



HAL
open science

Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions

M.B. Jaber, A. Couvert, A. Amrane, P. Le Cloirec, Eric Dumont

► **To cite this version:**

M.B. Jaber, A. Couvert, A. Amrane, P. Le Cloirec, Eric Dumont. Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions. *Journal of Environmental Chemical Engineering*, 2017, 5 (6), pp.5617-5623. 10.1016/j.jece.2017.10.029 . hal-01639689

HAL Id: hal-01639689

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01639689>

Submitted on 5 Dec 2017

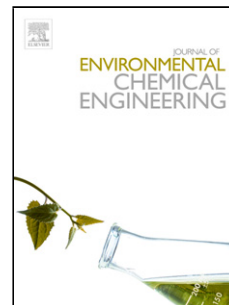
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

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.

Accepted Manuscript

Title: Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions

Authors: Mouna Ben Jaber, Annabelle Couvert, Abdeltif Amrane, Pierre Le Cloirec, Eric Dumont



PII: S2213-3437(17)30530-4
DOI: <https://doi.org/10.1016/j.jece.2017.10.029>
Reference: JECE 1939

To appear in:

Received date: 13-6-2017
Revised date: 11-10-2017
Accepted date: 13-10-2017

Please cite this article as: Mouna Ben Jaber, Annabelle Couvert, Abdeltif Amrane, Pierre Le Cloirec, Eric Dumont, Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions, Journal of Environmental Chemical Engineering <https://doi.org/10.1016/j.jece.2017.10.029>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Hydrogen sulfide removal from a biogas mimic by biofiltration under anoxic conditions

Mouna BEN JABER¹, Annabelle COUVERT¹, Abdeltif AMRANE¹, Pierre LE CLOIREC¹, Eric DUMONT^{2*}

¹ École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

² UMR CNRS 6144 GEPEA, IMT Atlantique, Campus de Nantes, La Chantrerie, 4 rue Alfred Kastler, CS 20722, 44307 Nantes Cedex 3, France

*: Corresponding author

Highlights

- H₂S removal from a biogas mimic in anoxic biofilters was investigated
- Two packing materials were used: expanded schist and cellular concrete waste
- Expanded schist is efficient for removing H₂S (up to 1100 ppmv) at an EBRT of 300 s
- Cellular concrete waste is also efficient (H₂S up to 900 ppmv) at an EBRT of 240 s
- Biofilters could be used instead of biotrickling filters for biogas cleaning

Abstract

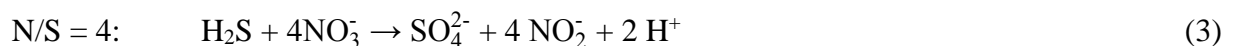
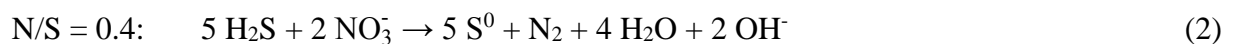
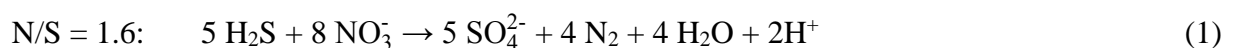
The biofiltration of hydrogen sulfide present in a biogas mimic under anoxic conditions was performed using expanded schist and cellular concrete waste as packing materials. The impact of various parameters, such as H₂S concentrations, Empty Bed Residence Time (EBRT) and molar ratio N/S, on the performances of biofilters was evaluated. At an EBRT of 300 s, expanded schist efficiently treated H₂S concentrations up to 1100 ppmv (maximum elimination capacity $EC_{\max} = 30.3 \text{ g m}^{-3} \text{ h}^{-1}$). At an EBRT of 240 s, cellular concrete waste was an effective material for the treatment of concentrations of H₂S up to 900 ppmv ($EC_{\max} = 25.2 \text{ g m}^{-3} \text{ h}^{-1}$). Whatever the molar ratio N/S selected, sulfate and elemental sulfur were produced in the biofilters. Both materials presented a satisfactory mechanical behavior with low pressure drops. Therefore, this study showed that biofilters could be used to treat moderate concentrations of H₂S in biogas under anoxic conditions.

Keywords: Biogas; Biofilter; Anoxic conditions; Cellular concrete waste; Expanded schist; H₂S

1. Introduction

Biogas is a renewable energy source that is produced during the anaerobic digestion of organic wastes (i.e., sewage sludge, municipal solid wastes, agricultural wastes, etc.). Typical biogas contains methane (CH_4 , 40 - 75 %), carbon dioxide (CO_2 , 15 - 60 %) and trace amounts of other constituents, such as hydrogen sulfide (H_2S), halogenated hydrocarbons, ammonia, nitrogen and siloxanes [1]. Hydrogen sulfide can be present at high concentrations (10 to 10,000 ppmv) depending on the composition of the organic substrate [2]. H_2S has a real impact on human health, corrodes engine parts and forms poisonous sulfur dioxide (SO_2) during its combustion. Before biogas can be used, H_2S must therefore be removed. A well-known method of biogas purification is absorption using amine solutions such as methyldiethanolamine (MDEA) and monoethanolamine (MEA) and alkaline solutions [3–5]. These technologies have been successfully applied. However, the major drawbacks of these processes are the high energy and operating costs due to the regeneration of the absorbent phase. Another biogas desulfurization method is adsorption using different porous and/or reactive materials such as activated carbon [6–9] and zeolite [10,11]. However, for high concentrations of H_2S in biogas, the adsorbing materials are saturated relatively quickly and need to be changed frequently, which results in high operational costs. Recently, the focus has shifted toward using bioreactors for biogas desulfurization. Such a technology appears an attractive process due to its effectiveness, low energy consumption and environmental acceptability. Bioreactors use microorganisms immobilized in the form of a biofilm for pollutant biodegradation. H_2S is transferred from the gaseous phase to the biofilm where it is metabolized. Pollutant transfer and biodegradation kinetics depend on the properties of the medium and operating conditions such as pH, water holding capacity, porosity, and mechanical stability. The packing material represents the cornerstone of the process. Synthetic media, such as polypropylene Pall rings and plastic fibers, are widely used for H_2S removal

due to their interesting mechanical behavior [12–14]. Hydrogen sulfide biodegradation in biogas has been mainly studied under aerobic conditions [15–17] but several studies using anoxic conditions have also been reported [12,14]. The main advantage of working in an anoxic environment is that biogas is not diluted with air so that the methane concentration is not reduced. Moreover, these conditions prevent the risk of explosion of the oxygen/methane mixture. In this case, nitrates (NO_3^-) can be used as electron acceptors instead of oxygen. In addition, anoxic bioreactors produce less biomass than aerobic bioreactors due to the inorganic nature of the reactants and the lower energy yield, resulting from the smaller oxidation potential of nitrate compared to oxygen [18]. Although the denitrification process using nitrates as electron acceptors to remove H_2S in wastewater is feasible, it has been paid little attention for biogas purification. Moreover, the interactions between H_2S oxidation and NO_3^- reduction are complex and there are many challenges to overcome before achieving the development of an industrial-scale pilot [19]. Depending on the molar ratio of nitrogen source to sulfide (N/S), a specific denitrifying bacteria, namely *Thiobacillus denitrificans*, carries out a double action: (i) H_2S oxidation with formation of sulfate [Eqs. (1) and (3)] or elemental sulfur (Eqs. (2) and (4)); (ii) NO_3^- reduction with formation of nitrogen [Eqs. (1, 2)] or nitrite [Eqs (3, 4)]. The overall reaction is given by Eq. (5).



To date, biological biogas cleaning under anoxic conditions has only been studied using biotrickling filters [14,16,20,21]. To the best of our knowledge, there is no study reporting the purification of biogas using biofilters. The purpose of this study was therefore to investigate

the performances of anoxic biofilters treating H₂S present in a biogas mimic using different packing materials, i.e. expanded schist and cellular concrete waste. Significant effort was focused on the impact of key parameters, such as Empty Bed Residence Time (EBRT), H₂S concentration, and the molar ratio N/S, on the performances of the process. The final objective was to demonstrate that when biogas is produced by on-farm anaerobic digesters, the simultaneous biological removal of H₂S from biogas and nitrates from wastewater could be coupled in a biofilter. The paper is organized as follows. The packing materials used in this study are described in the first part as well as the operating conditions selected for H₂S biofiltration. Then, the impact of the operating conditions on H₂S removal is reported in the second part.

2. Materials and methods

2.1. Filter media

Two different packing materials were tested in this study.

(i) Expanded schist is an inorganic support produced in Mayenne, France (Granulex Company; www.granulex.fr) [Fig. 1]. It has been efficiently used for H₂S biofiltration in air in several studies [22–24]. Recently, Ben Jaber et al. [25,26] proved that expanded schist could be successfully used for treating high H₂S concentrations in air under extreme acidic conditions due to its excellent mechanical behavior, which resulted in low pressure drops over a long period of operation. At an EBRT of 63 s, a removal efficiency higher than 95 % was thus achieved for concentrations up to 250 ppmv, corresponding to a maximum elimination capacity (EC_{max}) of 24.7 g m⁻³ h⁻¹.

(ii) Cellular concrete is a recycled mineral waste material provided by the Florentaise company (Nantes, France; www.florentaise.com) [Fig. 1]. It was used for the first time as a new packing material for H₂S biofiltration in air by Ben Jaber et al. [27]. At an EBRT of 63 s, a removal efficiency of 100 % was reached for H₂S concentrations up to 133 ppmv

(elimination capacity of $10.5 \text{ g m}^{-3} \text{ h}^{-1}$). Physicochemical and biological mechanisms explaining H_2S removal were evidenced and an EC_{max} value of $17.8 \text{ g m}^{-3} \text{ h}^{-1}$ was calculated. This recent study revealed that the packed bed of cellular concrete also presented a satisfactory mechanical behavior with low pressure drops (30 % lower than those measured with expanded schist in the same conditions).

The composition of the packing materials (Table 1) was determined using an Energy Dispersive X-ray Fluorescence Spectrometer (EDX-800HS, Shimadzu Company). The internal porosity and the apparent density were measured by a Micromeritics AutoPore IV 9500 mercury porosimeter. The specific surface area was measured by a Micromeritics ASAP 2020 Surface Area Analyzer. The physical characteristics of the two packing materials are presented in Table 2. The water retention capacity of a material represents the maximum mass of water retained per gram of dry material. The material was immersed for 1 h in water and then drained for 24 h. The difference in mass was used to calculate its water retention capacity. The pH of the packing material was measured with a pH electrode (Consort) connected to a multi-parameter analyzer Consort C561 (measurement accuracy $0.2 \% \pm 1$ digit).

Fig. 1 Pictures of expanded schist (left) and cellular concrete waste (right).

Table 1 Composition (% weight) of cellular concrete and expanded schist (the main components are given).

Composition (%)	Cellular concrete	Expanded schist
SiO₂	50.5	56.4
CaO	24.6	0.9
SO₃	19.7	1.6
Al₂O₃	2.2	20.5
P₂O₅	1.4	1.6
Fe₂O₃	1.3	12.4
K₂O	0.2	5.0

Table 2 Physical characteristics of cellular concrete and expanded schist.

Characteristics	Cellular concrete	Expanded schist
Median size of particles (mm)	11	12
Apparent density (kg m ⁻³)	547 ± 5	1248 ± 12
Specific surface area S _{BET} (m ² g ⁻¹)	44 ± 0.8	-
Initial pH	9.0 ± 0.1	7.0 ± 0.1
Water retention capacity (%)	56 ± 2	-

2.2. Analytical methods

The H₂S concentration was measured with a ProCeas[®] Biogas analyzer (from AP2E Company, Aix-en-Provence, France). This is a complete pre-calibrated laser infrared spectrometer of rapid real-time measurement of H₂S (0 - 2000 ppmv ± 1 %), CO₂ and CH₄ for methanization process monitoring.

Samples of leachate were taken periodically in order to determine (i) the sulfate concentration (by the turbidimetric method) and (ii) the nitrite concentration (by the photometric method) as described in the Standard Methods for the examination of Water and Wastewater [28].

2.3. Experimental set-up

The biofiltration unit [Fig. 2] consisted of three identical PVC columns (called “BF1”; “BF2” and “BF3”) with an internal diameter of 10 cm and a packed volume of 7.85 L (1 m height). Biofilters BF1 and BF2 were filled with 5.2 kg of expanded schist while BF3 was filled with 2.5 kg of cellular concrete waste. The biofilters were inoculated with 3 L of a diluted solution of activated sludge from a domestic wastewater treatment plant (Tougas, Nantes, France). The initial biomass was not acclimatized beforehand to H₂S treatment under anoxic conditions. For safety reasons, methane was replaced by nitrogen and the biogas mimic treated was a mixture of nitrogen and hydrogen sulfide. The replacement of methane by nitrogen in the biogas mimic has been successfully considered in several studies [16,29,30]. Since methane is barely soluble in water, it has been shown that it is not degraded during biogas purification

[12,17,21]. A nitrogen generator BrezzaNiGen LC-MS (40-1) (purity up to 99.9 %) from Gengaz Company (Wasquehal, France) was set up in order to provide a continuous supply of N₂ for biofilters. A stream of H₂S (99.7 % purity) controlled by a mass flow controller (Model 5850S, Brooks Instruments, Hatfield, USA) was mixed with N₂, and then introduced at the bottom of the biofilter. In order to maintain an optimal bed humidity and to provide nutrients for microorganisms, biofilters were sprinkled with a nutritive solution for 5 min each hour (80 mL h⁻¹). The composition of this solution was as follows: [KH₂PO₄], 0.025 g L⁻¹; [Na₂CO₃], 0.400 g L⁻¹; [NH₄Cl], 0.020 g L⁻¹; [FeSO₄.7H₂O], 0.014 g L⁻¹.

Under anoxic conditions, nitrates are used as electron acceptors. Sodium nitrate (NaNO₃) was used as the nitrate source. Depending on the molar ratio N/S selected, the same quantity of nitrate was added in BF1, BF2 and BF3, respectively.

Fig. 2 Experimental pilot-scale biofilters.

2.4. Operating conditions

The parameters used in this paper to describe the operating conditions and for the determination of the removal performances are given in Table 3.

For biofilter BF1 (expanded schist), different molar ratios N/S (0.4, 0.89 and 1.6) were tested in order to monitor the impact of this parameter on the performances of the process. The concentration was maintained at a constant level (300 ppmv) and the EBRT was 60 s.

For biofilters BF2 (expanded schist) and BF3 (cellular concrete waste), two parameters affecting the loading rate were studied during 213 days: (i) pollutant concentration was increased in order to compare biofilter removal efficiencies; (ii) the influence of the variation in EBRT as concentration increases. The H₂S concentrations considered (Table 4) were

selected according to a moderate concentration that can be present in a biogas (up to 1000 ppmv). A constant molar ratio N/S of 0.89 was applied. In fact, using such an N/S value, Manconi et al. [31] achieved the complete oxidation of sulfide to sulfate. As a result of an external disturbance (a problem with the BF3 flowmeter), a drop in process performance occurred from the 116th day. To restore the biofilter capacities, a lower concentration of H₂S up to 200 ppmv was applied from the 125th day.

Table 3 Parameters used in this paper.

	Definition	Nomenclature
Loading rate (g m ⁻³ h ⁻¹)	$LR = \frac{Q}{V} C_{in}$	C _{in} : inlet concentration (mg m ⁻³)
Elimination capacity (g m ⁻³ h ⁻¹)	$EC = \frac{Q}{V} (C_{in} - C_{out})$	C _{out} : outlet concentration (mg m ⁻³)
Removal efficiency (%)	$RE = \frac{(C_{in} - C_{out})}{C_{in}} 100$	Q: gas flow rate (m ³ h ⁻¹)
Empty Bed Residence Time (s)	$EBRT = \frac{V}{Q}$	V: packed bed volume (m ³)

Table 4 Operating conditions for biofilters BF2 and BF3.

BF2				BF3			
Duration (days)	[H ₂ S] (ppmv)	EBRT (s)	LR (g m ⁻³ h ⁻¹)	Duration (days)	[H ₂ S] (ppmv)	EBRT (s)	LR (g m ⁻³ h ⁻¹)
9	25	60	2.1	9	25	60	2.1
13	150	60	12.6	13	150	60	12.6
13	300	60	25.2	13	300	60	25.2
16	450	60	37.8	16	450	60	37.8
6	450	120	18.9	6	450	120	18.9
Technical problems (48 days)							
9	450	120	18.9	9	450	120	18.9
11	600	120	25.2	11	600	120	25.2
14	700	120	29.4	10	200	120	8.4
8	800	120	33.6	10	300	120	12.6
8	800	180	22.4	10	450	120	18.9
13	800	240	16.8	10	450	180	12.6
14	900	240	18.9	17	600	180	16.8

12	1000	240	21	12	800	180	22.4
10	1100	240	23.1	12	900	180	25.2
9	1100	300	18.5	7	900	240	18.9

3. Results and discussion

3.1. Impact of change in H₂S concentration and EBRT

The impact of an increase in the H₂S concentration from 25 to 450 ppmv (LR from 2.1 to 37.8 g m⁻³ h⁻¹) on the performances of biofilters BF2 (expanded schist) and BF3 (cellular concrete waste) is shown in Fig. 3. The acclimation period for the microbial population for both biofilters was short. H₂S was totally removed from the 3rd day (RE > 99 %). At an EBRT of 60 s and a constant molar ratio N/S of 0.89, for H₂S concentrations up to 300 ppmv, a removal efficiency of 100 % (corresponding to an EC of 25.2 g m⁻³ h⁻¹) was recorded in both biofilters proving the ability of expanded schist and cellular concrete waste to be used for biofiltration under anoxic conditions. Note that expanded schist has previously been demonstrated as efficient for treating moderate concentrations of H₂S in air [22–24]. Additionally, Ben Jaber et al. [25] recently highlighted that this material gives interesting performances for removing high concentrations of H₂S (up to 360 ppmv) present in waste gas at an EBRT of 63 s. Therefore, the present approach confirmed that this medium can also be successfully used to treat high concentrations of H₂S up to 450 ppmv at an EBRT of 60 s under anoxic conditions. A similar conclusion can be made for cellular concrete waste (RE = 100 % for H₂S concentrations up to 300 ppmv).

As shown in Fig. 3, the removal efficiencies in both biofilters started to decrease for H₂S concentrations of 450 ppmv. However, expanded schist (BF2) presented better performances than those found with cellular concrete (BF3) (a difference of 13 % in terms of removal efficiency was recorded). Such a difference between media performances was also evidenced by Ben Jaber et al. [27] in the case of H₂S biofiltration in air under aerobic conditions.

According to these authors, at a loading rate of $28.8 \text{ g m}^{-3} \text{ h}^{-1}$ (EBRT of 63 s and H_2S concentration of 360 ppmv), the removal efficiencies obtained for expanded schist and cellular concrete were 87 % and 63 %, respectively. They assumed that physicochemical and biological mechanisms explaining H_2S removal occurred simultaneously in the biofilter. However, physicochemical interactions between the main components (Table 1) of the packing materials and H_2S are not yet fully understood. Consequently, further investigations are necessary to identify the precise physicochemical mechanisms involved in H_2S removal and to determine the part played by these mechanisms regarding the overall H_2S removal. The decrease in the removal efficiency as concentration increases may be due to a direct inhibitory effect on the metabolism of some microorganisms or to mass transfer limitations owing to a too low EBRT [32–34].

At high H_2S concentration, the Empty Bed Residence Time (EBRT) is the key parameter to ensure a successful biofiltration operation. However, an increase in EBRT mechanically implies a decrease in the loading rate to be treated. The impact of the EBRT on the performances of biofilters BF2 and BF3 is shown in Figs. 4-5, respectively. The biofilter filled with expanded schist (BF2) was able to remove completely H_2S concentrations up to 1100 ppmv at an EBRT of 300 s. During the operation time (213 days), an experimental maximum elimination capacity (EC_{max}) of $30.3 \text{ g m}^{-3} \text{ h}^{-1}$ was achieved [Fig. 4]. Concerning the biofilter filled with cellular concrete waste (BF3), Fig. 5 shows that this material is efficient for the treatment of H_2S concentrations up to 900 ppmv at an EBRT of 240 s ($\text{EC}_{\text{max}} = 25.2 \text{ g m}^{-3} \text{ h}^{-1}$). These results confirm that expanded schist showed better performances than cellular concrete waste. Moreover, they indicate that the elimination capacities of the biofilters were around 25 and $30 \text{ g m}^{-3} \text{ h}^{-1}$ for BF3 and BF2, respectively, irrespective of the parameters used to change the loading rate (H_2S concentration or EBRT). In the literature,

only few data are available dealing with biogas purification using biofilters and these studies were carried out under aerobic conditions. Nonetheless, these results could be compared with those obtained using biotrickling filters under anoxic conditions. Although a direct comparison of bioreactor performances operating at different EBRTs has to be considered with caution, it appears that expanded schist and cellular concrete waste are promising materials to treat H_2S from biogas in terms of elimination capacity and removal efficiency. Thus, although better performances were reported by Montebello et al. [16] who achieved a maximum removal capacity of $142 \text{ g m}^{-3} \text{ h}^{-1}$ at an EBRT of 163 s using polyurethane foam as packing material, and by Fernandez et al. [20] who found a maximum removal capacity of $171 \text{ g m}^{-3} \text{ h}^{-1}$ at an EBRT of 144 s using polypropylene Pall rings, the present results are significantly higher than the performances obtained by Soreanu et al. [35] using plastic fibers and lava rock as packing materials in a biotrickling filter at an EBRT of 16 min (7.37 and $7.58 \text{ g m}^{-3} \text{ h}^{-1}$, respectively). In the same way, Soreanu et al. [21] reported a maximum removal capacity of $12.5 \text{ g m}^{-3} \text{ h}^{-1}$ for an EBRT of 18 min using plastic fibers as packing material. Therefore, the present study highlights that biofiltration using cheap materials such as expanded schist and cellular concrete waste can be an efficient technique to treat H_2S in biogas under anoxic conditions. However, the use of biofilters should be restricted to treating biogas moderately loaded in H_2S , i.e. for biogas containing a few hundreds of ppmv of H_2S .

Fig. 3 Removal efficiency of H_2S using expanded schist (BF2) and cellular concrete (BF3) as packing materials (H_2S concentrations from 25 to 450 ppmv; EBRT = 60 s; N/S = 0.89).

Fig. 4 EBRT influence on removal efficiency of H_2S using expanded schist (BF2) as packing material (H_2S concentrations from 25 to 1100 ppmv; N/S = 0.89).

Fig. 5 EBRT influence on removal efficiency of H₂S using cellular concrete waste (BF3) as packing material (H₂S concentrations from 25 to 900 ppmv; N/S = 0.89).

3.2. Accumulation of nitrites and sulfates

The selected N/S molar ratio for BF2 and BF3 was 0.89. This choice was based on the work of Manconi et al. [31] who observed the complete oxidation of hydrogen sulfide using this molar ratio. For the treatment of H₂S under anoxic conditions, a double activity is ideally expected in the biofilter, i.e. the complete oxidation of H₂S and the complete reduction of nitrates leading to N₂ generation. However, H₂S can usually be oxidized to sulfates (SO₄²⁻) according to Eqs. (1, 3) and to elemental sulfur (S⁰) according to Eqs. (2, 4). Moreover, the production of nitrites (NO₂⁻), by-products in the denitrification process, is also observed [Eqs. (3, 4)]. Figure 6 shows the leachate analysis in terms of sulfate and nitrite production. For both biofilters, nitrite production was low even at high concentrations of H₂S. Thus, at a concentration of 600 ppmv (corresponding to a loading rate of 25.2 g m⁻³ h⁻¹), the nitrite concentration was less than 0.8 mg L⁻¹, suggesting total denitrification. Such a value is a hundred times lower than that given by Fernandez et al. [20] who reported an accumulation of nitrite of less than 80 mg L⁻¹ in a biotrickling filter (N/S value of 0.77). However, the loading rate applied by these authors (201 g m⁻³ h⁻¹) was eight times higher than the one applied in the present study. Concerning the sulfate production, Fig. 6 shows that the concentration of SO₄²⁻ reached 6,593 and 5,252 mg L⁻¹ in BF2 (expanded schist) and BF3 (cellular concrete), respectively, for an H₂S concentration of 600 ppmv. This difference (around 20 %) can be explained by the higher removal efficiency recorded for BF2 than for BF3. For example, at an EBRT of 120 s and a pollutant concentration of 450 ppmv, H₂S was completely eliminated by the expanded schist (BF2) while a removal efficiency of 83 % was obtained for the cellular concrete (BF3).

In terms of the sulfur mass balance, using a constant molar ratio N/S, it can be seen that the conversion of H₂S to sulfates decreased when the H₂S concentration increased (Table 5). At a concentration of 600 ppmv, sulfate conversion rates of 59 and 47 % were obtained in BF2 (expanded schist) and BF3 (cellular concrete), respectively. From these findings, it can be concluded that a significant part of H₂S removed is converted into elemental sulfur S⁰, which can accumulate and form a deposit in packing materials. This accumulation was evidenced by a yellow deposit on the packing materials (Fig. 7). These results are in agreement with those found by Soreanu et al. [21], who reported that for sulfate concentrations higher than 2,500 mg L⁻¹, elemental sulfur became the major product of oxidation of H₂S under anoxic conditions. Fortuny et al. [29] also observed that the bed was almost completely clogged with elemental sulfur after 3 months of operation leading to an increase in pressure drops. The selected N/S molar ratio (0.89) may not be sufficient to achieve complete oxidation of H₂S. Moreover, the accumulation of elemental sulfur may also be due to high concentrations of H₂S continuously feeding the biofilters [21]. For instance, in BF2 (expanded schist), 92 % of H₂S was oxidized to sulfates at a concentration of 150 ppmv, while the sulfate conversion rate decreased to 59 % at a concentration of 600 ppmv (Table 5).

Fig. 6 Production of nitrites and sulfates in BF2 (expanded schist) and BF3 (cellular concrete) during H₂S biofiltration (N/S = 0.89).

Table 5 H₂S conversion to sulfates in BF2 (expanded schist) and BF3 (cellular concrete) (N/S = 0.89).

H ₂ S input		BF2 (expanded schist)		BF3 (cellular concrete)	
[H ₂ S] (ppmv)	mg S-H ₂ S/day	mg S-SO ₄ ²⁻ /day	Conversion to sulfates (%)	mg S-SO ₄ ²⁻ /day	Conversion to sulfates (%)
150	2229	2058	92	1794	80
300	4459	2800	63	3049	68
450	6688	4566	68	3610	54
600	8918	5274	59	4202	47

Fig. 7 Elemental sulfur accumulation in BF2 (expanded schist) and BF3 (cellular concrete) (N/S = 0.89).

3.3. Impact of the molar ratio N/S

In order to evaluate the impact of the molar ratio N/S on the by-products obtained from H₂S oxidation, different values were tested (0.4, 0.89 and 1.6). As expected, the value of the N/S ratio did not affect the removal efficiency. Table 6 shows that, irrespective of the N/S ratio, H₂S was totally removed from BF1 (RE = 100 %) at a constant H₂S concentration of 300 ppmv and at an EBRT of 60 s. This finding is in agreement with the results of Almenglo et al. [36] who showed no impact of nitrate concentration on the removal efficiency for N/S in the range of 0.96 to 1.25. However, surprisingly, sulfate concentrations were similar for the three molar ratios tested. The average percentage of conversion of H₂S to sulfate was 55 % (Table 6) whereas Manconi et al. [31] achieved the complete oxidation of sulfide to sulfate with an N/S ratio of 0.89. Nonetheless, this result is in agreement with the overall reaction given by Eq. (5). Testing different N/S molar ratios (between 0.34 and 1.74) in a biotrickling filter, Almenglo et al. [36] observed a sulfate production of between 8 % and 95 %, respectively. Thus, increasing the nitrate supply can avoid elemental sulfur production. However, the present results differ significantly from the data reported in the literature devoted to H₂S removal in biotrickling filters. In fact, Soreanu et al. [21] showed that when the system was overloaded by a high H₂S input, elemental sulfur became the primary reaction product. When working with a molar ratio N/S of 0.78, the elemental sulfur accumulated in the bed packing material [14]. Similarly, Fernandez et al. [12] observed the production of elemental sulfur (68.4 ± 15.7 %) for a molar ratio N/S of 0.77 ± 0.32. Consequently, it can be assumed that the part of H₂S not oxidized into sulfate was probably converted into elemental sulfur as evidenced by the appearance of yellow deposits on the packing material after H₂S biofiltration

[Fig. 7]. Nonetheless, the lack of influence of the N/S ratio value on H₂S conversion into S⁰ or SO₄²⁻ in biofilters remains to be investigated.

Table 6 Impact of molar ratio N/S on sulfate production in BF1 (expanded schist) ([H₂S] = 300 ppmv).

N/S	mg S-SO₄²⁻/day	Conversion into sulfate (%)	RE (%)
0.4	2439	55	100
0.89	2410	54	100
1.6	2531	57	100

3.4. Pressure drops

Pressure drops ΔP in biofilters depend mainly on the superficial gas velocity U_0 , the particle size, and biofilm development [23,37]. However, the accumulation of elemental sulfur in the biofilter can gradually clog the packing material, causing the biofilter pressure drop to increase. This deposit of elemental sulfur in the packed bed is therefore an issue for practical applications. For biofilters BF2 and BF3, the pressure drops (ΔP) were measured daily between the ports located at 20 and 100 cm from the bottom of the packing material. At the beginning of the operation, pressure drops were identical for both biofilters and varied between 3 and 14 Pa m⁻¹ for gas velocities ranging from 23 to 115 m h⁻¹. After 213 days of operation, the pressure drops increased to reach values between 22 and 39 Pa m⁻¹ and 3 and 16 Pa m⁻¹ for expanded schist (BF2) and cellular concrete (BF3), respectively. These values remain significantly low compared to those found for other packing materials used for biofiltration (Table 7). As a result, this finding highlights that expanded schist as well as cellular concrete waste are interesting materials for biofiltration in terms of bed mechanical stability.

4. Conclusion

The removal of H₂S from biogas in anoxic biofilters using expanded schist and cellular concrete waste as packing materials was evaluated. At an EBRT of 300 s, expanded schist efficiently treated high concentrations of H₂S in biogas up to 1100 ppmv (RE = 100 %; EC_{max} = 30.3 g m⁻³ h⁻¹). At an EBRT of 240 s, cellular concrete was also an effective material for the treatment of concentrations of H₂S up to 900 ppmv (EC_{max} = 25.2 g m⁻³ h⁻¹). Whatever the molar ratio N/S selected (0.4, 0.89 and 1.6), sulfate was produced (about 55 %) and elemental sulfur accumulated in the biofilters (about 45 %). In spite of this production of elemental sulfur due to H₂S oxidation, the pressure drops in biofilters were significantly lower than those obtained using other packing materials assessed in several studies. Expanded schist and cellular concrete waste are therefore interesting materials for biofiltration in terms of bed mechanical stability and treatment efficiency. In addition, this study presents experimental evidence that classic biofilters can be used as an alternative to biotrickling filters to treat moderate concentrations of H₂S up to 1100 ppmv in biogas under anoxic conditions.

Table 7 Pressure drops using different packing materials.

Packing materials	$\Delta P/H$ (Pa m ⁻¹)	U ₀ (m h ⁻¹)	References
Pine bark	15 - 388	65 - 520	[38]
Compost	500 - 1000	72 - 1000	[39]
Compost	368 - 760	76 - 534	[40]
Mixture of composted pig manure and sawdust	15 - 460	100 - 200	[41]
Open pore polyurethane (PU) foam	2452	8.6	[29]
Polyurethane foam	637	105	[42]
Coconut fiber	550	230	[43]

Granulated sludge	2000	100	[44]
Peat fiber	385	200	[45]
Expanded schist	22 - 39	23 - 115	Present study
Cellular concrete waste	3 - 16	23 - 115	Present study

Acknowledgements

The authors would like to thank Franck ROUXEL and the TCPLASTIC Company for their financial support.

References

- [1] E. Ryckebosch, M. Drouillon, H. Vervaeren, Techniques for transformation of biogas to biomethane, *Biomass Bioenergy*. 35 (2011) 1633–1645. doi:10.1016/j.biombioe.2011.02.033.
- [2] N. Abatzoglou, S. Boivin, A review of biogas purification processes, *Biofuels Bioprod. Biorefining*. 3 (2009) 42–71. doi:10.1002/bbb.117.
- [3] L. Dubois, D. Thomas, Comparison of Various Alkaline Solutions for H₂S/CO₂-Selective Absorption Applied to Biogas Purification, *Chem. Eng. Technol.* 33 (2010) 1601–1609. doi:10.1002/ceat.201000171.
- [4] M.S. Horikawa, F. Rossi, M.L. Gimenes, C.M.M. Costa, M. Da Silva, Chemical absorption of H₂S for biogas purification, *Braz. J. Chem. Eng.* 21 (2004) 415–422.
- [5] N. Tippayawong, P. Thanompongchart, Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor, *Energy*. 35 (2010) 4531–4535. doi:10.1016/j.energy.2010.04.014.
- [6] 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.
- [7] S. Pipatmanomai, S. Kaewluan, T. Vitidsant, Economic assessment of biogas-to-electricity generation system with H₂S removal by activated carbon in small pig farm, *Appl. Energy*. 86 (2009) 669–674. doi:10.1016/j.apenergy.2008.07.007.
- [8] L. Sigot, M. Fontseré Obis, H. Benbelkacem, P. Germain, G. Ducom, Comparing the performance of a 13X zeolite and an impregnated activated carbon for H₂S removal from biogas to fuel an SOFC: Influence of water, *Int. J. Hydrog. Energy*. 41 (2016) 18533–18541. doi:10.1016/j.ijhydene.2016.08.100.
- [9] R. Sitthikhankaew, S. Predapitakkun, R. (Wibulswas) Kiattikomol, S. Pumhiran, S. Assabumrungrat, N. Laosiripojana, Comparative Study of Hydrogen Sulfide Adsorption by using Alkaline Impregnated Activated Carbons for Hot Fuel Gas Purification, *Energy Procedia*. 9 (2011) 15–24. doi:10.1016/j.egypro.2011.09.003.
- [10] A. Alonso-Vicario, J.R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi, C.A. Ramírez-López, J. Torrecilla-Soria, A. Domínguez, Purification and upgrading of biogas by pressure swing

- adsorption on synthetic and natural zeolites, *Microporous Mesoporous Mater.* 134 (2010) 100–107. doi:10.1016/j.micromeso.2010.05.014.
- [11] P. Cosoli, M. Ferrone, S. Pricl, M. Fermeglia, Hydrogen sulphide removal from biogas by zeolite adsorption: Part I. GCMC molecular simulations, *Chem. Eng. J.* 145 (2008) 86–92. doi:10.1016/j.cej.2008.07.034.
- [12] M. Fernández, M. Ramírez, R.M. Pérez, J.M. Gómez, D. Cantero, Hydrogen sulphide removal from biogas by an anoxic biotrickling filter packed with Pall rings, *Chem. Eng. J.* 225 (2013) 456–463. doi:10.1016/j.cej.2013.04.020.
- [13] G. Rodriguez, A.D. Dorado, M. Fortuny, D. Gabriel, X. Gamisans, Biotrickling filters for biogas sweetening: Oxygen transfer improvement for a reliable operation, *Process Saf. Environ. Prot.* 92 (2014) 261–268. doi:10.1016/j.psep.2013.02.002.
- [14] G. Soreanu, M. Béland, P. Falletta, K. Edmonson, P. Seto, Investigation on the use of nitrified wastewater for the steady-state operation of a biotrickling filter for the removal of hydrogen sulphide in biogas, *J. Environ. Eng. Sci.* 7 (2008) 543–552. doi:10.1139/S08-023.
- [15] S. Chairapat, R. Mardthing, D. Kantachote, S. Karnchanawong, Removal of hydrogen sulfide by complete aerobic oxidation in acidic biofiltration, *Process Biochem.* 46 (2011) 344–352. doi:10.1016/j.procbio.2010.09.007.
- [16] A.M. Montebello, M. Fernández, F. Almenglo, M. Ramírez, D. Cantero, M. Baeza, D. Gabriel, Simultaneous methylmercaptan and hydrogen sulfide removal in the desulfurization of biogas in aerobic and anoxic biotrickling filters, *Chem. Eng. J.* 200–202 (2012) 237–246. doi:10.1016/j.cej.2012.06.043.
- [17] D. Ramírez-Sáenz, P.B. Zarate-Segura, C. Guerrero-Barajas, E.I. García-Peña, H₂S and volatile fatty acids elimination by biofiltration: Clean-up process for biogas potential use, *J. Hazard. Mater.* 163 (2009) 1272–1281. doi:10.1016/j.jhazmat.2008.07.129.
- [18] L.M. Prescott, *Microbiology, Fifth Edition*, 5 edition, McGraw-Hill Science/Engineering/Math, Boston, 2002.
- [19] E. Dumont, H₂S removal from biogas using bioreactors: a review, *Int. J. Energy Environ.* 6 (2015) 479–498.
- [20] M. Fernández, M. Ramírez, J.M. Gómez, D. Cantero, Biogas biodesulfurization in an anoxic biotrickling filter packed with open-pore polyurethane foam, *J. Hazard. Mater.* 264 (2014) 529–535. doi:10.1016/j.jhazmat.2013.10.046.
- [21] G. Soreanu, M. Béland, P. Falletta, K. Edmonson, P. Seto, Laboratory pilot scale study for H₂S removal from biogas in an anoxic biotrickling filter, *Water Sci. Technol.* 57 (2008) 201–208. doi:10.2166/wst.2008.023.
- [22] A. Courtois, Y. Andrès, É. Dumont, H₂S biofiltration using expanded schist as packing material: influence of packed bed configurations at constant EBRT, *J. Chem. Technol. Biotechnol.* 90 (2015) 50–56. doi:10.1002/jctb.4456.
- [23] E. Dumont, L.M. Ayala Guzman, M.S. Rodríguez Susa, Y. Andrès, H₂S biofiltration using expanded schist as packing material: performance evaluation and packed-bed tortuosity assessment, *J. Chem. Technol. Biotechnol.* 87 (2012) 725–731. doi:10.1002/jctb.3713.
- [24] A.C. Romero Hernandez, M.S. Rodríguez Susa, Y. Andrès, E. Dumont, Steady- and transient-state H₂S biofiltration using expanded schist as packing material, *New Biotechnol.* 30 (2013) 210–218. doi:10.1016/j.nbt.2012.07.003.
- [25] M. Ben Jaber, A. Couvert, A. Amrane, F. Rouxel, P. Le Cloirec, E. Dumont, Biofiltration of high concentration of H₂S in waste air under extreme acidic conditions, *New Biotechnol.* 33 (2016) 136–143. doi:10.1016/j.nbt.2015.09.008.
- [26] M. Ben Jaber, A. Couvert, A. Amrane, F. Rouxel, P. Le Cloirec, E. Dumont, Biofiltration of H₂S 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.
- [27] 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.

- [28] American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 14th ed., APHA, Washington, DC, 1975.
<http://www.sciencedirect.com/science/article/pii/S1385894715015636> (accessed June 15, 2016).
- [29] M. Fortuny, J.A. Baeza, X. Gamisans, C. Casas, J. Lafuente, M.A. Deshusses, D. Gabriel, Biological sweetening of energy gases mimics in biotrickling filters, *Chemosphere*. 71 (2008) 10–17. doi:10.1016/j.chemosphere.2007.10.072.
- [30] J.P. Maestre, R. Rovira, F.J. Álvarez-Hornos, M. Fortuny, J. Lafuente, X. Gamisans, D. Gabriel, Bacterial community analysis of a gas-phase biotrickling filter for biogas mimics desulfurization through the rRNA approach, *Chemosphere*. 80 (2010) 872–880. doi:10.1016/j.chemosphere.2010.05.019.
- [31] I. Manconi, A. Carucci, P. Lens, S. Rossetti, Simultaneous biological removal of sulphide and nitrate by autotrophic denitrification in an activated sludge system, *Water Sci. Technol. J. Int. Assoc. Water Pollut. Res.* 53 (2006) 91–99.
- [32] Y.-C. Chung, C. Huang, C.-P. Tseng, Biological elimination of H₂S and NH₃ from wastegases by biofilter packed with immobilized heterotrophic bacteria, *Chemosphere*. 43 (2001) 1043–1050. doi:10.1016/S0045-6535(00)00211-3.
- [33] H. Kim, Y.J. Kim, J.S. Chung, X. Quan, Long-Term Operation of a Biofilter for Simultaneous Removal of H₂S and NH₃, *J. Air Waste Manag. Assoc.* 52 (2002) 1389–1398.
- [34] A.H. Wani, R.M.R. Branion, A.K. Lau, Effects of periods of starvation and fluctuating hydrogen sulfide concentration on biofilter dynamics and performance, *J. Hazard. Mater.* 60 (1998) 287–303. doi:10.1016/S0304-3894(98)00154-X.
- [35] G. Soreanu, M. Béland, P. Falletta, B. Ventresca, P. Seto, Evaluation of different packing media for anoxic H₂S control in biogas, *Environ. Technol.* 30 (2009) 1249–1259. doi:10.1080/09593330902998314.
- [36] F. Almenglo, T. Bezerra, J. Lafuente, D. Gabriel, M. Ramírez, D. Cantero, Effect of gas-liquid flow pattern and microbial diversity analysis of a pilot-scale biotrickling filter for anoxic biogas desulfurization, *Chemosphere*. 157 (2016) 215–223. doi:10.1016/j.chemosphere.2016.05.016.
- [37] E. Dumont, S. Woudberg, J. Van Jaarsveld, Assessment of porosity and biofilm thickness in packed beds using porous media models, *Powder Technol.* 303 (2016) 76–89. doi:10.1016/j.powtec.2016.08.060.
- [38] E. Dumont, Y. Andrès, P. Le Cloirec, F. Gaudin, Evaluation of a new packing material for H₂S removed by biofiltration, *Biochem. Eng. J.* 42 (2008) 120–127. doi:10.1016/j.bej.2008.06.012.
- [39] Y. Yang, E.R. Allen, Biofiltration Control of Hydrogen Sulfide 1. Design and Operational Parameters, *Air Waste*. 44 (1994) 863–868. doi:10.1080/1073161X.1994.10467287.
- [40] J.M. Morgan-Sagastume, A. Noyola, Hydrogen sulfide removal by compost biofiltration: Effect of mixing the filter media on operational factors, *Bioresour. Technol.* 97 (2006) 1546–1553. doi:10.1016/j.biortech.2005.06.003.
- [41] A. Elias, A. Barona, A. Arreguy, J. Rios, I. Aranguiz, J. Peñas, Evaluation of a packing material for the biodegradation of H₂S and product analysis, *Process Biochem.* 37 (2002) 813–820. doi:10.1016/S0032-9592(01)00287-4.
- [42] M. Ramírez, J.M. Gómez, G. Aroca, D. Cantero, Removal of hydrogen sulfide by immobilized *Thiobacillus thiooparus* in a biotrickling filter packed with polyurethane foam, *Bioresour. Technol.* 100 (2009) 4989–4995. doi:10.1016/j.biortech.2009.05.022.
- [43] J.L.R.P. Filho, L.T. Sader, M.H.R.Z. Damianovic, E. Foresti, E.L. Silva, Performance evaluation of packing materials in the removal of hydrogen sulphide in gas-phase biofilters: Polyurethane foam, sugarcane bagasse, and coconut fibre, *Chem. Eng. J.* 158 (2010) 441–450. doi:10.1016/j.cej.2010.01.014.
- [44] L. Malhautier, C. Gracian, J.-C. Roux, J.-L. Fanlo, P. Le Cloirec, Biological treatment process of air loaded with an ammonia and hydrogen sulfide mixture, *Chemosphere*. 50 (2003) 145–153. doi:10.1016/S0045-6535(02)00395-8.

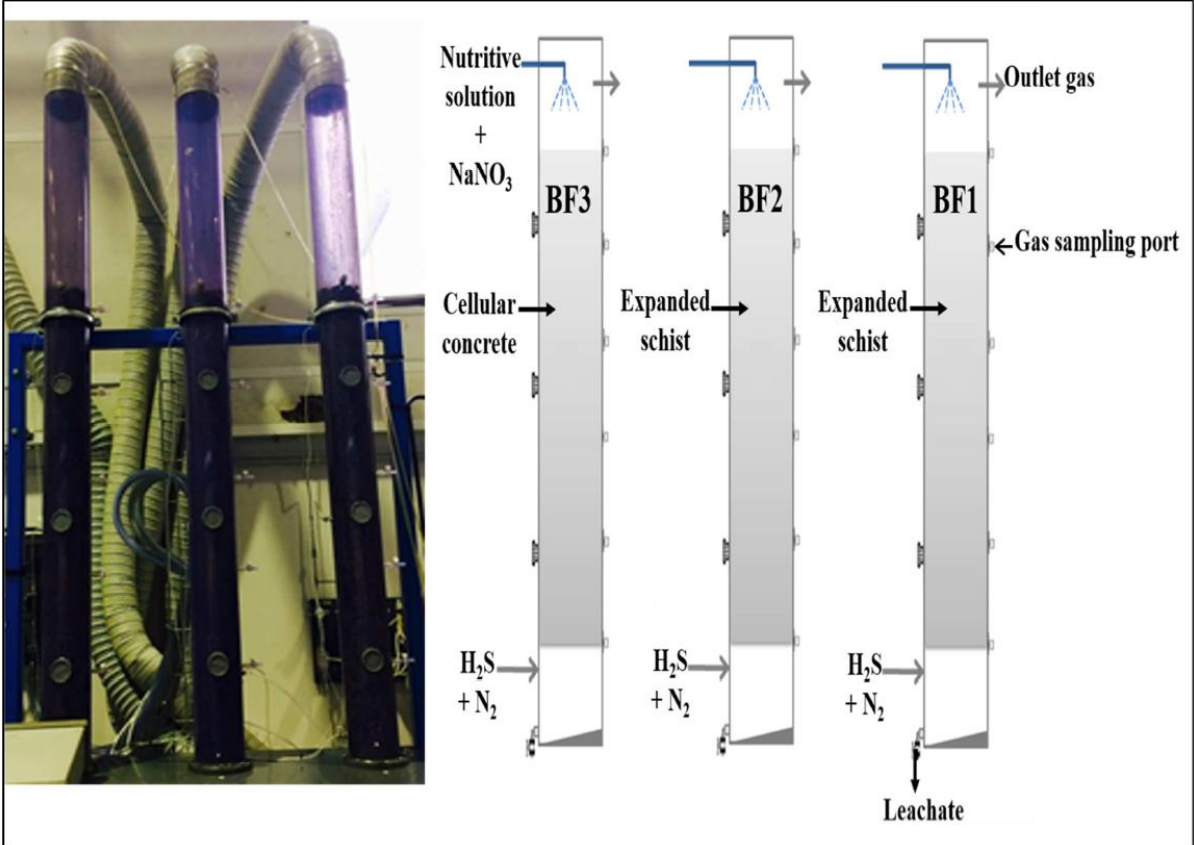
- [45] H. Van Langenhove, E. Wuyts, N. Schamp, Elimination of hydrogen sulphide from odorous air by a wood bark biofilter, *Water Res.* 20 (1986) 1471–1476. doi:10.1016/0043-1354(86)90109-0.

Figure Caption

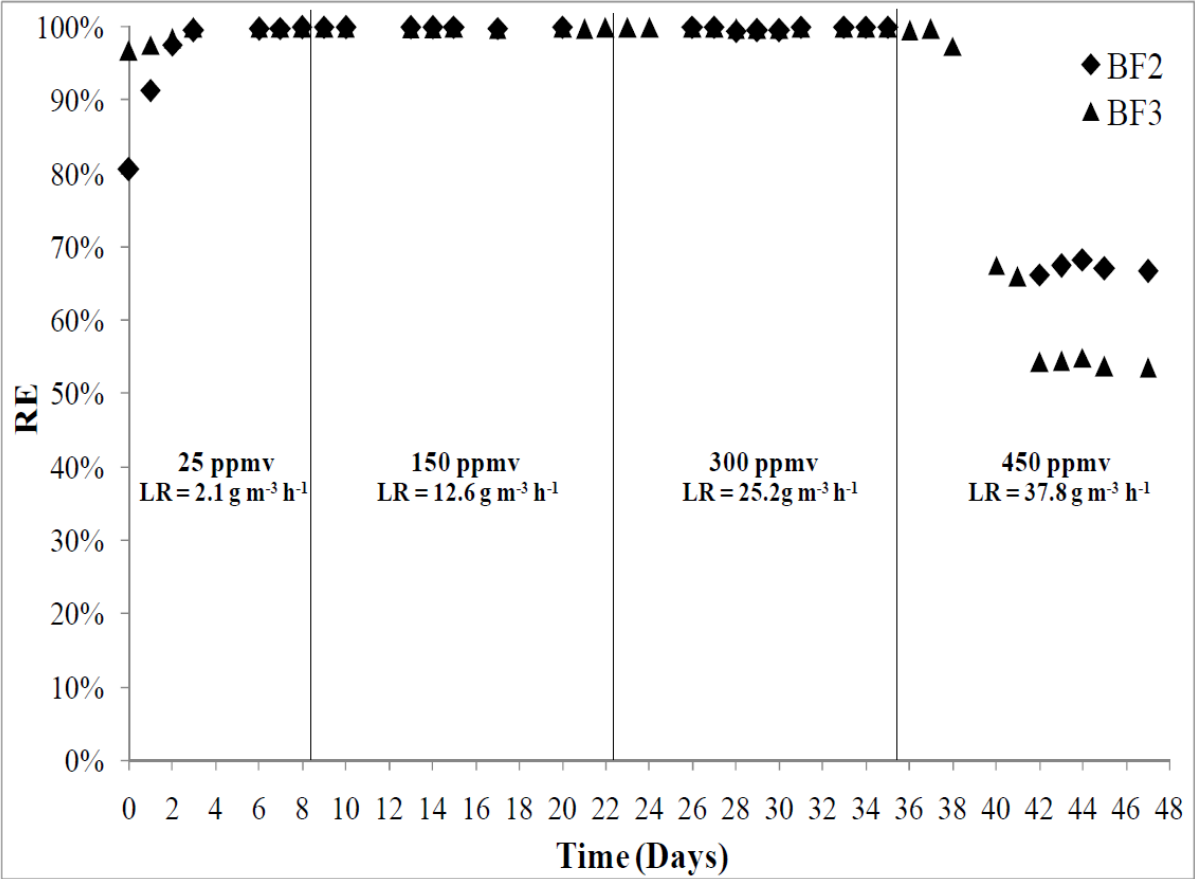
Figr-1



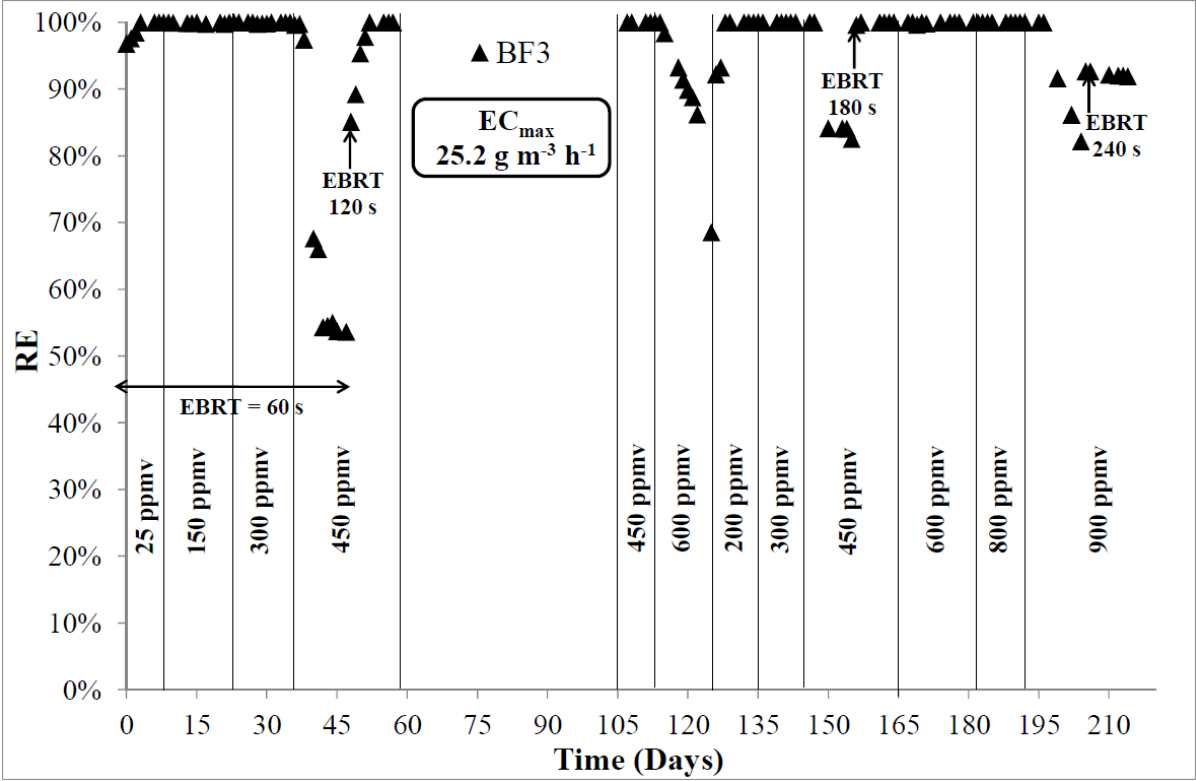
Figr-2



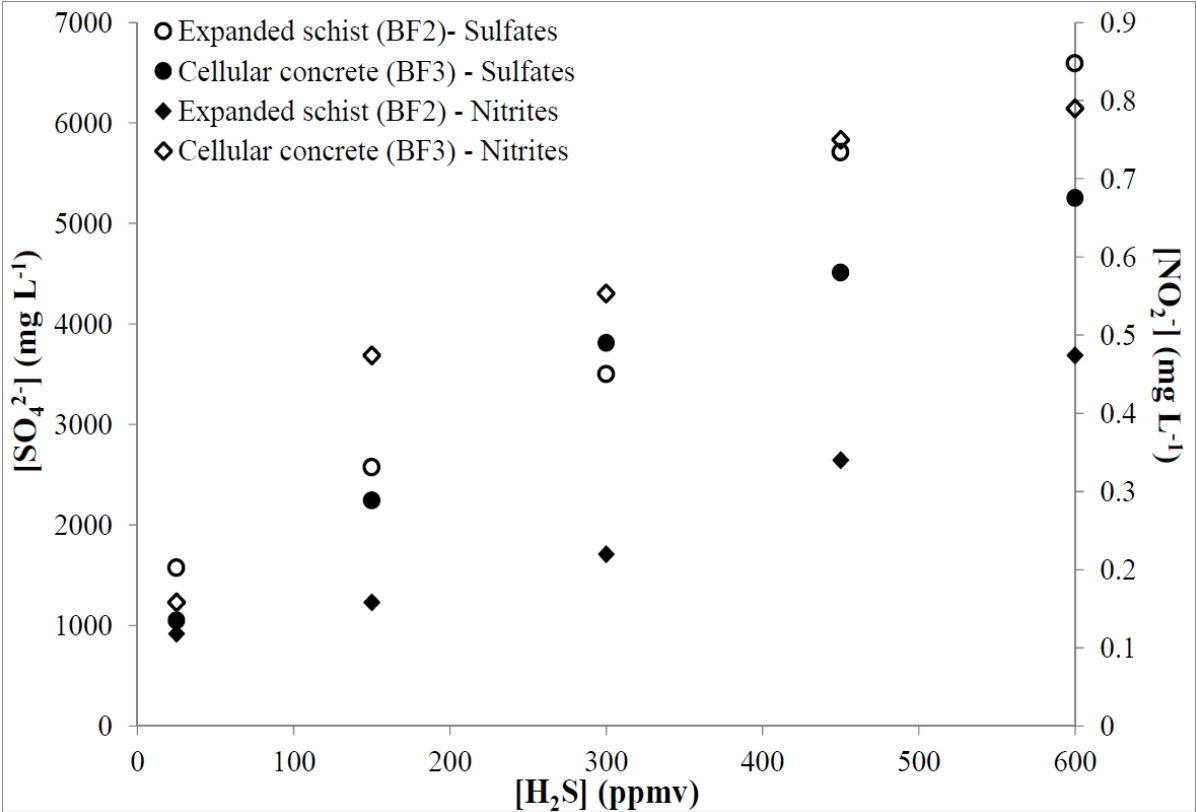
Figr-3







Figr-5



Figr-6



Figr-7

	Before H₂S biofiltration	After H₂S biofiltration
Expanded schist	 A pile of reddish-brown, angular, porous expanded schist particles.	 A pile of expanded schist particles that have turned a yellowish-tan color, indicating sulfur coating.
Cellular concrete waste	 A pile of light-colored, porous, irregularly shaped cellular concrete waste particles.	 A pile of cellular concrete waste particles that have turned a yellowish-tan color, indicating sulfur coating.

Figr-8

Fig. 1 Pictures of expanded schist (left) and cellular concrete waste (right).

Fig. 2 Experimental pilot-scale biofilters.

Fig. 3 Removal efficiency of H₂S using expanded schist (BF2) and cellular concrete (BF3) as packing materials (H₂S concentrations from 25 to 450 ppmv; EBRT = 60 s; N/S = 0.89).

Fig. 4 EBRT influence on removal efficiency of H₂S using expanded schist (BF2) as packing material (H₂S concentrations from 25 to 1100 ppmv; N/S = 0.89).

Fig. 5 EBRT influence on removal efficiency of H₂S using cellular concrete waste (BF3) as packing material (H₂S concentrations from 25 to 900 ppmv; N/S = 0.89).

Fig. 6 Production of nitrites and sulfates in BF2 (expanded schist) and BF3 (cellular concrete) during H₂S biofiltration (N/S = 0.89).

Fig. 7 Elemental sulfur accumulation in BF2 (expanded schist) and BF3 (cellular concrete) (N/S = 0.89).