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# A Two-Stage Biogas Desulfurization Process Using Cellular Concrete Filtration and an Anoxic Biotrickling Filter

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**Abstract:** A two-stage desulfurization process including an abiotic filtration using cellular concrete waste (first stage) and an anoxic biotrickling filter filling with an inoculated expanded schist material (second stage) was investigated to remove $H_2S$ in mimic biogas with limited $O_2$ amount (ranged from 0.5 to 0.8%). The two-stage process was able to satisfactorily remove $H_2S$ for all experimental conditions (RE > 97%; $H_2S$ concentration = 1500 mg $m^{-3}$; total Empty Bed Residence Time (EBRT) = 200 s; removal capacity (RC) = 26 g $m^{-3}$ $h^{-1}$). Moreover, at a total EBRT = 360 s (i.e., 180 s for each stage), the $H_2S$ loading rate (LR) was almost treated by the bed of cellular concrete alone, indicating that abiotic filtration could be applied to satisfactorily remove $H_2S$ contained in the gas. According to the $H_2S$ concentration entering the biotrickling filter, the majority end-product was either elemental sulfur ($S^0$) or sulfate ($SO_4^{2-}$). Thus, the ability of the abiotic filter to remove a significant part of $H_2S$ would avoid the clogging of the biotrickling filter due to the deposit of $S^0$. Consequently, this two-stage desulfurization process is a promising technology for efficient and economical biogas cleaning adapted to biogas containing limited $O_2$ amounts, such as landfill biogas.

**Keywords:** $H_2S$; cellular concrete; biotrickling filter; biogas; desulfurization



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## 1. Introduction

According to the European directives, such as the Directive (EU) 2018/2001, the energy from renewable sources constitutes an important part of the package of measures needed to reduce greenhouse gas emissions and comply with the 2015 Paris Agreement on Climate Change (Union 2030 energy and climate framework). Moreover, the increased use of energy from renewable sources also has a fundamental part to play in promoting the security of energy supply and sustainable energy at affordable prices [1]. The most important renewable energy sources are wind power, solar photovoltaics and biomass energy [2]. Among the biomass energy sources, biogas from anaerobic digestion is largely used both on European and global scales. Depending on its production origin (anaerobic digestion, landfills), methane ($CH_4$) and carbon dioxide ($CO_2$) are the major constituents of biogas. However, trace amounts of other components such as nitrogen ($N_2$), water vapor ($H_2O$), ammonia ($NH_3$), oxygen ($O_2$), hydrogen sulfide ($H_2S$) and other sulfur compounds are also found [3,4]. In order to avoid $SO_2$ formation during biogas combustion, protect combined heat and power and avoid $H_2S$ injection in natural gas network, $H_2S$ removal is needed. Indeed, $H_2S$ is known as a corrosive and hazardous pollutant whose gaseous concentrations in biogas can vary significantly from some ppm to several thousands of ppm [3,5]. According to the fields of biogas utilization, different purification stages are applied to remove unwanted gases and substances [6]. The first stage involves the removal of $H_2S$ (<1000 ppmv [7]), which is sufficient for the production of heat and steam in boilers, as well as combustion in cogeneration engines. The second stage of purification includes

the removal of $CO_2$. The third stage involves the removal of various components and pollutants (biogas to biomethane) to levels required for the injection into the natural gas grid and uses as a vehicle fuel [8–11]. The present paper is dedicated to the first stage of biogas purification. $H_2S$ can be removed using physical–chemical methods (scrubbing, adsorption processes, etc.) and biotechnological ones [3,4,12,13]. By considering these latter, it was established that biofiltration, mainly biofilters and biotrickling filters, is a mature technology to efficiently remove $H_2S$ in the air, whereas biological desulfurization of biogas is currently considered a promising technology [14]. In the air, i.e., in the presence of atmospheric oxygen acting as an electron acceptor, the ability of bioreactors to remove $H_2S$ is largely reported in the literature, even under extremely acidic conditions [15]. However, for biogas desulfurization in aerobic conditions, i.e., using atmospheric oxygen from air flow rate additions, significant efforts have to be still placed on developing control strategies to avoid biogas dilution [16]. In the absence of atmospheric oxygen, solutions based on alternative electron acceptors, such as nitrates, exist to biologically remove $H_2S$ under anoxic conditions. Consequently, anaerobic biotrickling filtration appears a suitable solution to overcome the main drawbacks of aerobic bioprocesses, i.e., biogas dilution with nitrogen and safety problems due to potential explosive mixtures of oxygen/methane. In both cases, $H_2S$ must be first absorbed in the aqueous phase in which sulfide oxidizing bacteria carry out the substrate oxidation. The products of the oxidation are either elemental sulfur ($H_2S + 0.5O_2 \rightarrow S^0 + H_2O$) or sulfate ($H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$) according to the $H_2S$/electron acceptor ratio. Between the air addition way and the anoxic way, a third way consisting of taking advantage of the possible presence of oxygen in the raw gas also has to be considered since oxygen concentrations up to 1% are reported in landfill gases [3]. The amount of oxygen is usually lower in biogas produced through anaerobic digestion since preventive treatment based on a simple micro-aeration of the digester headspace allows the development of aerobic *thiobacteria* oxidizing $H_2S$ into elemental sulfur $S^0$ [5,7,17]. According to the stoichiometric equations abovementioned, the first product of the $H_2S$ oxidation is elemental sulfur $S^0$, which can be converted into sulfate $SO_4^{2-}$ in the case of excess oxygen amounts ($S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$). It was admitted that the accumulation of $S^0$ in a biotrickling filter leading to bed clogging is the main drawback of these bioreactors [18,19]. As the washing of the filter bed is difficult, and as $S^0$ is insoluble in the recirculating liquid, it is preferable to operate in oxygen excess to oxidize $S^0$ into $SO_4^{2-}$ [20,21]. Moreover, the literature reports that $H_2S$ removal efficiency (RE) depends on the $O_2/H_2S$ molar ratio. Thus, RE of 95% was obtained for an $O_2/H_2S$ ratio of 2:1, against 63% and 50% for 1:1 and 1:2 ratios, respectively [22]. As a result, according to the $H_2S$ and $O_2$ concentrations characterizing the biogas, efficient desulfurization could be directly achieved in a biotrickling filter without any electron acceptor addition, atmospheric oxygen or nitrates. The objective of this study was consequently to study the feasibility of a biotrickling filter filled with expanded schist as packing material to removed $H_2S$ from a biogas with trace amounts of oxygen. Among the materials commonly used in $H_2S$ biofiltration (peat, pouzzolane, wood bark, etc.), expanded schist has widely proved to be a good carrier material, showing high removal $H_2S$ performances both in aerobic and anoxic conditions, but also good lifetime due to its mechanical resistance and its non-alteration during chemical or biological reactions [15,23,24]. However, as biotrickling filters are sensitive to $H_2S$ loading rate changes due to concentration or flow rate fluctuations, a basic filtration using cellular concrete, an inexpensive waste material from construction, was used beforehand to buffer the shock loads and avoid the inhibition of the bacterial community. Indeed, cellular concrete waste was demonstrated to be efficient for partial $H_2S$ removal in abiotic conditions, i.e., without any microbial population [25,26]. Chemical reactions involving the components of the cellular concrete (mainly CaO, $CaCO_3$ and $Fe_2O_3$) would explain the ability of this material to react with $H_2S$. The $H_2S$ removal was therefore investigated using a two-stage desulfurization process for different operating conditions of $H_2S$ concentrations and Empty Bed Residence Time (EBRT).

## 2. Materials and Methods

### *2.1. Materials*

Both of the materials, expanded schist and cellular concrete waste, were described in previous studies [25,26]. Expanded schist is an inorganic material provided by the Granulex company (France), and cellular concrete waste, called "copolight", is a mineral material provided by the Florentaise company (France). Properties and pictures of both materials are given in Table 1 and Figure 1, respectively. The ability of biotrickling filters filled with expanded schist to remove $H_2S$ was demonstrated in aerobic and anoxic conditions, as well as under extremely acidic conditions in relation to the production of large amounts of $SO_4^{2-}$ [15]. Maximum removal capacity $RC_{max}$ of 30.3 g $m^{-3}$ $h^{-1}$ was recorded for $H_2S$ concentrations up to 1100 ppmv (EBRT of 300 s) [23]. Moreover, compared with other biofiltration materials, the good mechanical stability of the expanded schist observed over time is a great advantage in avoiding technical maintenance. As no bed compaction was observed during long-running periods, bed pressure drops are limited to some Pa per meter of material [15].

**Table 1.** Physico-chemical properties and composition of materials (Adapted with permission from Refs. [23,25]).

| Properties | Cellular Concrete Waste | Expanded Schist |
|---|---|---|
| Density (kg $m^{-3}$) | 547 ± 5 | 1248 ± 12 |
| Porosity (%) | 64 | 47 |
| pH of surface | 9.0 ± 0.1 | 7.0 ± 0.1 |
| **Composition (weight %)** | | |
| $SiO_2$ | 50.5 | 56.4 |
| $Fe_2O_3$ | 1.3 | 12.4 |
| $Al_2O_3$ | 2.2 | 20.5 |
| CaO | 24.6 | 0.9 |
| $K_2O$ | 0.2 | 5 |
| $SO_3$ | 19.7 | 1.6 |
| $TiO_2$ | (nd) | (nd) |
| $P_2O_5$ | 1.4 | 12.4 |

(**a**) (**b**)

**Figure 1.** Materials used in this study; (**a**) cellular concrete waste; (**b**) expanded schist.

The ability of cellular concrete waste to react with $H_2S$ in air and in abiotic conditions was recently highlighted [26]. It was reported that in wet conditions, reactions occurring between $H_2S$ and calcium carbonate lead to gypsum formation ($CaSO_4 \cdot 2H_2O$). This abiotic $H_2S$ filtration could thus be beneficially used as a first step of biofiltration systems, e.g., to soften the change in $H_2S$ loading rate. To date, cellular concrete waste has not yet been studied for $H_2S$ biogas filtration.

### 2.2. Experimental Setup

The experimental setup is described in Figure 2. The pilot plant consisted of 2 PVC cylindrical columns (internal diameter of 100 mm) filled with 7.8 L of material (1 m in height). The "abiotic filter" was filled with cellular concrete waste (Figure 1), and the "biotrickling filter" was filled with expanded schist inoculated with 4 L of activated sludge from a wastewater treatment plant (Procanar, Lauzach, France). Prior to inoculation, sludge was not $H_2S$ acclimatized. For safety reasons, mimic biogas was used, and $CH_4$ was replaced by $N_2$. The use of mimic biogas without $CH_4$ and $CO_2$ was successfully considered in several studies, with the presence or absence of methane having no effect on the microorganisms using $H_2S$ as substrate [22]. A nitrogen generator BrezzaNiGen LC–MS (40-1) (purity up to 99.9%) from Gengaz Company (Wasquehal, France) was used to supply $N_2$ continuously into the columns. In spite of the ability of the generator to efficiently purify $N_2$ from the air, a weak fraction of oxygen ranging from 0.5 to 0.8% was always measured in the nitrogen gas. The $N_2$ flow rate entering the two-stages process was controlled and measured by a mass flowmeter (Model 58500, Brooks Instruments, Hatfield, MA, USA). A stream of $H_2S$ (99.7% purity) controlled by another mass flow meter (Model 5850S, Brooks Instruments, Hatfield, PA, USA) was mixed with the $N_2$ flow rate before entering the abiotic filter. As a result, the gas entering the two-stage process was a mixture of $N_2$-$H_2S$-$O_2$ mimicking raw biogas. Thermocouples (K type) were installed on each column to measure temperatures. In order to maintain optimal bed humidity, both columns were fed with tap water. For the abiotic filter, cellular concrete waste was humidified by a drop-by-drop system. For the biotrickling filter, expanded schist was sprinkled (water flow rate of 60 mL $min^{-1}$) by water recirculating in the column. The water was discharged once a week to prevent its electrical conductivity from exceeding 10 mS $cm^{-1}$. As a result, all experiments were carried out in wet conditions controlled by humidity sensors (Model EE08, E + E Electronik, Sevres, France) located at the top of columns. Relative humidity measurements of the gas at the outlet of the first stage were always higher than 94%. $H_2S$ and $O_2$ concentrations were measured by an electrochemical analyzer (Biogas 5000, QED Environmental Systems Ltd., Coventry, UK) along all the columns, which were equipped with 6 sampling ports located at 0, 20, 40, 60, 80 and 100 cm from the bottom. These sampling ports were also used to measure the pressure drops (pressure sensor Setra, Setra Systems, Inc, Boxborough, MA, USA; 0–700 Pa). No nutritive solution was added to the tap water for the inoculated biotrickling filter. Indeed, it was assumed that the minerals contained in the tap water would be sufficient for the growth of autotrophic biomass.

The biotrickling filter washing liquid parameters, such as (i) temperature, (ii) pH and (iii) electrical conductivity, were measured daily using a multi-channel analyzer consort C834 (Consort bvba, Turnhout, Belgium) with temperature correction. The sulfate concentration was measured daily using a High-Pressure Ion Chromatography (940 Professional IC Vario, Metrohm, detection by conductivity, eluent: 3.2 mM $Na_2CO_3$ + 1 mM $NaHCO_3$, column: metrosep A supp 5 150/4.0). For this study, no specific measurement were made on the abiotic filter washing liquid.

The cellular concrete composition over time (at days 0 and 43) was determined using an Energy Dispersive X-ray Fluorescence Spectrometer (EDX-800HS, Shimadzu Company, Kyoto, Japan).

### 2.3. Operating Parameters

The parameters used to determine the performance of the two-stage process are detailed in Table 2. Two parameters influencing the $H_2S$ loading rate were studied during the 68 days of operation: (i) the influence of pollutant concentration change at a constant EBRT; (ii) the influence of the change in EBRT for a given $H_2S$ concentration. The $H_2S$ concentrations selected for the study (up to 1500 mg $m^{-3}$) were chosen according to the concentrations usually encountered in raw biogas. The operating conditions of the study are summarized in Table 3. Temperatures of gas and materials were measured, not controlled. For the running period, recorded temperatures ranged from 17 to 27 °C according to

the climatic conditions (June to August 2021). Before the beginning of this measurement campaign (June 2021), the two-stage process was operated continuously for several months in order to fix the different problems encountered. Consequently, it can be considered that the biomass inoculating the biotrickling filter was $H_2S$ acclimatized.

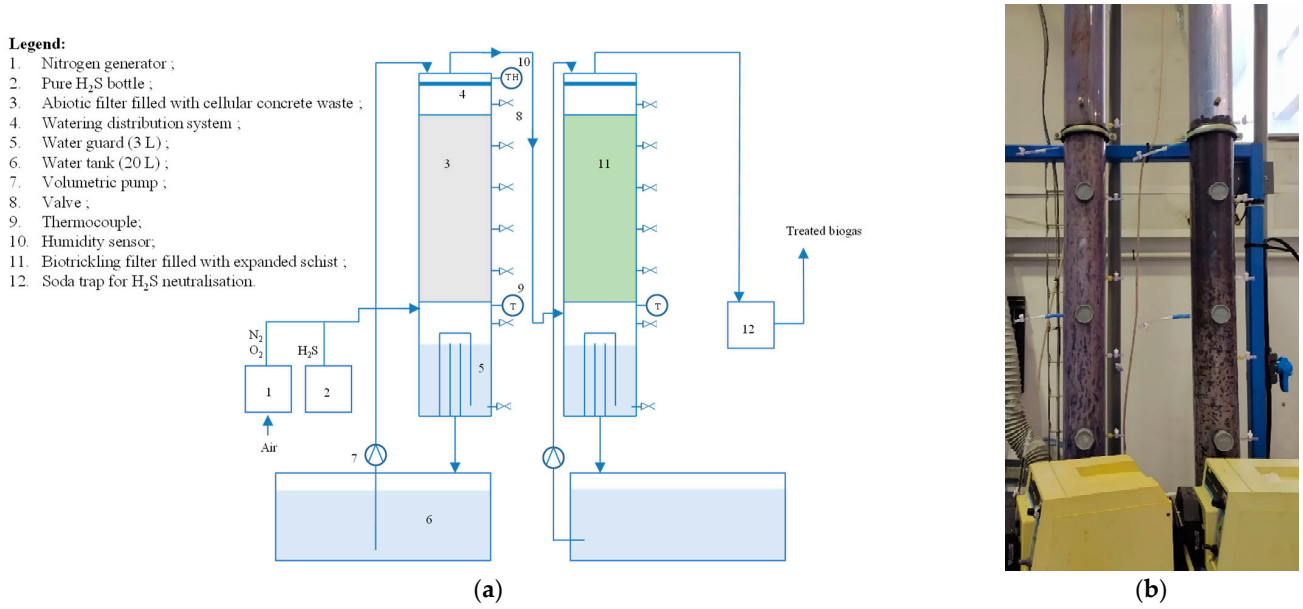



**Figure 2.** Experimental setup; (**a**) flow sheet; (**b**) picture of experimental columns (left: first stage, abiotic filter; right: second stage, biotrickling filter).

**Table 2.** Parameters used in this study.

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

**Table 3.** Operating conditions.

| Duration (Day) | Inlet $H_2S$ Concentration (mg $m^{-3}$) | Abiotic Filter EBRT (s) | Biotrickling Filter EBRT (s) | Total EBRT (s) | Loading Rate LR (g $m^{-3}$ $h^{-1}$) |
|---|---|---|---|---|---|
| 8 | 350 | 180 | 180 | 360 | 3.5 |
| 8 | 500 | | | | 5.0 |
| 8 | 900 | | | | 9.0 |
| 6 | 1200 | | | | 12.0 |
| 8 | 1500 | | | | 14.5 |
| 11 | 1500 | 150 | 150 | 300 | 18.0 |
| 10 | | 120 | 120 | 240 | 22.5 |
| 10 | | 100 | 100 | 200 | 27.0 |

### *2.4. Analysis of Microbial Community*

Biofilm samples were taken on day 0 (after acclimatization) and after 55 days in operation. They were centrifuged at 3000× *g* for 10 min, the supernatant was removed, and the pellet was stored at −20 °C until DNA extraction.

DNA was extracted from 200 mg of pellet using the Macherey Nagel NucleoSpin Soil kit according to the manufacturer's instructions. The extracted DNA was eluted in 100 µL of sterile water and stored at −20 °C for further analysis. Microbial community dynamics were investigated by high throughput DNA sequencing using Ion Torrent Personal Genome Machine methods and technologies (ThermoFisher Scientific, MA, USA) as described in Madigou et al. [27] with a few adaptations. The analysis targeted the V4-V5 hypervariable regions of the bacterial and archaeal 16S rRNA genes using PCR amplification (Platinium SuperFi PCR protocol from Life Technologies) and fusion primers 515F (5′-Ion A adapter–Barcode–GTGYCAGCMGCCGCGGTA-3′) and 928R (5′-Ion trP1 adapter–CCCCGYCAATTCMTTTRAGT-3′) [28], which includes a barcode and sequencing adapters. The resulting amplicons were purified and quantified according to the manufacturer's instructions using, respectively, the Agencourt AMPure XP magnetic beads (Beckman Coulter, Lane Cove West, NSW, Australia), DNA 1000 kit and 2100 Bioanalyzer (Agilent Technologies, Les Ulis, France). Template preparation for emulsion PCR and subsequent sequencing were performed using the Ion PGM Hi-Q View OT2 Kit and Ion PGM Hi-Q View Sequencing kit (Life Technologies, West Sacramento, CA, USA) as described in [27]. The high-throughput DNA sequencing produced an average of 3369/10071 +/− 2291 sequence reads of about 380 base pairs length for each sample.

These sequences were processed with the FROGS pipeline [29], following the authors' recommendations on the MIGALE Galaxy instance (INRAE, Jouy-en-Josas, France). Operational Taxonomic Unit (OTUs) abundance and microbial community diversity indices calculations were performed using Easy16S (https://shiny.migale.inrae.fr/app/easy16S (accessed on 7 April 2022)), a shiny web interface based on the phyloseq R package [30].

## 3. Results and Discussion

Results of the two-stage process are reported in Figure 3. The two-stage process was able to satisfactorily remove $H_2S$ (RE > 97%) for all experimental conditions. Basically, the measured $H_2S$ outlet concentration was never higher than 14 mg $m^{-3}$. At EBRT = 360 s, $H_2S$ removal was mainly achieved by the abiotic filter, whereas at lower EBRT, most of the removal was performed by the biotrickling filter. Figure 4a shows that the removal capacity (RC) was always close to the loading rate (LR) for the two-stage process, in agreement with the high RE value. Therefore, it can be concluded that a total EBRT of 200 s is sufficient for the complete $H_2S$ removal. Moreover, it can be argued that lower EBRT would make it possible to efficiently treat $H_2S$ concentrations higher than 1500 mg $m^{-3}$. It is interesting to note that RC of 26 g $m^{-3}$ $h^{-1}$ was achieved by the abiotic filter alone at EBRT of 180 s (Figure 4b). In this case, RE ranged from 75 to 100%. These results are significantly higher than those reported in air by Lebrun et al. [26] (RC = 7.8 g $m^{-3}$ $h^{-1}$ at EBRT of 56 s, $C_G^{in}$ = 70 mg $m^{-3}$) and Ben Jaber et al. [25] (RC = 5.6 g $m^{-3}$ $h^{-1}$ at EBRT of 63 s, $C_G^{in}$ = 140 mg $m^{-3}$). Indeed, in these previous studies, the humidity of the material was not controlled, and consequently, recorded performances were not optimized. It can thus be concluded that an efficient $H_2S$ filtration through only a bed of cellular concrete waste is possible at moderate $H_2S$ concentrations. In other words, this abiotic $H_2S$ filtration could be used instead of biofiltration for many $H_2S$ gas treatment applications with equal performance. For LR > 30 g $m^{-3}$ $h^{-1}$, the removal efficiency dropped to values lower than 50% in relation to the decrease in EBRT (Figure 4b). Consequently, it can be suggested that EBRT seems to be the main parameter governing $H_2S$ removal in the abiotic filter, rather than $H_2S$ concentration. However, investigations must be continued to refine the parameters influencing $H_2S$ removal.

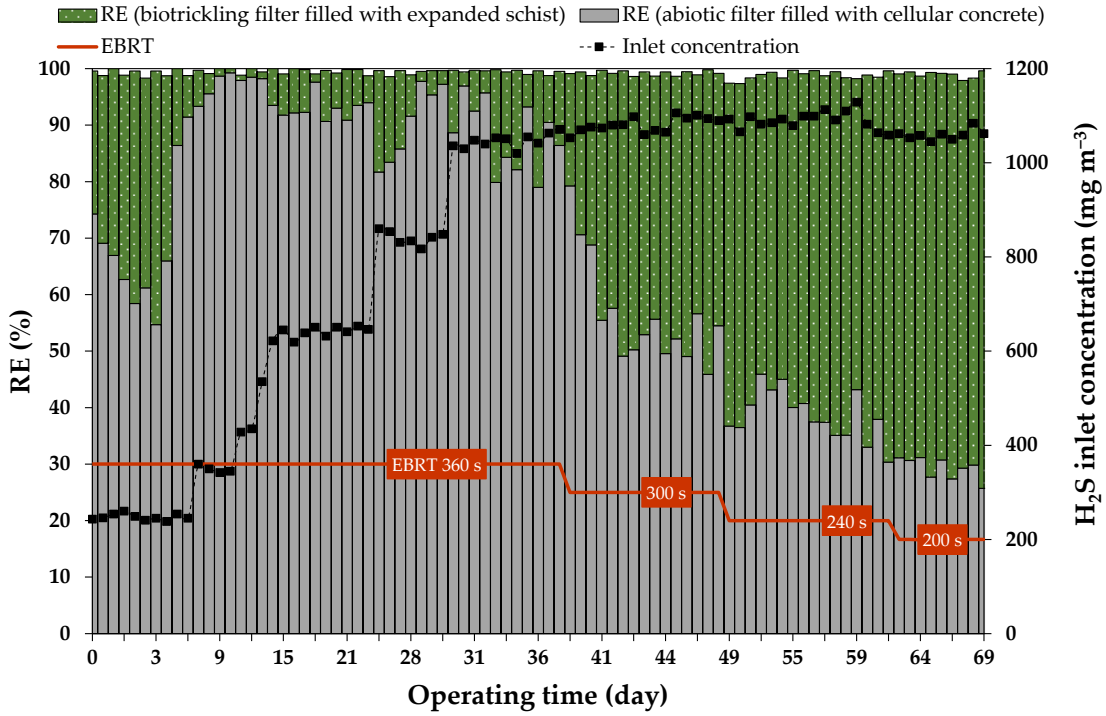



**Figure 3.** $H_2S$ removal efficiency of the two-stage process.

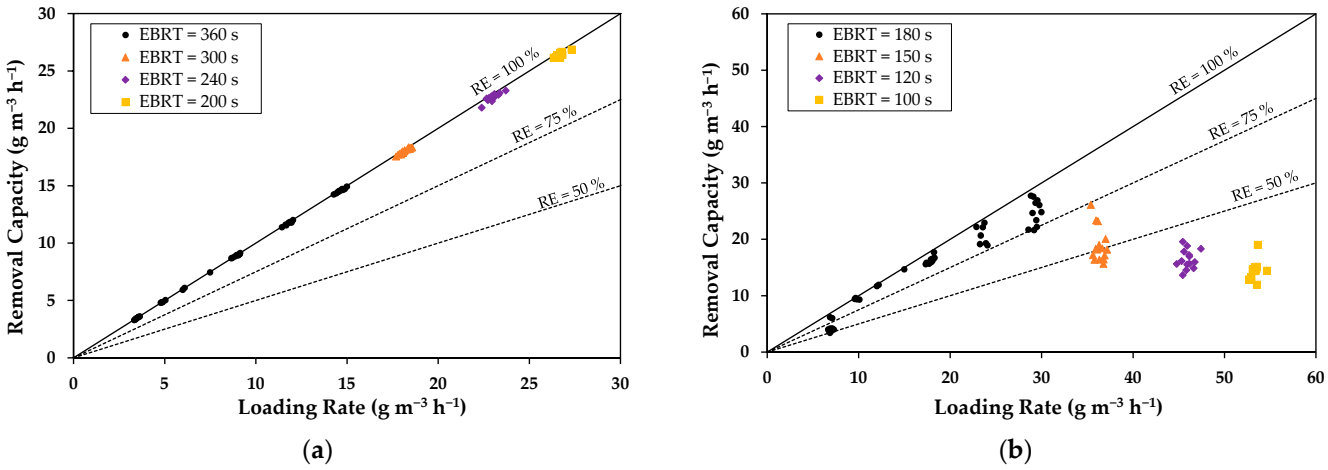



**Figure 4.** RC vs. LR: (**a**) two-stage process (LR and RC calculated using both the abiotic filter bed and the biotrickling filter bed); (**b**) abiotic filter only (EBRT, LR and RC calculated using the abiotic filter bed volume only).

By considering results achieved in the biotrickling filter alone during the first 37 days of operation (Figure 5), the $H_2S$ inlet concentration was lower than 200 mg $m^{-3}$ because part of $H_2S$ was previously removed by the cellular concrete filter. As a result, the loading rate to be treated was limited to 5 g $m^{-3}$ $h^{-1}$. However, for days 37 to 68, corresponding to a decrease in the total EBRT, the $H_2S$ inlet concentration reached up to 1000 mg $m^{-3}$, and consequently, LR increased to 35 g $m^{-3}$ $h^{-1}$. As observed in Figure 5, the removal capacity was always close to LR, confirming the ability of the biotrickling filter to remove $H_2S$. In terms of RE and RC values, these results are in the same order of magnitude as those reported in the recent literature dedicated to the anoxic removal of $H_2S$ using conventional biotrickling filters [31–34]. Bearing in mind that the maximal RC of the two-stage process was not reached, these results can be compared with those obtained by means of others technologies. For instance, using an anoxic bioscrubber (absorption column + stirred tank),

Quijano et al. [35] reported a maximum RC of 35.7 ± 2.0 g $m^{-3}$ $h^{-1}$ (RE from 92 to 99%). Using a 3D-printed honeycomb monolith as a biotrickling filter, Qiu and Deshusses [22] obtained for the first time an RC of 122 g $m^{-3}$ $h^{-1}$ (RE 95%). However, after the cleaning procedure, the performance of the system decreases significantly (RC = 63 g $m^{-3}$ $h^{-1}$ and RE = 49%) to reach some values close to RC obtained in this study. Anoxic desulfurization was also performed by González-Cortés et al. in a 3 L inner loop jacketed gas-lift bioreactor fed with mimic biogas ($N_2$ + $H_2S$) and nitrogen species ($NO_2^-$, $NO_3^-$) as the electron acceptor [36]. A maximum RC of 141.18 g $m^{-3}$ $h^{-1}$ (RE = 95.0%) was achieved. However, these authors indicated that the high operating costs of this technology, due to the high requirements of nitrite or nitrate, make its full-scale application difficult. Thus, the major difference between the results of the present study and the literature data lies in the fact that $H_2S$ removal under anoxic conditions was obtained without any addition of electron acceptors such as nitrates or nitrites. Thus, it can be reasonably suggested that the amount of oxygen present in the mimic biogas is sufficient for $H_2S$ oxidation (it is unlikely that oxygen comes from reactions occurring between $H_2S$ and the cellular concrete during the abiotic filtration [26]). EBRT applied in the biotrickling filter was high enough to provide both the mass transfer of $H_2S$ and oxygen from the gas phase to the liquid phase and the $H_2S$ biodegradation by microorganisms, as revealed by high RE values. However, the oxygen availability in relation to the $H_2S$ concentration to be treated determines the degradation products ($S^0$ or $SO_4^{2-}$). Elemental sulfur $S^0$, the first product of the $H_2S$ degradation, is transformed into $SO_4^{2-}$ if $O_2$ is in excess. The oxygen fraction in the mimic biogas entering the biotrickling filter ranged from 0.5 to 0.8%, i.e., from 5000 to 8000 ppm. According to the $H_2S$ concentration entering the biotrickling filter, it can then be argued that the $O_2/H_2S$ ratio value was around 50–100 at the bottom for low $H_2S$ concentrations (some ppm) and close to 5–10 for high concentrations (some hundreds of ppm). As $O_2$ is progressively consumed along all the biotrickling filter, values lower than five can be reasonably assumed at the outlet, especially as oxygen is 80 times less soluble in water than $H_2S$ [31]. According to the literature, half of $H_2S$ degraded is converted into $S^0$ for an $O_2/H_2S$ ratio of 6 [21], and complete $H_2S$ oxidation to $SO_4^{2-}$ is achieved for an $O_2/H_2S$ ratio of 23.6 [37]. The sulfate production, expressed as the ratio ($S–SO_4^{2-}$ accumulated in the leachate/$S–H_2S$ removed from the biogas) as a function of the $H_2S$ concentration entering the biotrickling filter is displayed in Figure 6. As observed, $SO_4^{2-}$ production decreased with the increase in the $H_2S$ concentrations and the removal capacity, in agreement with the literature data. $SO_4^{2-}$ production, ranged between 70% and 100% for $H_2S$ concentrations lower than 100 mg $m^{-3}$ (corresponding to RC lower than 2 g $m^{-3}$ $h^{-1}$), tended to a plateau of around 25–30% for $H_2S$ concentrations reaching 1000 mg $m^{-3}$ (RC tending toward 40 g $m^{-3}$ $h^{-1}$). In parallel of these findings, it can be added that the concentration of sulfate in the leachate, measured from ion chromatography, can also be deduced from the measurement of the electrical conductivity of water, on the basis that $SO_4^{2-}$ is the majority ionic species in water since other sulfur ionic species, which could derive from $H_2S$ oxidation, such as sulfide ($S_2^-$), sulfite ($SO_3^{2-}$) and thiosulfate ($S_2O_3^{2-}$), are insignificant in water. Indeed, Qiu and Deshusses [22] measured that sulfide produced by $H_2S$ oxidation was less than 1% of the total species detected in the liquid. Moreover, formation of thiosulfate ($S_2O_3^{2-}$) is unfavorable at pH lower than 8 [38]. Thus, in acidic conditions (pH = 1.8), Rodriguez et al. [21] observed that the presence of sulfite and thiosulfate was below the detection limit of the analyzer. In the present study, the pH value ranged between 1.5 and 3 during the operating conditions. As a result, it can be claimed that the change in the electrical conductivity of water was due to change in the sulfate concentration in water ($SO_4^{2-}{}_{(gS/L)}$ = 0.058 × electrical conductivity$_{(mS/cm)}$; $R^2$ = 0.98; not shown). Note that a part of leachate was periodically removed and replaced by fresh water in order to keep the pH higher than 1.5; such a condition avoiding a performance decay. Acidic conditions also influenced the microbial communities in the biotrickling filter. Figure 7 exhibits genus level NGS (next-generation sequencing) analysis results for microbial diversity in the biofilm harvested at the surface of the expanded

schist sampled in the middle of the biotrickling filter. After the acclimatization period, Illumina Miseq sequencing revealed that the microbial community at the beginning of experiment (day 0) contained high abundance of $H_2S$-affinity genera including mainly *Alicyclobacillus*, *Thionomas*, *Acidithiobacillus* and *Metallibacterium*. The total proportion of these four genera exceeded 95%, which indicated a microbial community with low diversity, but high enrichment of functional bacteria proving that the activated sludge used to inoculate the biotrickling filter was well $H_2S$ acclimatized. All these OTUs are involved in the sulfur cycle and were previously described in acid mining environments as sulfur-oxidizing bacteria [39]. Amongst the most common genera are acidophiles which exhibit mesophilic growth optima. These bacteria possess chemolithotrophic metabolism, by which they are able to use sulfur under oxic conditions. Therefore, high $H_2S$ concentrations and low pH helped shape a microbial community well adapted to $H_2S$ degradation, as reported in the literature [40,41]. After 55 days in operation under severe acidic conditions (pH 1.5–3), the microbial diversity was simplified to extremophile *Acidithiobacillus* spp. and *Metallibacterium* spp., with *Acidithiobacillus* being the most abundant bacterial group (95%), confirming that this genus dominates for this range of acidic pH [42]. These two genera are acidophile bacteria with optimal growth at pH 2–3 and autotrophic metabolism.

Pictures of the two packing materials extracted from columns at the end of the experiment are displayed in Figure 8. The yellow color suggests a sulfur deposit, which was confirmed by the analysis of cellular concrete composition over time. For this material, the mass percentage of sulfur was 6.8% at the beginning of the study and increased progressively to reach 15.4% on day 43. For the biotrickling filter, a sulfur deposit was clearly observed on the material pieces extracted at the bottom of the bed (Figure 8b), whereas the material pieces extracted at the top were cleaner. This finding is consistent with the explanation given above for Figure 6 concerning the predominant $S^0$ production at high loading rates due to high $H_2S$ inlet concentration. Despite the sulfur deposits, no clogging was observed on both bed materials, as illustrated by the measurement of pressure drops. Thus, at the end of the experiment, pressure drops were below 20 Pa $m^{-1}$ for the biotrickling filter and below 30 Pa $m^{-1}$ for the abiotic filter, respectively. These results are in agreement with those reported by Ben Jaber et al. [25] and Lebrun et al. [26], where pressure drops were less than 40 Pa $m^{-1}$ and around 12 Pa $m^{-1}$, respectively.

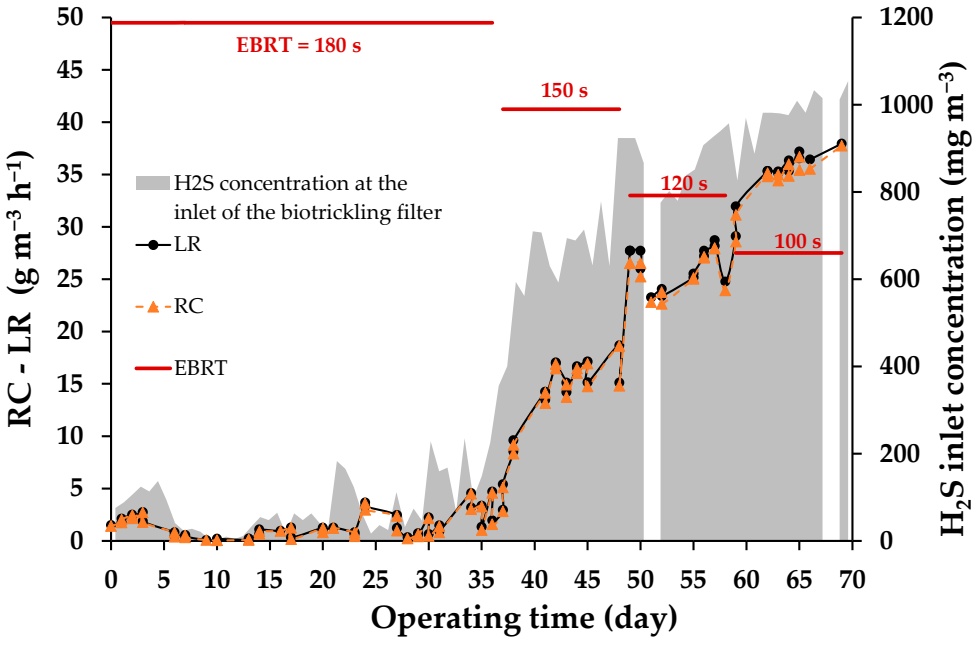



**Figure 5.** Loading rate (LR) and removal capacity (RC) of the biotrickling filter alone at different EBRT and $H_2S$ inlet concentrations.

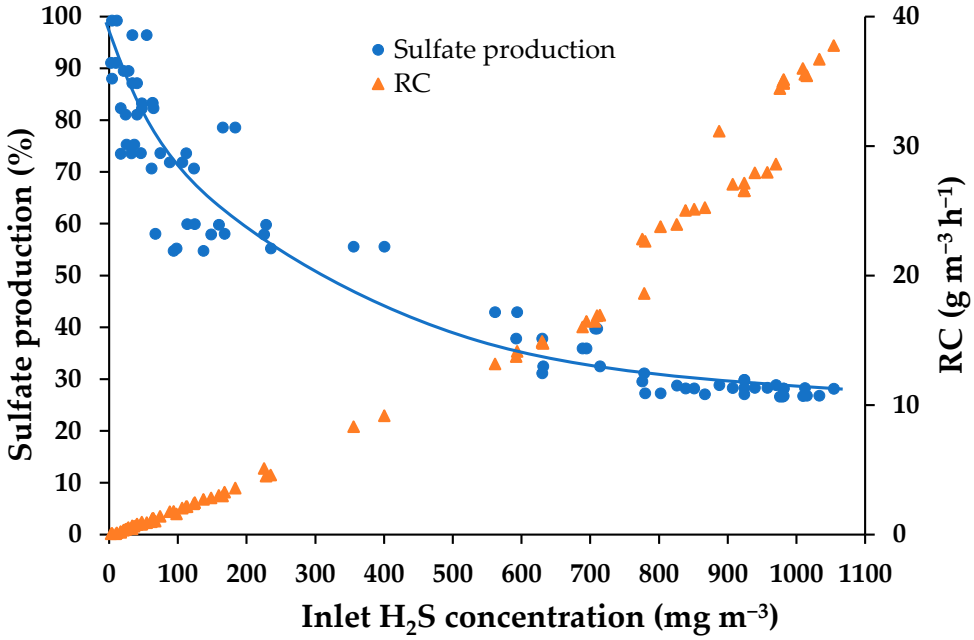



**Figure 6.** Biotrickling filter results: sulfate production and removal capacity according to the $H_2S$ concentration at the inlet of the second stage.

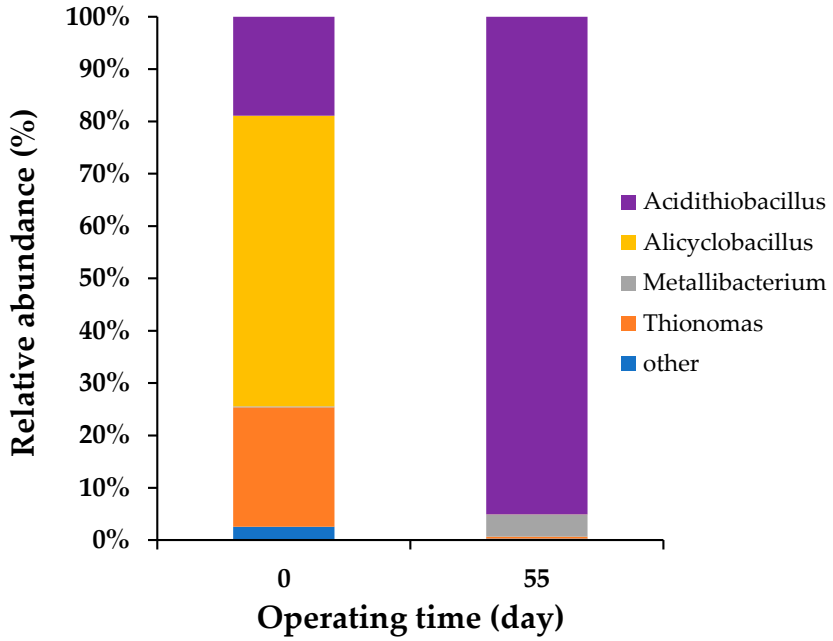
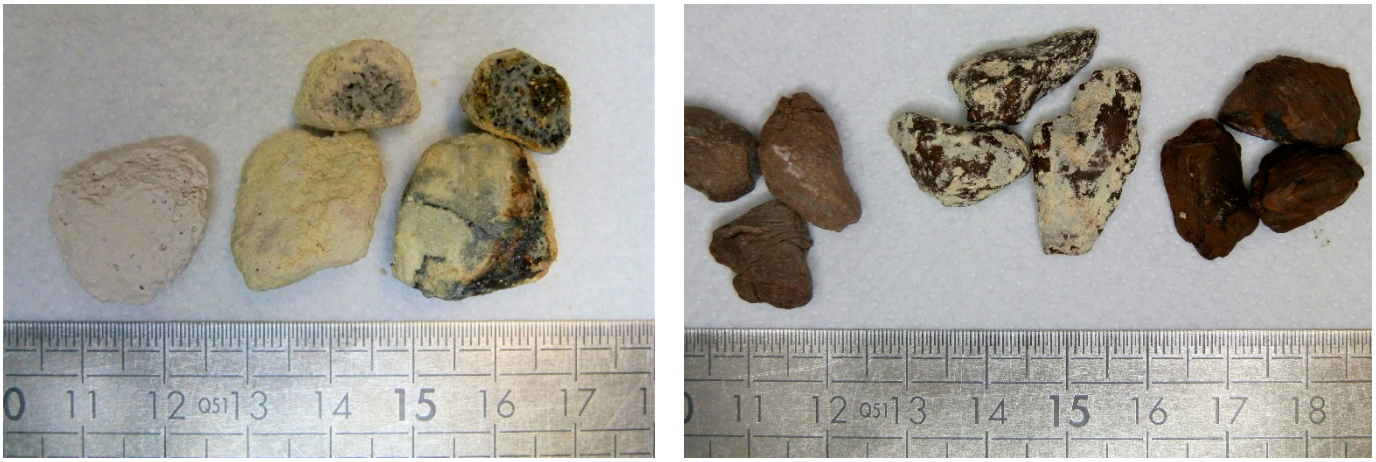



**Figure 7.** Genus level NGS analysis results for microbial diversity in biotrickling filter using the prokaryotic universal primer. The bar charts show taxonomic profiles obtained at the beginning of experiment (day 0) and after 55 days in operation.

Moreover, given that the sulfate production by the biotrickling filter mainly depends on the $H_2S$ concentration at the inlet of the column, i.e., at the outlet of the abiotic filter filled with cellular concrete, it is possible to consider that the ability of the abiotic filter to remove a significant part of $H_2S$ would allow reducing the clogging of the biotrickling filter. Indeed, Rodriguez et al. [21] demonstrated that it is possible to partially remove the deposited $S^0$ by bio-oxidation (40.3%) when the biotrickling filter is not fed by biogas. In other words, the expanded schist filling the biotrickling filter could be partially cleaned, thus regenerated, during phases when the abiotic filter would be highly effective, depending on the fluctuations of the $H_2S$ loading rate of the two-stage process.



(**a**) (**b**)

**Figure 8.** Change in aspect of both packing materials over time; (**a**) Cellular concrete waste (left to right: blank material, extracted from the top of the abiotic filter, extracted from the bottom); (**b**) expanded schist (left to right: blank material, extracted from the bottom of the biotrickling filter, extracted from the top).

EBRT is one of the critical parameters for the mass transfer of $H_2S$ required for high removal efficiency. The objective is always to find a good compromise between short EBRT in order to limit the size of the equipment and high RE. At a total EBRT of 200 s (100 s for each stage), the present study demonstrated that the two-stage process was efficient in treating $H_2S$ concentration of 1500 mg $m^{-3}$ (RE > 97%; Figure 3). Consequently, future works will be performed to reduce the total EBRT. However, for these operating conditions, Figure 3 reveals that the part of $H_2S$ removed by the abiotic filtration stage was around 30%. Considering the ability of the cellular concrete to react with $H_2S$, it could be emphasized to adapt the EBRT of the first stage in order to reduce the EBRT of the second stage. Indeed, the design of the two stages is significantly different since the first one is based on chemical reactions, whereas the second one is based on biological reactions. Thus, the first stage could be designed as a compact horizontal mode system allowing to easily adjust the EBRT to operating changes, while the second stage would be designed as a more classical biofiltration system governed by a given EBRT value imposed by the height of expanded schist filling the system.

The two-stage process could be an interesting way to overcome current difficulties with typical desulfurization bioprocesses of landfill gas. Bioprocesses such as BTF are simple, environmentally benign, cost-effective and ease scalability [4], but some issues can be encountered, such as (i) handling bacteria during high inlet $H_2S$ concentration or stops, (ii) controlling the chemicals nutrients feeding and (iii) avoiding the premature clogging due to sulfur accumulation. Therefore, the cellular concrete as a first-stage abiotic filter could be a solution to protect the biotrickling filter from $H_2S$ shock loads and reduce the premature clogging risk of the second-stage BTF concomitantly. Moreover, as expanded schist has widely proved to be a good carrier material with a long lifetime due to its mechanical resistance during biological reactions, the management of the BTF is limited, and the possible handling of the saturated or degraded media will be avoided. Admittedly, the cellular concrete should be changed periodically, but the management of the first abiotic stage is largely easier than the BTF management. Currently, this two-stage desulfurization process allows reaching the maximal $H_2S$ concentration for numerous applications, i.e., fuel cells, heating and Stirling engines, internal combustion engine, turbines and microturbines [3]. Moreover, the process probably reduces the amount of oxygen in the biogas. Consequently, it can be considered an alternative to biogas purification based on activated carbon. Pragmatically, the process should be tested in situ

on real biogas to assess the efficiency of the process, to evaluate its ability to remove other elements such as $NH_3$ and $CO_2$, and to carry out an economic study.

## 4. Conclusions

It was demonstrated that a two-stage desulfurization process including an abiotic filtration using cellular concrete waste and an anoxic biotrickling filter using an inoculated expanded schist material is efficient in removing $H_2S$ in mimic biogas without any addition of electron acceptors such as nitrite or nitrate (RE > 97%; $H_2S$ concentration = 1500 mg $m^{-3}$). Bio-oxidation of $H_2S$ is achieved provided that the biogas to be treated contains a small fraction of oxygen (up to 0.8% in the present study). The drop in pH in the biotrickling filter (1.5–3) simplified the microbial diversity mainly to extremophile *Acidithiobacillus* spp. At EBRT = 200 s, the removal capacity of the two-stage process was 26 g $m^{-3}$ $h^{-1,}$ and consequently, it appears as a promising technology for efficient and economical biogas cleaning adapted to biogas containing limited $O_2$ amounts, such as landfill biogas. Moreover, at $H_2S$ concentrations up to 1200 mg $m^{-3}$ and longer EBRT (180 s for the first stage only), the abiotic $H_2S$ filtration alone using cellular concrete waste was shown to be equally efficient. Therefore, this abiotic filtration could be used instead of biofiltration for many $H_2S$ gas treatment applications (not limited to biogas) in aerobic or anoxic conditions.

This promising two-stage desulfurization process has to be now investigated in situ in real conditions for the treatment of real biogas containing $CH_4$, $CO_2$, $NH_3$, $O_2$ and $H_2S$. Only the use in real conditions will allow studying the influence of EBRT and $H_2S$ concentration, the main operating parameters.

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