \text{ kJ mol}^{-1}$
$\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}$	$\Delta_r G^\circ = - 61.8 \text{ kJ mol}^{-1}$
$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{Al}_2\text{S}_3 + 3\text{H}_2\text{O}$	$\Delta_r G^\circ = + 284 \text{ kJ mol}^{-1}$
$\text{K}_2\text{O} + \text{H}_2\text{S} \rightarrow \text{K}_2\text{S} + \text{H}_2\text{O}$	$\Delta_r G^\circ = - 237.1 \text{ kJ mol}^{-1}$
$\text{FeO} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{O}$	$\Delta_r G^\circ = - 67.4 \text{ kJ mol}^{-1}$

It is known that iron oxides are currently used to remove H<sub>2</sub>S in sour gas at industrial scale. In such a case, gas is contacted with a liquid containing soluble ferric ions Fe<sup>3+</sup>. H<sub>2</sub>S is then oxidized to elemental sulfur and Fe<sup>3+</sup> is reduced to ferrous ions Fe<sup>2+</sup> according to the reaction:

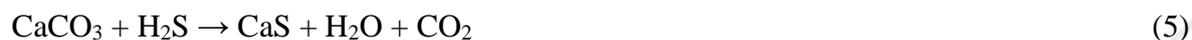


The liquid can be regenerated. Thus, Fe<sup>2+</sup> can subsequently be reconverted to Fe<sup>3+</sup> by oxidation with air (e.g. the Shell Iron Redox process SulFerox®) or via a biological means using *Thiobacillus ferrooxidans* [9].

Additionally, cheap materials containing iron oxides, like laterite [10], waste pyrolysis chars [11], sewage-sludge [12], red mud [13], municipal solid waste incineration bottom ash [14] or steel slags [15], have been recently identified as potentially interesting media for H<sub>2</sub>S removal. Moreover, synthetic biofiltration media containing iron was also developed to speed up the biological oxidation of H<sub>2</sub>S [16]. Reactions between H<sub>2</sub>S and iron oxide then lead to the formation of FeS and FeS<sub>2</sub>:



H<sub>2</sub>S can also react with calcium oxide (CaO; oxide sulfidation) and calcium carbonate (CaCO<sub>3</sub>; carbonate sulfidation) leading to the formation of calcium sulfide (CaS) and calcium sulfate, i.e. gypsum (CaSO<sub>4</sub> 2H<sub>2</sub>O):



The gypsum formed can then react with aluminates to form ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O) known to be an expansive material causing the disintegration of concrete [17]. Note that Ca-based sorbents (Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>) are applied to remove H<sub>2</sub>S from fuel gases at high temperatures [18] but it seems that there are only few available data at ambient temperature. For instance, the reactivity of (CaCO<sub>3</sub>)-based solid wastes for the removal of H<sub>2</sub>S from simulated biogas matrix was investigated using triphasic gas/liquid/solid process at room temperature and atmospheric pressure [19]. In the absence of oxygen in the biogas, this study suggested that dissolved H<sub>2</sub>S is neutralized by CO<sub>3</sub><sup>2-</sup> released by dissolution of CaCO<sub>3</sub>. However, as CaCO<sub>3</sub> is only slightly soluble in water, H<sub>2</sub>S removal would not be efficient in this case. Calcium oxide and calcium carbonate have been also used for the development of synthetic media enabling the removal of H<sub>2</sub>S by biofiltration. A cylindrical-shaped extrudate, called UP20, containing mainly calcium carbonate, an organic binder, and nutrients, has thus been specifically developed for the treatment of H<sub>2</sub>S. Several studies have highlighted that UP20 can offer a real advantage for H<sub>2</sub>S treatment, either alone, or in association with others packing materials [20–23]. However, the ability of UP20 to improve H<sub>2</sub>S removal has been attributed rather to a slow-release of nutrients and to a buffering effect than to possible reactions between H<sub>2</sub>S and CaCO<sub>3</sub>. Another composite packing material, called CM-5, mainly consisting of compost (17% w) with functional microorganisms, calcium

carbonate (13% w), perlite (18% w), cement (18% w), plant fiber (7% w), and inorganic binder (27% w) was developed for H<sub>2</sub>S biofiltration [24,25]. A comparison between two identical biofilters filled with original CM-5 (i.e. medium embedded with microorganisms) and sterilized CM-5 (i.e. medium without microorganisms) was carried out. Based on the maximum elimination capacity (EC<sub>max</sub>) determined from the Michaelis-Menten model, it was highlighted that performance of the biofilter filled with sterilized CM-5 was eight times lower than that of the biofilter filled with original CM-5 (8 and 62 g m<sup>-3</sup> h<sup>-1</sup>, respectively). Consequently, the ability of CM-5 to remove H<sub>2</sub>S is mainly due to the presence of functional microorganisms rather than to possible reactions with the material. Nonetheless, it has to be noted that performance of the sterilized CM-5 is not insignificant. This could be due to reactions between H<sub>2</sub>S and several components of compost, calcium carbonate, perlite, cement, plant fiber, or due to synergic interactions between all of them. However, no information about the role of calcium carbonate was reported in these studies.

The comparison between experimental results obtained for the 3 abiotic filters could then be used to identify which components, either iron oxides or calcium oxides, are mainly involved in H<sub>2</sub>S removal.

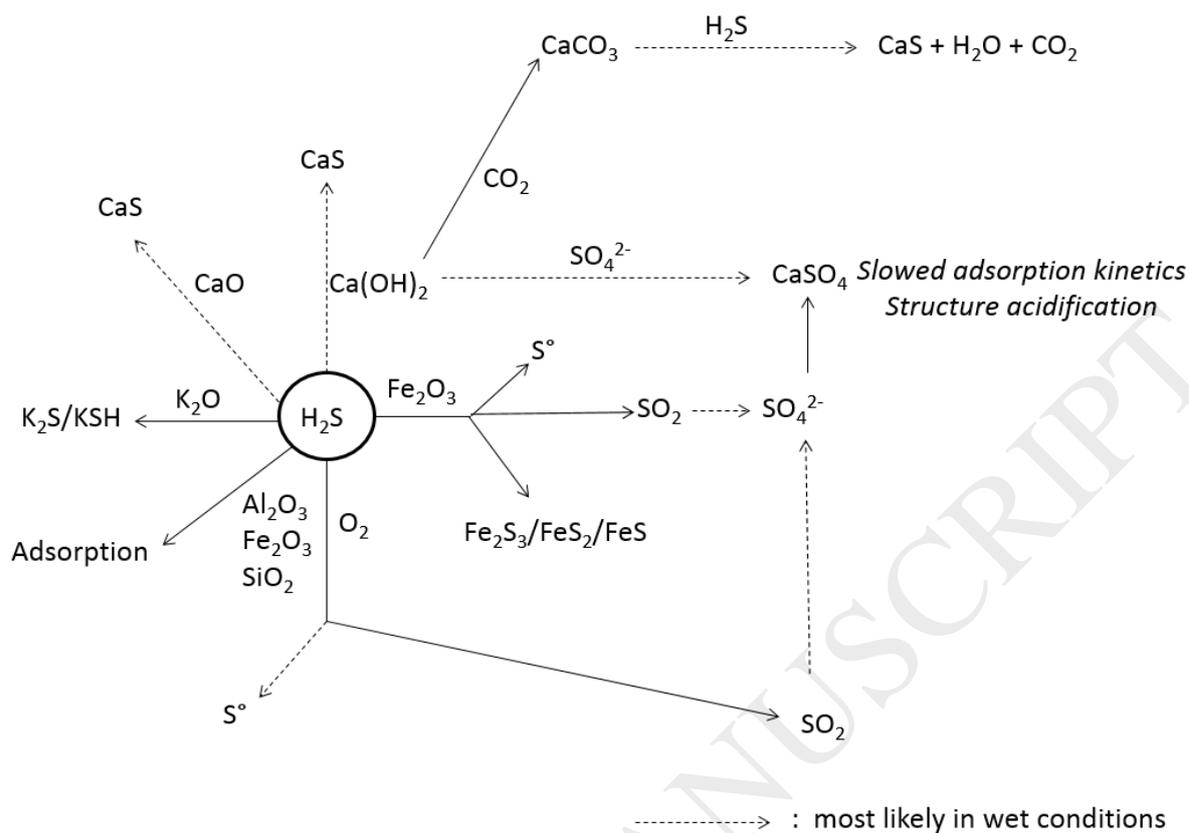


Figure 1: Possible interactions between  $\text{H}_2\text{S}$  and cellular concrete components.

## 4 Materials and methods

### 4.1 Experimental set up

The experimental set up is shown in Figure 2. It consisted of 3 PVC cylindrical columns (internal diameter 100 mm) filled with a volume of 7.8 L of material (1 m height). Filter “BF1” was filled with a mixture of cellular concrete waste and expanded schist (54%/46% weight, corresponding respectively to 65%/35% in volume). Filters “BF2” and “BF3” were filled with 100% expanded schist and 100% cellular concrete waste, respectively (Table 4). Materials were sieved and fractions exceeding 10 mm and less than 5 mm were removed. Thermocouples (K type) were installed on each column to measure temperatures. For each

column, the air flow was generated using a regulated fan. If necessary, it bubbled through a humidification system (internal diameter of 200 mm and 30 cm height) filled with tap water. A stream of  $\text{H}_2\text{S}$  (99.7% purity), controlled by a mass flow meter (5850S, Brooks Instruments, Hatfield, USA) was diluted in the air after the humidification system and before entering the column. The  $\text{H}_2\text{S}$  concentration was measured by an Onyx 5220 analyser (Cosma, France, measurement accuracy  $\pm 1\%$ ) all along the column, which was equipped with 9 sampling ports located at 0, 5, 20, 40, 50, 60, 80, 90, 95 and 100 cm from the bottom. These sampling ports could also be used to measure the pressure drops (using a pressure sensor Setra, Setra Systems, Inc, Boxborough, USA; 0-700 Pa).

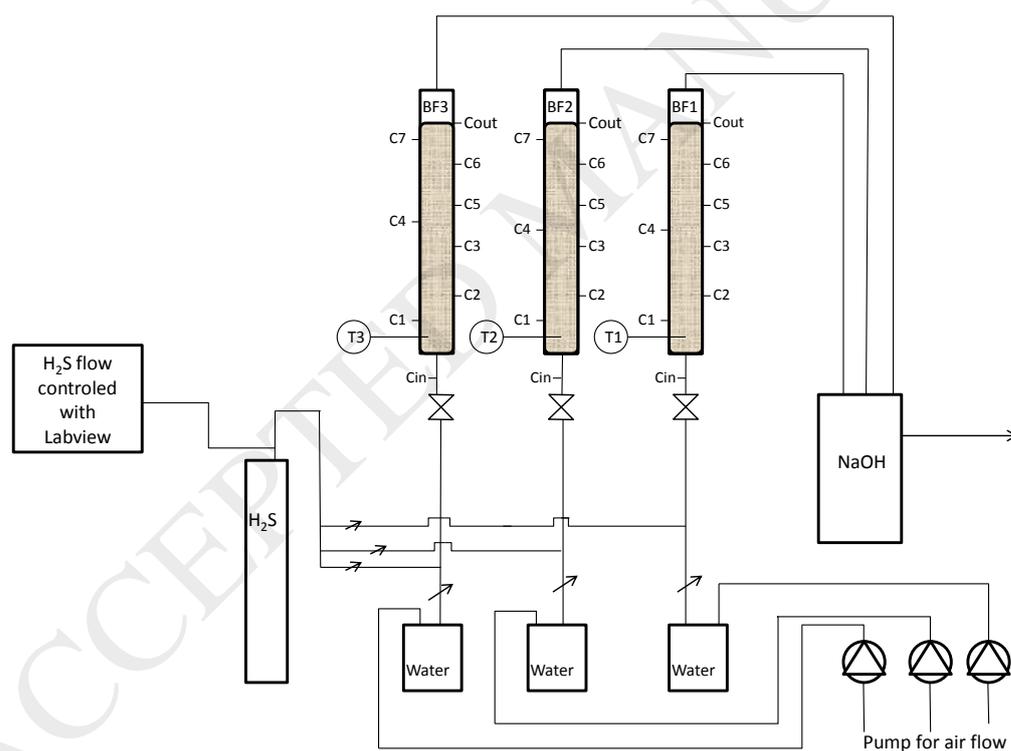


Figure 2: Flowsheet of the filters used for  $\text{H}_2\text{S}$  removal.

Table 4: Composition of filters

Filter	Material (weight)	Main Components (weight)
BF1	54% Cellular concrete 46% Expanded schist	SiO <sub>2</sub> (53%)
		CaO (14%)
BF2	100% Expanded schist	SO <sub>3</sub> (11%)
		Al <sub>2</sub> O <sub>3</sub> (10%)
		Fe <sub>2</sub> O <sub>3</sub> (6%)
		P <sub>2</sub> O <sub>5</sub> (6%)
		SiO <sub>2</sub> (56%)
BF3	100% Cellular concrete	Al <sub>2</sub> O <sub>3</sub> (20%)
		Fe <sub>2</sub> O <sub>3</sub> (12%)
		P <sub>2</sub> O <sub>5</sub> (12%)
		SiO <sub>2</sub> (50%)
BF3	100% Cellular concrete	CaO (25%)
		SO <sub>3</sub> (20%)
		Al <sub>2</sub> O <sub>3</sub> (2%)
		Fe <sub>2</sub> O <sub>3</sub> (1%)
		SiO <sub>2</sub> (50%)

## 4.2 Operating conditions

In order to identify the possible reactions occurring between the cellular concrete components and H<sub>2</sub>S, the polluted gas was firstly flowed through the packing filters in dry conditions, i.e without the humidification system, at a constant airflow (0.5 m<sup>3</sup> h<sup>-1</sup> corresponding to an EBRT of 56 s) and inlet H<sub>2</sub>S concentration (50 ppmv). Experiments were carried out over five days from 8:00 AM to 18:00 PM each day. H<sub>2</sub>S filtration was afterwards investigated in wet conditions for various operating conditions over 4 months (Table 5). For these conditions, the three packing materials were initially sprayed one time. The moisture of the bed materials were then only maintained by the humidity of the gas flow entering the columns. Experiments in wet conditions were usually carried out from 8:00 AM to 18:00 PM each day (experiments were not carried out after 18:00 PM during the week nor during the weekend for security reasons). Nonetheless, some experiments were carried out continuously for 80 h in order to determine the variation in measurements and to check the “steady state”

condition. Parameters used to describe the operating conditions and to determine the removal performances are defined in Table 6.

Table 5: Operating conditions

Conditions	Air flowrate (m <sup>3</sup> h <sup>-1</sup> )	Inlet concentration (ppm)	H <sub>2</sub> S LR (g m <sup>-3</sup> h <sup>-1</sup> )	EBRT (s)
Dry	0.5	50	4.5	56
		100	9.0	56
		200	17.9	56
		300	26.9	56
		400	35.9	56
Wet	0.5	500	44.9	56
		1.0	9.0	28
		1.5	13.5	19
		2.0	18.0	14
		3.0	26.9	9
	4.0	50	35.9	7

Table 6: Parameters used in this paper

Parameter	Definition	Nomenclature
Loading Rate LR (g m <sup>-3</sup> h <sup>-1</sup> )	$\frac{Q}{V} C_G^{\text{in}}$	$C_G^{\text{in}}$ : Inlet concentration (g m <sup>-3</sup> )
Elimination Capacity EC (g m <sup>-3</sup> h <sup>-1</sup> )	$\frac{Q}{V} (C_G^{\text{in}} - C_G^{\text{out}})$	$C_G^{\text{out}}$ : Outlet concentration (g m <sup>-3</sup> )
Empty Bed Residence Time EBRT (s)	$\frac{V}{Q}$	Q: Gas flow rate (m <sup>3</sup> s <sup>-1</sup> )
Removal Efficiency RE (%)	$100 \frac{C_G^{\text{in}} - C_G^{\text{out}}}{C_G^{\text{in}}}$	V: Packing bed volume (m <sup>3</sup> )

## 5 Results and discussion

### 5.1 H<sub>2</sub>S treatment in dry conditions vs wet conditions

In dry conditions, H<sub>2</sub>S removal efficiency was relatively low. At EBRT = 56 s, RE = 18% was obtained for filters using cellular concrete waste whereas no removal was recorded for expanded schist (Figure 3). In wet conditions, H<sub>2</sub>S removal efficiency was significantly

achieved for cellular concrete waste whereas a slight H<sub>2</sub>S removal was measured for expanded schist (Figure 4). For each filter, results given in this figure correspond to 17 measurements carried out regularly between 2 and 79 h after the beginning of the experiment, which explains why results are relatively dispersed. On average, H<sub>2</sub>S removal efficiency was 47% and 4% for filters BF3 and BF2, respectively, whereas 28% was obtained for the filter BF1 (mixture). Results obtained for cellular concrete waste alone were nonetheless lower than those reported in Ben Jaber et al. [5], i.e. RE = 70% for an H<sub>2</sub>S concentration of 100 ppm at EBRT = 63 s. In terms of sulphur proportion (in % weight), analysis using X-ray Fluorescence spectrometer reveals that H<sub>2</sub>S reacted with the components of the materials (Table 7). Results obtained are in agreement with removal efficiencies. For cellular concrete waste used alone (BF3), sulphur proportion increased from 6.8% at the beginning to reach 20.9% at the end of the experiment in wet conditions. It has to be noted that the pH of each material measured after H<sub>2</sub>S exposition was unchanged in regards to initial value. Overall, it was calculated that 130 mg of H<sub>2</sub>S was captured per g of cellular concrete waste during the 4 months of experiment. For expanded schist used alone (BF2), the increase was less noticeable, in agreement with the low RE recorded, but demonstrated nonetheless that expanded schist reacted with H<sub>2</sub>S. Regarding both materials used as a mixture in filter BF1, the increase in H<sub>2</sub>S proportion in the cellular concrete waste is similar to that recorded for filter BF3, albeit in a lesser extent (19.7% and 20.9%, respectively). Conversely, the H<sub>2</sub>S proportion in the expanded schist in BF1 was double that in BF2 (14.2% vs 7.1%) showing probable interactions between both materials used in the mixture. Differences between these results will be discussed hereafter.

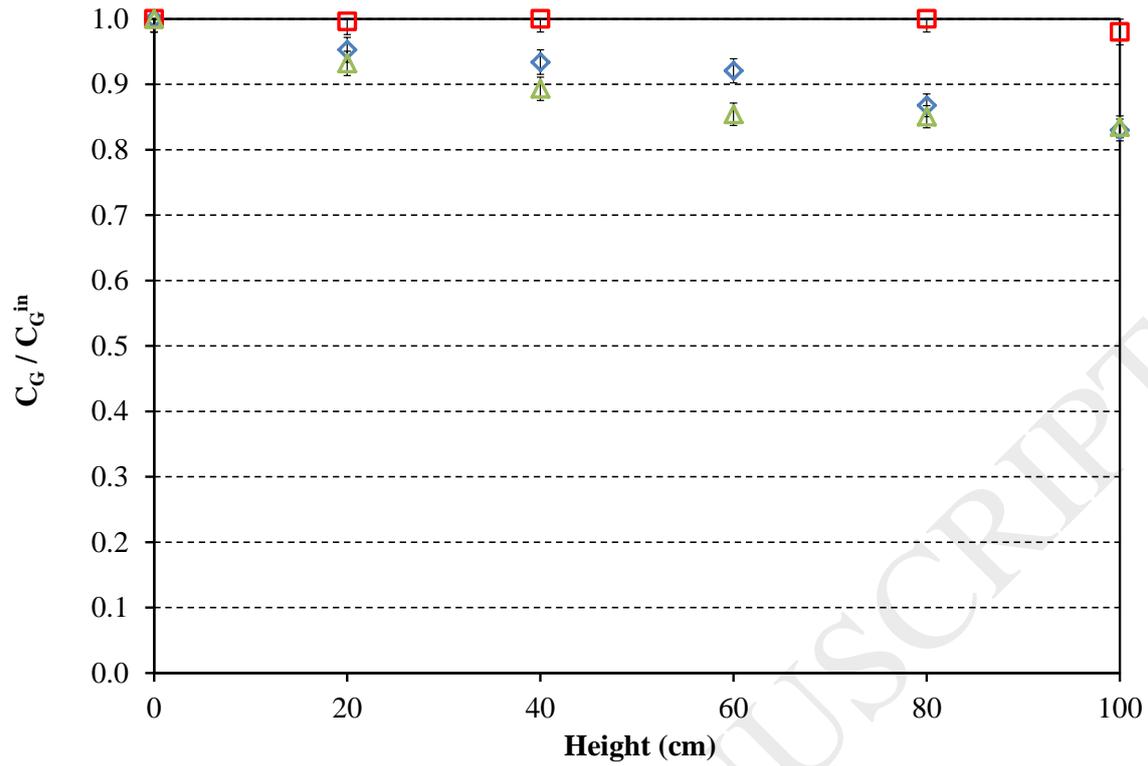


Figure 3: H<sub>2</sub>S relative concentration along the three filters in dry conditions (blue diamond: cellular concrete waste; green triangle: mixture of cellular concrete waste and expanded schist; red square: expanded schist).  $C_G^{\text{in}} = 50$  ppm; EBRT = 56 s.

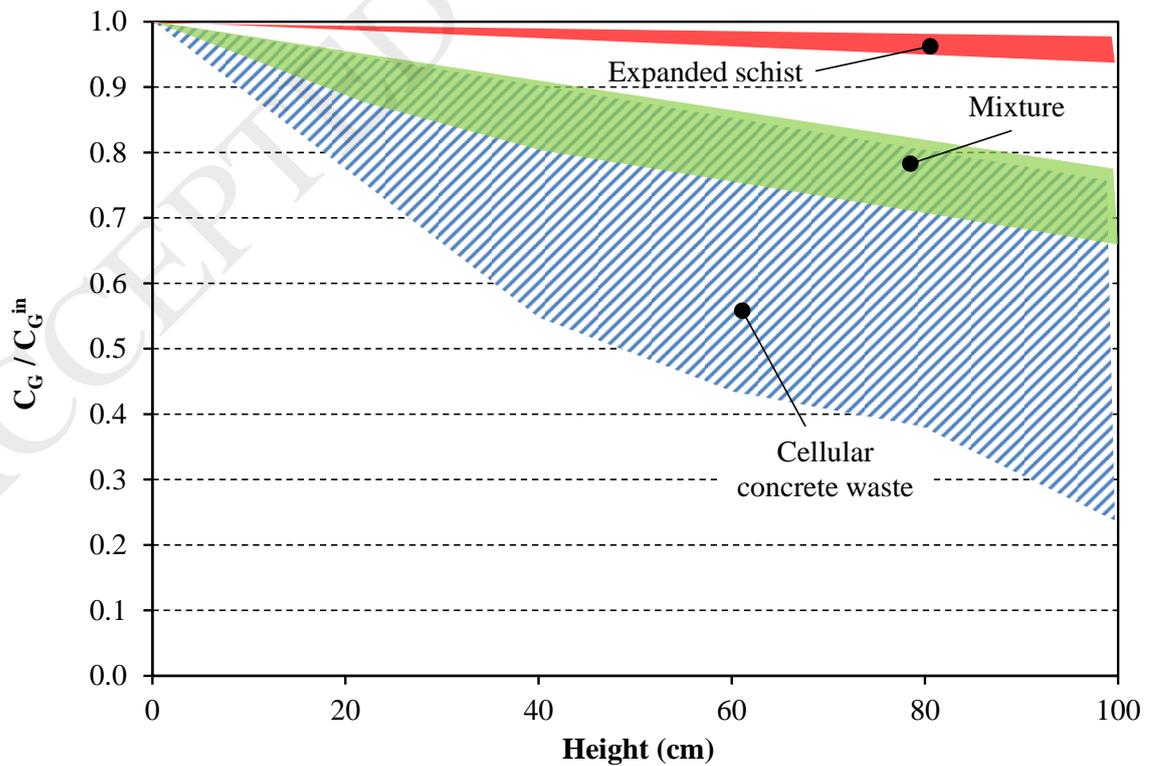


Figure 4: H<sub>2</sub>S relative concentration along the three filters in wet conditions ( $C_G^{\text{in}} = 50$  ppm; EBRT = 56 s).

Table 7: Change in sulphur proportion (% weight) in packing materials during filtration experiment.

Filter	Material	Before exposure	After exposure dry conditions	After exposure wet conditions
<b>BF3</b>	Cellular concrete	6.8	9.9	20.9
<b>BF1</b>	Cellular concrete	6.8	7.6	19.7
	Expanded schist	2.3	4.5	14.2
<b>BF2</b>	Expanded schist	2.3	1.8	7.1

All these findings suggest that one or several compounds, mainly present in cellular concrete and present at a negligible concentration in expanded schist, are reacting with H<sub>2</sub>S. According to Table 4, CaO and SO<sub>3</sub>, might be involved. SO<sub>3</sub> can be excluded since it is not identified as a possible reactant with H<sub>2</sub>S (Figure 1). Moreover, it can be assumed that components like Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, largely present in expanded schist and marginally present in cellular concrete (Table 1), are therefore only slightly involved in H<sub>2</sub>S removal. Considering that materials containing iron oxides are usually identified as potential interesting media for H<sub>2</sub>S removal, this last finding may seem surprising at first. Besides, as better removal efficiencies were recorded in wet conditions, results can be explained by the appearance of CaCO<sub>3</sub>, formed according to reactions that occur naturally in concrete surface in wet conditions.



As a result, cellular concrete waste used in this study should not act as an iron sponge with iron regeneration. Chemical reactions between H<sub>2</sub>S and calcium oxides leading to the formation of gypsum according to equations 4-6 are mostly probable. The formation of the

components  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ , although slightly soluble in water, could explain the double proportion of sulphur measured in the expanded schist in the BF1 filter in regard to BF2. It could be assumed that during the formation of calcium compounds, a part of these compounds moved by lixiviation from the cellular concrete waste to the expanded schist. In regards to literature data, reactions that occur between  $\text{CaCO}_3$  and  $\text{H}_2\text{S}$  could also explain the ability of synthetic media developed specifically for biofiltration, and containing  $\text{CaCO}_3$  such as UP20 [21,26] and CM-5 [24,25], to improve biofilter performances. Moreover, in the case of UP20, these physical reactions could explain the ability of biofilters to withstand sudden high load  $\text{H}_2\text{S}$  changes [23]. As previously indicated, the use of Ca-based sorbents in the removal of  $\text{H}_2\text{S}$  from fuel gases was extensively studied at high temperatures, i.e. 650-1300°C [18], but the use of carbonaceous materials for gas desulfurization at ambient temperature is only now starting to be studied [11]. To date, and from the current state of our knowledge, reported results have been obtained in the presence of water. For instance, crushed oyster shells, mainly composed of  $\text{CaCO}_3$ , were used to remove  $\text{H}_2\text{S}$  in water [27]. Mechanisms of adsorption followed by an oxidation to obtain  $\text{S}^0$ ,  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^-$  were suggested. Therefore, based on the study of Asaoka and co-workers [27], an attempt to remove  $\text{H}_2\text{S}$  using a filter filled with crushed oyster shells was carried out. Filter BF2 was used for this purpose (Figure 2), expanded schist being replaced by crushed oyster shells (particle size distribution: 3-6 mm). For the operating conditions  $\text{EBRT} = 56 \text{ s}$  and  $C_G^{\text{in}} = 50 \text{ ppm}$ , removal efficiencies were 7.5% and 21.5% in dry and wet conditions, respectively, which is lower than results obtained for cellular concrete waste (Figure 5). However, it has to be noted that the oyster shell used in this study is a smooth material. Consequently, from these findings, it can be argued that: (i) the porosity of the material is a parameter that also has to be considered; (ii) the ability of the cellular concrete to react with  $\text{H}_2\text{S}$  in wet conditions is mainly due to the presence of calcium

oxides, but reaction could be catalyzed by the presence of other trace metal elements not present in the oyster shell. Both arguments can obviously be conjugated.

## 5.2 Impact of experimental conditions

The influence of inlet  $\text{H}_2\text{S}$  concentration was studied in wet conditions at a constant EBRT of 56 s. Results are reported in Figure 5. For both filters filled with cellular concrete waste, the removal efficiency logically decreased with the increase in  $C_G^{\text{in}}$ , the shapes of the curves being quite similar. The drop in RE were significant for inlet concentrations up to 200 ppm and moderate for higher concentrations. For a filter filled with cellular concrete only, RE was around 40-45% for an  $\text{H}_2\text{S}$  inlet concentration of 50 ppm. This result confirms the potential advantage of using cellular concrete waste as a first stage in treatment of gaseous  $\text{H}_2\text{S}$  effluents. For expanded schist, RE ranged from 1.5% to 5.8% irrespective of the  $\text{H}_2\text{S}$  inlet concentration.

The influence of EBRT change in the removal efficiency is clearly highlighted in Figure 6 for filters filled with cellular concrete waste. For BF1 and BF3, RE increased significantly with EBRT. As the change in EBRT was obtained by varying the gas flow-rate, the maximum EBRT value was 56 s, corresponding to a minimum flow-rate of  $0.5 \text{ m}^3 \text{ h}^{-1}$ . In this case, RE was around 40-45% for the filter filled with cellular concrete waste. Considering that measured pressure drops were low for this material (around  $12 \text{ Pa m}^{-1}$ ), it will be interesting to investigate the impact of higher EBRT obtained by increasing the height of the packing material. Furthermore, it could be argued that  $\text{H}_2\text{S}$  filtration through a long horizontally packed filter (several meters leading to high EBRT values) could be very efficient. For BF1 (mixture), it can be considered that  $\text{H}_2\text{S}$  removal is mainly due the presence of cellular concrete waste. Since the contact time between the gas phase and this material in BF1 is approximately half that in BF3 (due to the presence of expanded schist in BF1), it can be

considered that the performances of both filters were similar (on the basis of the amounts of cellular concrete waste in filters) as it will be shown hereafter from the determination of parameter  $\alpha_{\text{lump}}$  using the Ottengraf model.

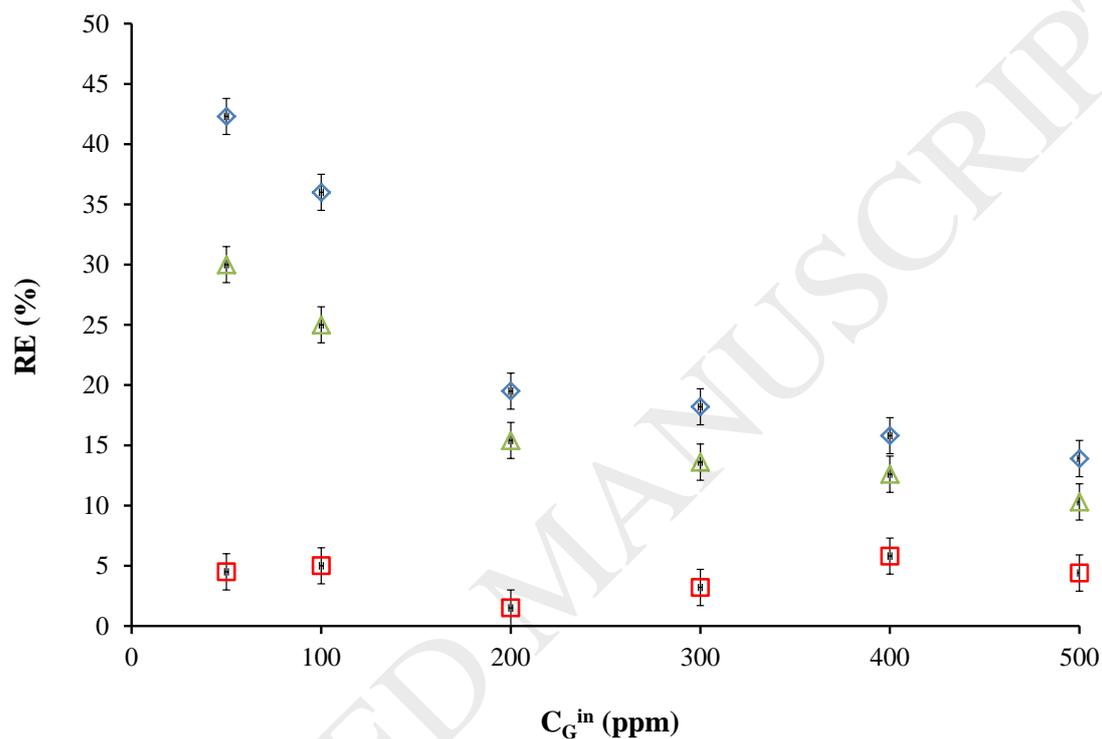


Figure 5: Removal efficiency vs  $\text{H}_2\text{S}$  concentration at the inlet of filters in wet conditions at  $\text{EBRT} = 56$  s (blue diamond: cellular concrete waste; green triangle: mixture of cellular concrete waste and expanded schist; red square: expanded schist).

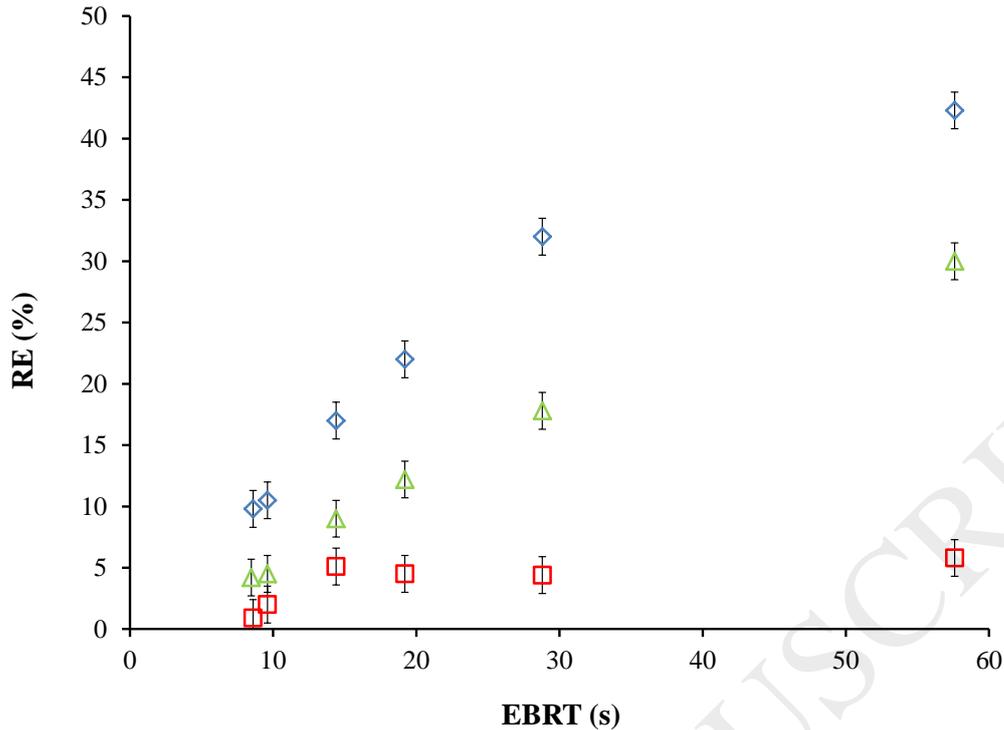


Figure 6: Removal efficiency vs EBRT in wet conditions at  $C_g^{\text{in}} = 50$  ppm (blue diamond: cellular concrete waste; green triangle: mixture of cellular concrete waste and expanded schist; red square: expanded schist).

### 5.3 Performances of packing materials

In order to assess the performances of the packing materials filling the filters in wet conditions, the Ottengraf and Michaelis-Menten models have been applied, respectively. Experimental results were fitted to determine the parameters  $\alpha_{\text{lump}}$ ,  $EC_{\text{max}}$  and  $K_s$ . The choice to use these models to determine the filter performances in abiotic conditions may seem surprising at first but can easily be explained. Firstly, it should be noted that the equation of the Michaelis-Menten model describes physically the rate of a reaction by relating the reaction rate to the concentration of the substrate. This equation describes the biochemical reactions involving a single substrate but may also be formally applied to other physical reactions. In the present case, the form of the equation of the Michaelis-Menten model is:

$$EC = EC_{\max} \frac{C_{\ln}}{K_s + C_{\ln}} \quad (9)$$

With:

$$C_{\ln} = \frac{C_G^{\text{in}} - C_G^{\text{out}}}{\ln\left(\frac{C_G^{\text{in}}}{C_G^{\text{out}}}\right)} \quad (10)$$

It has to be noted that equations (9-10) have been successfully applied to describe the performances of different packing materials used in H<sub>2</sub>S biofiltration [3,20,21,28,29].

Secondly, it has to be remembered that the Ottengraf model, developed by Ottengraf and Van den Oever [30] to describe the mechanisms of transfer and biodegradation in a biofilter, is based on the Michaelis-Menten equation. Thus, one of the main assumptions of this model is 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  $K_s$ . However, the same assumption of a zero-order reaction rate could be made in the absence of biofilm provided that a chemical reaction occurs between H<sub>2</sub>S and the components of the material. Usually, zero-order kinetics are encountered at high concentrations of H<sub>2</sub>S, which is generally the case in laboratory experiments. Two situations were then considered by the Ottengraf model: zero-order kinetics with diffusional limitation and zero-order kinetics with biological limitation in the biofilm. Considering that H<sub>2</sub>S reaction limitation or H<sub>2</sub>S diffusion limitation can also occur in the present case due to a physical reaction between H<sub>2</sub>S and the components of the material in place of a biological degradation in a biofilm, it therefore appeared interesting to apply this model to determine the parameter  $\alpha_{\text{lump}}$ . This parameter is interesting because it was demonstrated that it is a suitable tool to determine the performance of a biofilter as a whole whatever its composition (mixture or layers of different packing materials) and whatever the EBRT [3]. Thus, assuming that the reaction rate is diffusion limited, the relation between the loading rate and the removal capacity of the filter is given by the relation (the way to obtain this relation is extensively described in [3]):

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

From Equation (11), the parameter  $\alpha_{\text{lump}}$  is obtained by drawing the curve  $(1-EC/LR)^{1/2}$  versus  $(EBRT/LR)^{1/2}$ . A linear curve with an intercept of 1, and a slope corresponding to  $-\alpha_{\text{lump}}$  has to be obtained. Using the definitions of LR and EC given in Table 6 (i.e.  $\text{g m}^{-3} \text{h}^{-1}$ ) and EBRT in h, the unit of  $\alpha_{\text{lump}}$  is then in  $\text{g}^{1/2} \text{m}^{-3/2} \text{h}^{-1/2}$ .

Experimental data and modeled curves provided by the Michaelis-Menten and Ottengraf models are displayed in Figures 7 and 8, respectively. From Figure 7, it is shown that data obtained for filters containing cellular concrete waste (i.e. BF1 and BF3) can be satisfactorily described by the model of Michaelis-Menten (Microsoft® Excel solver was used to determine  $EC_{\text{max}}$  and  $K_s$  values). For BF2, data cannot be modeled (calculated  $EC_{\text{max}}$  being an unrealistic value) which is not surprising since RE was close to zero whatever the operating conditions. As indicated in Table 8,  $EC_{\text{max}}$  value determined for cellular concrete waste was in the same order of magnitude as the value obtained for sterilized CM-5, a synthetic material specifically developed for  $\text{H}_2\text{S}$  treatment, and significantly lower than the value obtained using laboratory-scale biofilters. Nonetheless, this result reinforces the idea that cellular concrete waste could be used as a first stage in  $\text{H}_2\text{S}$  treatment.

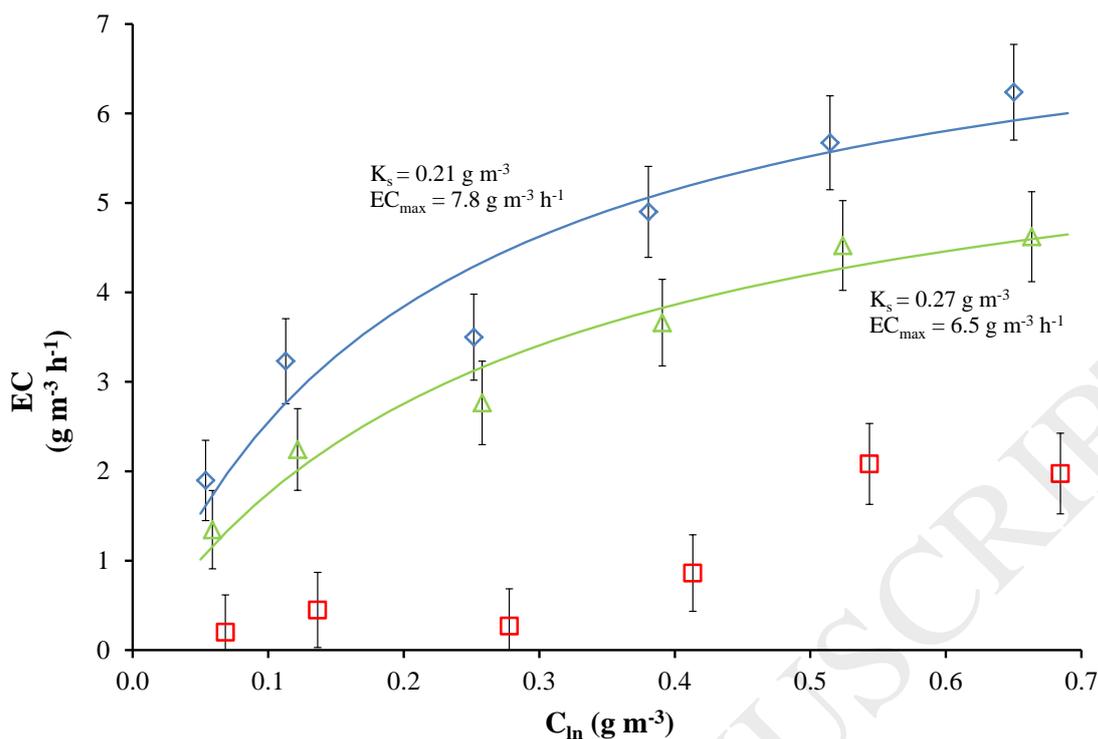


Figure 7: Elimination capacity vs  $H_2S$  concentration. Experimental points (blue diamond: cellular concrete waste; green triangle: mixture of cellular concrete waste and expanded schist; red square: expanded schist) and the Michaelis-Menten model (continuous lines).

Figure 8 shows that the experimental data for cellular concrete waste can also be modelled using the Ottengraf model. Consequently, it can be considered that  $H_2S$  reaction with cellular concrete is of zero-order kinetic with diffusional limitation. As the parameter  $\alpha_{lump}$  allows to characterize the performance of a filter as a whole whatever its composition (mixture of different packing materials for instance), it seems reasonable that  $\alpha_{lump}$  value for BF1 was lower than for BF3 ( $2.70$  vs  $4.26\ g^{1/2}\ m^{-3/2}\ h^{-1}$ , respectively). The ratio between  $\alpha_{lump}$  values corresponds well to the ratio of the amounts of cellular concrete waste filling each filter (65% and 100% in volume, respectively). The comparison between  $\alpha_{lump}$  values determined for biofilters (Table 9) and cellular concrete waste in abiotic conditions are in agreement with the findings deduced from the analysis of  $EC_{max}$  values. Even if the  $\alpha_{lump}$  value determined for cellular concrete waste is lower than the values reported in the literature in the case of a

biofilter filled with inoculated materials, the potential advantages of using this waste material for H<sub>2</sub>S treatment is nonetheless proved.

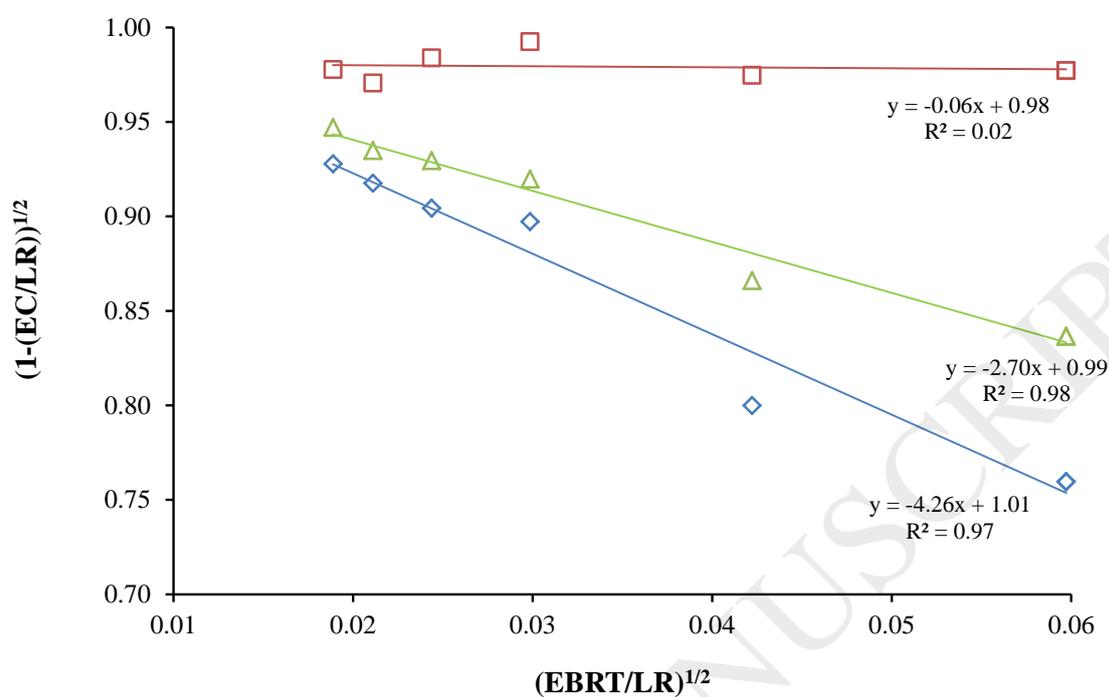


Figure 8:  $\alpha_{lump}$  determination from the Ottengraf model (blue diamond: cellular concrete waste; green triangle: mixture of cellular concrete waste and expanded schist; red square: expanded schist).

Table 8: Parameters  $EC_{max}$  et  $K_s$  reported in the literature.

	<b>EBRT</b> (s)	<b><math>K_s</math></b> (g m <sup>-3</sup> )	<b><math>EC_{max}</math></b> (g m <sup>-3</sup> h <sup>-1</sup> )	<b>Reference</b>
Cellular concrete waste (abiotic)	56	0.21	7.8	Present study
Expanded schist + microorganisms	63	0.070	28.6	[4]
Expanded schist + microorganisms	35	0.050	32.8	[23]
Peat + microorganisms		0.113	53.4	
Sapwood + microorganisms	57	0.017	8.3	[22]
Pine bark + microorganisms		0.036	16.5	
Sterilized CM-5 (abiotic)		0.030	8.4	
CM-5 + microorganisms	48	0.080	62.2	[25]

Table 9:  $\alpha_{\text{lump}}$  values of different packing materials used in biofiltration [3,22].

Packing materials filling the biofilter	$\alpha_{\text{lump}}$ ( $\text{g}^{1/2} \text{m}^{-3/2} \text{h}^{-1}$ )
Sapwood	7.9
Sapwood + UP20 (2 layers)	8.4
Pine bark	11.4
Pozzolan + UP20 (2 layers)	11.9
Peat	15.3
Peat + UP20 (2 layers)	15.9
Peat + UP20 (mixed)	21.3
Expanded schist + UP20 (2 layers)	26.4

## 6 Conclusion

The ability of an abiotic filter filled with cellular concrete waste as packing material to treat  $\text{H}_2\text{S}$  in air was investigated. It was demonstrated that wet conditions are required to obtain  $\text{H}_2\text{S}$  removal. Removal efficiency around 40-45% was obtained at an EBRT of 56 s and for a  $\text{H}_2\text{S}$  concentration of 50 ppm. This result was mainly due to reactions occurring between  $\text{H}_2\text{S}$  and calcium carbonate leading to gypsum formation. A maximum elimination capacity of  $7.8 \text{ g m}^{-3} \text{ h}^{-1}$  was calculated using the Michaelis-Menten model. Therefore,  $\text{H}_2\text{S}$  filtration using cellular concrete waste could be carried out beneficially as the humidification step of biofiltration systems. Additionally, this mode of filtration could be used as a first step treatment to remove  $\text{H}_2\text{S}$  from biogas. Considering that pressure drops were low for this material (around  $12 \text{ Pa m}^{-1}$ ), it can be assumed that a  $\text{H}_2\text{S}$  filtration through a long packed filter would be very efficient (a horizontal mode would be more appropriate than a very high column). However, the fact that the gypsum formed can potentially react with aluminates to form ettringite causing the disintegration of concrete has to be investigated in order to determine the lifetime of the material for such applications.

## REFERENCES

- [1] K. Vikrant, S.K. Kailasa, D.C.W. Tsang, S.S. Lee, P. Kumar, B.S. Giri, R.S. Singh, K.-H. Kim, Biofiltration of hydrogen sulfide: Trends and challenges, *J. Clean. Prod.* 187 (2018) 131–147. doi:10.1016/j.jclepro.2018.03.188.
- [2] M. Ben Jaber, A. Couvert, A. Amrane, P. Le Cloirec, E. Dumont, Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions, *J. Environ. Chem. Eng.* 5 (2017) 5617–5623. doi:10.1016/j.jece.2017.10.029.
- [3] M. Ben Jaber, A. Couvert, A. Amrane, F. Rouxel, P. Le Cloirec, E. Dumont, Biofiltration of H<sub>2</sub>S in air—Experimental comparisons of original packing materials and modeling, *Biochem. Eng. J.* 112 (2016) 153–160. doi:10.1016/j.bej.2016.04.020.
- [4] M. Ben Jaber, A. Couvert, A. Amrane, F. Rouxel, P. Le Cloirec, E. Dumont, Biofiltration of high concentration of H<sub>2</sub>S in waste air under extreme acidic conditions, *New Biotechnol.* 33 (2016) 136–143. doi:10.1016/j.nbt.2015.09.008.
- [5] M. Ben Jaber, A. Couvert, A. Amrane, P. Le Cloirec, E. Dumont, Removal of hydrogen sulfide in air using cellular concrete waste: Biotic and abiotic filtrations, *Chem. Eng. J.* 319 (2017) 268–278. doi:10.1016/j.cej.2017.03.014.
- [6] A. Grandclerc, M. Guéguen-Minerbe, I. Nour, P. Dangla, T. Chaussadent, Impact of cement composition on the adsorption of hydrogen sulphide and its subsequent oxidation onto cementitious material surfaces, *Constr. Build. Mater.* 152 (2017) 576–586. doi:10.1016/j.conbuildmat.2017.07.003.
- [7] D. Martemianov, B.-B. Xie, T. Yurmazova, M. Khaskelberg, F. Wang, C.-H. Wei, S. Preis, Cellular concrete-supported cost-effective adsorbents for aqueous arsenic and heavy metals abatement, *J. Environ. Chem. Eng.* 5 (2017) 3930–3941. doi:10.1016/j.jece.2017.07.063.
- [8] E. Oguz, Adsorption of fluoride on gas concrete materials, *J. Hazard. Mater.* 117 (2005) 227–233. doi:10.1016/j.jhazmat.2004.09.020.
- [9] E. Dumont, H<sub>2</sub>S removal from biogas using bioreactors: a review, *Int. J. Energy Environ.* (2015) 479–498.
- [10] N. Thanakunpaisit, N. Jantarachatt, U. Onthong, Removal of Hydrogen Sulfide from Biogas using Laterite Materials as an Adsorbent, *Energy Procedia.* 138 (2017) 1134–1139. doi:10.1016/j.egypro.2017.10.215.
- [11] M. Hervy, D. Pham Minh, C. Gérente, E. Weiss-Hortala, A. Nzihou, A. Villot, L. Le Coq, H<sub>2</sub>S removal from syngas using wastes pyrolysis chars, *Chem. Eng. J.* 334 (2018) 2179–2189. doi:10.1016/j.cej.2017.11.162.
- [12] F.J. Gutiérrez Ortiz, P.G. Aguilera, P. Ollero, Biogas desulfurization by adsorption on thermally treated sewage-sludge, *Sep. Purif. Technol.* 123 (2014) 200–213. doi:10.1016/j.seppur.2013.12.025.
- [13] R.C. Sahu, R. Patel, B.C. Ray, Removal of hydrogen sulfide using red mud at ambient conditions, *Fuel Process. Technol.* 92 (2011) 1587–1592. doi:10.1016/j.fuproc.2011.04.002.
- [14] M. Fontseré Obis, P. Germain, H. Bouzahzah, A. Richioud, H. Benbelkacem, The effect of the origin of MSWI bottom ash on the H<sub>2</sub>S elimination from landfill biogas, *Waste Manag.* 70 (2017) 158–169. doi:10.1016/j.wasman.2017.09.014.
- [15] L. Sarperi, A. Surbrenat, A. Kerihuel, F. Chazarenc, The use of an industrial by-product as a sorbent to remove CO<sub>2</sub> and H<sub>2</sub>S from biogas, *J. Environ. Chem. Eng.* 2 (2014) 1207–1213. doi:10.1016/j.jece.2014.05.002.

- [16] Z. Shareefdeen, Development of a biofilter media for removal of hydrogen sulphide, *Glob. NEST J.* 11 (2009) 218–222. doi:10.30955/gnj.000583.
- [17] L. Zhang, D.A. Dzombak, D.V. Nakles, S.B. Hawthorne, D.J. Miller, B.G. Kutchko, C.L. Lopano, B.R. Strazisar, Characterization of pozzolan-amended wellbore cement exposed to CO<sub>2</sub> and H<sub>2</sub>S gas mixtures under geologic carbon storage conditions, *Int. J. Greenh. Gas Control.* 19 (2013) 358–368. doi:10.1016/j.ijggc.2013.09.004.
- [18] R. Agnihotri, S.S. Chauk, S.K. Mahuli, L.-S. Fan, Mechanism of CaO reaction with H<sub>2</sub>S: Diffusion through CaS product layer, *Chem. Eng. Sci.* 54 (1999) 3443–3453. doi:10.1016/S0009-2509(98)00339-X.
- [19] O.W. Awe, D.P. Minh, N. Lyczko, A. Nzihou, Y. Zhao, Laboratory-scale investigation of the removal of hydrogen sulfide from biogas and air using industrial waste-based sorbents, *J. Environ. Chem. Eng.* 5 (2017) 1809–1820. doi:10.1016/j.jece.2017.03.023.
- [20] E. Dumont, L.M. Ayala Guzman, M.S. Rodríguez Susa, Y. Andrès, H<sub>2</sub>S 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.
- [21] E. Dumont, Y. Andrès, P. Le Cloirec, F. Gaudin, Evaluation of a new packing material for H<sub>2</sub>S removed by biofiltration, *Biochem. Eng. J.* 42 (2008) 120–127. doi:10.1016/j.bej.2008.06.012.
- [22] E. Dumont, Y. Andrès, Evaluation of innovative packing materials for the biodegradation of H<sub>2</sub>S: a comparative study, *J. Chem. Technol. Biotechnol.* 85 (2010) 429–434. doi:10.1002/jctb.2334.
- [23] A.C. Romero Hernandez, M.S. Rodríguez Susa, Y. Andrès, E. Dumont, Steady- and transient-state H<sub>2</sub>S biofiltration using expanded schist as packing material, *New Biotechnol.* 30 (2013) 210–218. doi:10.1016/j.nbt.2012.07.003.
- [24] R. Zhu, S. Li, Z. Wu, É. Dumont, Performance evaluation of a slow-release packing material-embedded functional microorganisms for biofiltration, *Environ. Technol.* 38 (2017) 945–955. doi:10.1080/09593330.2016.1214624.
- [25] R. Zhu, S. Li, X. Bao, É. Dumont, Comparison of biological H<sub>2</sub>S removal characteristics between a composite packing material with and without functional microorganisms, *Sci. Rep.* 7 (2017) 42241. doi:10.1038/srep42241.
- [26] C. Corre, C. Couriol, A. Amrane, E. Dumont, Y. Andrès, P. Le Cloirec, Efficiency of Biological Activator Formulated Material (BAFM) for volatile organic compounds removal – preliminary batch culture tests with activated sludge, *Environ. Technol.* 33 (2012) 1671–1676. doi:10.1080/09593330.2011.641592.
- [27] S. Asaoka, T. Yamamoto, S. Kondo, S. Hayakawa, Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments, *Bioresour. Technol.* 100 (2009) 4127–4132. doi:10.1016/j.biortech.2009.03.075.
- [28] A. Courtois, Y. Andrès, É. Dumont, H<sub>2</sub>S biofiltration using expanded schist as packing material: influence of packed bed configurations at constant EBRT: H<sub>2</sub>S biofiltration using expanded schist as packing material, *J. Chem. Technol. Biotechnol.* 90 (2015) 50–56. doi:10.1002/jctb.4456.
- [29] 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 H<sub>2</sub>S removal, *Environ. Technol.* 34 (2013) 1123–1129. doi:10.1080/09593330.2012.736691.
- [30] 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.