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Article

Hybrid Filtration Process for Gas Desulfurization

Christelle Germain¹, Morgane Poser^{1,2} , Pascal Peu³ , Annabelle Couvert¹ and Eric Dumont^{4,*} 

¹ Ecole Nationale Supérieure de Chimie de Rennes, CNRS, University of Rennes, ISCR, UMR 6226, 35000 Rennes, France; christelle.germain@sigma-clermont.fr (C.G.); morgane.poser@gmail.com (M.P.); annabelle.couvert@ensc-rennes.fr (A.C.)

² Agence de l'environnement et de la Maîtrise de l'Energie, 20 avenue du Grésillé, BP 90406, CEDEX 01, 49004 Angers, France

³ INRAE, UR OPAALE, 17 Avenue de Cucillé, CS 64427, 35044 Rennes, France; pascal.peu@inrae.fr

⁴ IMT Atlantique, CNRS, Nantes Université, GEPEA UMR 6144, 44000 Nantes, France

* Correspondence: eric.dumont@imt-atlantique.fr

Abstract: A hybrid desulfurization process combining a physical filtration stage on cellular concrete (CC abiotic filter, called CCAF) and a biotrickling filter (called BTF) filled with expanded schist as packing material was used to remove high H₂S concentrations from a synthetic gas containing dinitrogen (N₂), dioxygen (O₂) and H₂S without the addition of a nutritive solution. Provided that small amounts of oxygen are present in the gas (1.2 ± 0.1% in volume), the global removal efficiency was 100%, and the global removal capacity reached 35 ± 2 gH₂S m⁻³ h⁻¹ for a total empty bed residence time (EBRT) of 120 s (CCAF + BTF). The resilience of the desulfurization process was demonstrated by applying severe changes in the H₂S concentrations, from 160 to 1150 ± 20 mg m⁻³ for an EBRT = 120 s. According to the performances of the abiotic filter, which can decline over time due to the lifetime of the cellular concrete (137 days), the biotrickling filter reacted either as a refining system or as an efficient system able to treat significant H₂S loading rates (up to 45 ± 3 gH₂S m⁻³ h⁻¹). Depending on the operating conditions, the increase in the pressure drops of the biotrickling filter (from 45 ± 3 to 234 ± 8 Pa m⁻¹) highlighted biomass accumulation, especially extremophilic *Acidithiobacillus sp.* Considering the cellular concrete abiotic filter alone, removal capacities of up to 56 ± 3 gH₂S m⁻³ h⁻¹ were recorded for an EBRT of 60 s, demonstrating that gases such as landfill biogas or household biogas could be efficiently treated using this simple technique.

Keywords: desulfurization; gas; biotrickling filter; cellular concrete; H₂S



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1. Introduction

Climate change is no longer a hypothetical threat but a tangible reality. Some consequences of climate change are already irreversible, while others, such as hydrological changes from the retreat of glaciers, are approaching irreversibility. Thus, climate change significantly slows down efforts to reach global sustainable development goals [1]. Consequently, a massive effort in affordable, clean and renewable energy expansion is needed to reach these goals [2]. In such a context, biogas is presented as a renewable energy source of great interest. It is produced through the anaerobic digestion of industrial, agricultural or municipal waste and it is used as a heat source, electricity source or as fuel once purified [3]. Biogas is usually valorized directly on the production site, by combustion or cogeneration (combined production of heat and electricity) [4]. Methane (CH₄, 53–70% vol) and carbon dioxide (CO₂, 30–47% vol) are the primary constituents of biogas produced by anaerobic digestion, but it also contains other compounds in smaller quantities, including water vapor (H₂O), hydrogen sulfide (H₂S), siloxanes, Volatile Organic Compounds (VOCs), ammonia (NH₃) and oxygen (O₂) [3]. As H₂S is a corrosive gas, it must be removed before biogas combustion to avoid sulfur dioxide formation (SO₂) and equipment damages (engines, boilers, etc.). The H₂S concentrations in biogas typically range from 0.1 to 1%, but higher

concentrations are possible [5]. Biogas purification is a multistage process including desulfurization (removal of H₂S), dehydration (removal of H₂O) and decarbonation (removal of CO₂). These three upgrading steps are mandatory to make biogas an affordable sustainable power source [4,6,7].

The existing widespread desulfurization techniques [8–11] are absorption (usually chemical scrubbing using sodium hydroxide), adsorption [12], membrane filtration and biofiltration [13], mostly on biotrickling filters (BTF). A life cycle assessment of desulfurization techniques comparing biological filtration, chemical scrubbing and adsorption on impregnated activated carbon (AC) demonstrated that BTFs are more favorable in terms of environmental impact compared to other techniques, with chemical scrubbing being the worst technique [14]. Desulfurization using BTF consists of treating biogas by passing it through a packed bed column colonized by microorganisms that are able to degrade H₂S. A recirculating liquid phase contacting the biogas is used to transfer H₂S from the exhausted gas to the microorganisms and to remove the oxidized by-products (mainly sulfate anions SO₄²⁻). H₂S removal using BTF is usually an aerobic technique, but the need for atmospheric oxygen from air leads to biogas dilution and explosion risks. Therefore, anoxic bioreactors, in which nitrate (NO₃⁻) or nitrite (NO₂⁻) anions are used as electron acceptors instead of atmospheric O₂, are preferred. Since the first study regarding anoxic desulfurization in 2008 [15], a large number of studies using BTF were carried out, but other bioreactors were also investigated (stirred tank reactors, gas-lift, bubble columns, etc.) [5,16–18]. Nitrate or nitrite can be purchased from a commercial supplier (chemical source), but this solution is expensive [19], and recent studies suggest using local and biogenic nitrogen sources instead. Nitrate or nitrite is thus produced *in situ* in a nitrification bioreactor through the biological oxidation of ammonium-rich effluent [5,20]. The pairing of a bioreactor treating ammonium with an anoxic BTF purifying biogas would therefore be beneficial for removing the pollutants H₂S, NO₃⁻ and NO₂⁻ simultaneously [5,15]. But there are still many key operational aspects to overcome before this attractive solution can be implemented on an industrial scale.

It was also recently evidenced that the addition of nitrate or nitrite as an electron acceptor could be avoided when small amounts of O₂ are present in the gas [21]. This solution would consequently be the simplest biological method of biogas purification. But further studies are needed to confirm the feasibility of this solution in terms of the empty bed residence time of the gas (EBRT), the variation of H₂S concentrations, pressure drops (ΔP) and resilience. Moreover, it was recently demonstrated that H₂S can be efficiently removed by a simple filter filled with cellular concrete (CC) waste [22]. As the H₂S concentration in some biogases can be very high (several thousands of ppm), which can be detrimental to a biological system, a pre-treatment step may be necessary to limit the concentration to be treated. Therefore, an innovative hybrid process combining a physico-chemical purification stage and a biological degradation stage without the addition of nitrate or nitrite would be an attractive solution for removing H₂S. This desulfurization process could be implemented on different scales, from household to industrial plants, for the treatment of gases of various compositions, especially for gases containing small amounts of O₂. In this case, the new process would have the advantage of removing both H₂S and O₂ from the gas. In addition, for gases with moderate H₂S concentrations, the first stage of the process can be expected to achieve complete H₂S purification, making it a particularly interesting application for small decentralized domestic biogas digesters, such as those encountered in India or China.

The objective of this study was, consequently, to study a hybrid desulfurization process coupling abiotic and biotic modes without oxygen addition from air or nitrate/nitrite. First, a physical filtration stage on cellular concrete (called “cellular concrete abiotic filter” CCAF) was implemented, followed by a biotrickling filter (BTF) filled with expanded schist as a packing material. The influences of the main parameters, the EBRT and H₂S concentrations, were investigated.

2. Materials and Methods

2.1. Materials

Cellular concrete (CC) and expanded schist (ES) are materials with several advantages for use as packing materials for abiotic filtration and for biofiltration, respectively [21]. They are mechanically interesting as they are light and inorganic materials, which are two characteristics that help to reduce the risk of compaction in filtration columns, thus reducing pressure drops in the long term.

Cellular concrete is a light mineral and porous material with a whitish appearance (Figure 1). CC is named after its alveolar structure, since it contains an abundance of non-communicating small spherical cavities in the mm size range. It is made by mixing sand, water, lime, cement and an expansion reactant (usually aluminum sulfate), leading to the release of hydrogen gas, which gives CC its characteristic alveolar structure. The process ends with an autoclave thermal treatment at 10 bars and 180 °C to harden the material. CC used in this study (provided by the Florentaise compagny, Nantes, France) is a recycled waste material from the building of industry production plants. Before its use as a packing material, CC was sieved to use only pieces around 10 mm in diameter. CC is mainly composed of SiO₂ (50.5% in weight), CaO (24.6%), SO₃ (19.7%), Al₂O₃ (2.2%), P₂O₅ (1.4%) and Fe₂O₃ (1.3%). It was evidenced that in the presence of H₂S, and under wetted conditions, complex physico-chemical mechanisms occur between H₂S and the CC components, simultaneously leading to the H₂S removal and a modification in the composition of the material [22,23]. The ability of the CC to remove H₂S as well as its lifetime were predicted from experimental results [22].



Figure 1. Materials used for biogas desulfurization. (Left) Cellular concrete (CC). (Right) Expanded schist (ES).

Expanded schist (Granulex company, Mayenne, France, www.granulex.fr), a light reddish-brown material with a smooth surface, is a type of rock with a characteristic lamellar foliated structure. The manufacturing process of ES is based on the material expansion due to a gas release caused by the high temperature firing of clay. Simultaneously, an outer layer is formed by vitrification on the surface of the material. ES is mainly composed of SiO₂ (55.3% in mass), Al₂O₃ (20.2%), Fe₂O₃ (13.3%) and K₂O (5.1%) [21]. ES was also sieved to use only pieces around 10 mm in diameter. Expanded schist is recognized as a good material for H₂S biotic filtration both in aerobic and anoxic conditions, as well as under extremely acidic conditions. Compared to other biofiltration materials, its good mechanical stability over time is a great advantage to avoid technical maintenance since the bed pressure drops are limited to a few Pa per meter of material.

2.2. Experimental Setup

The experimental setup is displayed in Figure 2. Two packed bed columns were operated in series. Cylindrical polyvinyl chloride columns (internal diameter of 10 cm) were packed with 7.8 L (corresponding to 1 m height) of their respective packing materials. First, the gas circulated through the packed bed of cellular concrete (CCAF), and then

passed through the BTF packed with expanded schist. CCAF was humidified by a drop-by-drop system (flow rate 27 mL min^{-1}), while the BTF was continuously sprinkled with water (flow rate 114 mL min^{-1}). For both columns, water was circulated from top to bottom in a closed loop between the water tank and the column, while the gas circulated from bottom to top (countercurrent flow) in an open loop. The BTF water was renewed regularly (approximately once a week) to ensure sulfate accumulation did not reach values greater than $12 \text{ mg S-SO}_4^{2-} \text{ g}_{\text{material}}^{-1}$, corresponding to an electrical conductivity of 10 mS cm^{-1} [21]. Exceeding this limit leads to a negative impact on the bacterial population, which leads to a significant decrease in efficiency. The expanded schist filling the BTF was inoculated with 4 L of activated sludge from a wastewater treatment plant (Procanar, Lauzach, France), but no nutritive solution was added to the water since it was assumed that the minerals contained in the tap water were sufficient for the growth of autotrophic microorganisms. The average properties of tap water were as follows: pH = 8.0–8.8; electrical conductivity = 0.42 mS cm^{-1} ; $\text{Cl}^- = 57 \text{ mg L}^{-1}$; $\text{Na}^+ = 34.2 \text{ mg L}^{-1}$; $\text{SO}_4^{2-} = 6.6 \text{ mg L}^{-1}$; $\text{NO}_3^- = 4.1 \text{ mg L}^{-1}$. A gas containing dinitrogen (N_2), dioxygen (O_2) and H_2S was circulated through the columns. This gas could mimic landfill biogas or household biogas, as dinitrogen replaces methane CH_4 . A dinitrogen gas generator (BrezzaNiGen LC-MS, Gengaz Company, Wasquehal, France) produced N_2 by purifying ambient air. However, a residual O_2 concentration could still be measured, and the higher the gas flow rate, the higher the residual O_2 concentration. The N_2 flow rate was controlled and measured using a mass flowmeter (Model 58500, Brooks Instruments, Hatfield, MA, USA). A stream of H_2S (99.7% purity), controlled and measured using another mass flowmeter (Model 5850S, Brooks Instruments, Hatfield, PA, USA), was mixed with the N_2 flow prior to entering the CCAF. Each column was equipped with sampling ports located at the inlet and outlet for H_2S concentration measurement (C_{in} and C_{out}) and performance determination (Table 1). Thermocouples (K type) were installed on each column to measure the inner temperature on several measuring points, as described in Figure 2.

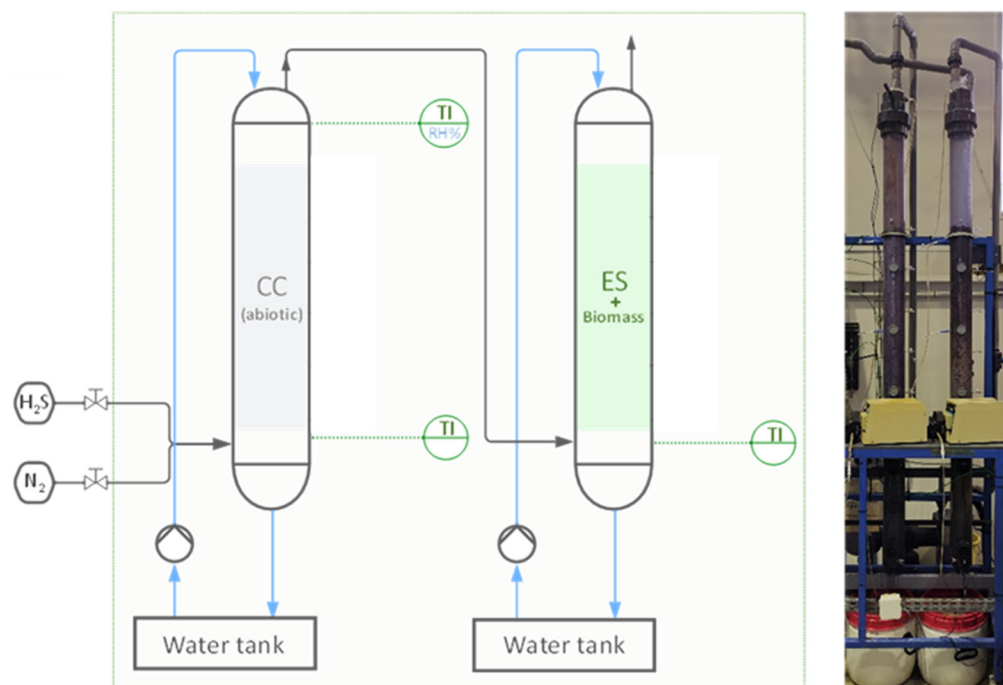


Figure 2. Experimental setup; (left) flow sheet of the desulfurization process (cellular concrete abiotic filter—CCAF—and expanded schist biotrickling filter—BTF-; TI: temperature indicator); (right) picture of the pilot.

Table 1. Parameters used to determine the performance of the desulfurization process.

Parameter	Definition	Nomenclature
Loading Rate LR ($\text{gH}_2\text{S m}^{-3} \text{ h}^{-1}$)	$\frac{Q}{V} C_{\text{in}}$	C_{in} ($\text{gH}_2\text{S m}^{-3}$): Inlet concentration
Removal Capacity RC ($\text{gH}_2\text{S m}^{-3} \text{ h}^{-1}$)	$\frac{Q}{V} (C_{\text{in}} - C_{\text{out}})$	C_{out} ($\text{gH}_2\text{S m}^{-3}$): Outlet concentration
Empty Bed Residence Time EBRT (s)	$\frac{V}{Q}$	Q ($\text{m}^3 \text{ s}^{-1}$): Gas flow rate
Removal Efficiency RE (%)	$\frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}}$	V (m^3): Packing bed volume

2.3. Operating Conditions

The parameters used to determine the performance of the desulfurization process are given in Table 1. Different operating conditions were applied during 5 phases of the experiment. During phase 1, the goal was to test different EBRT (from 64 to 322 s) and H_2S concentrations (C_{in} was increased incrementally every four days: 500, 800, 1000 and then 1300 mg m^{-3}). During phase 2, fluctuating H_2S loading rates were tested at a constant EBRT of 120 s (H_2S concentrations varying from 100 to 1200 mg m^{-3}). During phases 3 to 5, shock loads were applied at a constant EBRT (120 s) to test the resilience of the desulfurization process: H_2S concentrations, C_{in} , were increased abruptly from 160 to 1150 mg m^{-3} , and then sharply decreased to 550 mg m^{-3} , and finally raised again to 1150 mg m^{-3} . To avoid confusion, the following denomination was used in the paper to distinguish the gas residence time in the CCAF ($\text{EBRT}_{\text{CCAF}}$) and the gas residence time in the BTF filled with ES (EBRT_{BTF}), with the overall EBRT being the sum of $\text{EBRT}_{\text{CCAF}}$ and EBRT_{BTF} (or twice $\text{EBRT}_{\text{CCAF}}$ since both columns have the same volume). Similar denomination was used for removal efficiency, RE, loading rate, LR, and removal capacity, RC.

2.4. Gas Analysis

H_2S concentrations were measured using an electrochemical gas analyzer (Biogas 5000, QED Environmental Systems Ltd., Coventry, UK), which also quantified O_2 content. Pressure drops were measured using the sampling ports C_{in} and C_{out} (pressure sensor Setra, Setra Systems, Inc., Boxborough, MA, USA; 0–700 Pa).

2.5. Water Analysis

Water from both tanks were sampled once every day. The pH, conductivity and temperature were measured with a pH electrode and a conductivity electrode connected to a multiparameter analyzer, Consort C834 (Consort bvba, Turnhout, Belgium), with temperature correction. The sulfate content (SO_4^{2-}) was quantified using high-pressure ion chromatography (940 Professional IC Vario, Metrohm, Herisau, Switzerland; detection by conductivity, column metrosep A supp 5150/4.0, eluent 3.5 mM Na_2CO_3 + 3.0 mM NaHCO_3 + 10% MeOH).

2.6. Microbial Community Analysis

A sample of expanded schist covered by biofilm was collected at the middle of the BTF for microbial community analysis, namely DNA extraction performed using NucleoSpin Soil kit according to the manufacturer's instructions (Macherey Nagel, Hoerdt, France). Microbial community dynamics were investigated by high throughput DNA sequencing detailed in [21,24–26]. Operational Taxonomic Unit (OTU) abundance and microbial community diversity indices' calculations were performed using Easy16S (<https://shiny.migale.inrae.fr/app/easy16S>, accessed on 7 December 2022), a shiny web interface based on the phyloseq R package [27].

3. Results and Discussion

3.1. Performance of the Process

Figure 3 shows the performance of the desulfurization process during the five phases of experiment. During phase 1, the H_2S concentration was increased gradually from 500 ± 10 to $1260 \pm 20 \text{ mg m}^{-3}$, and different overall EBRTs were applied for each stage (from 64 to

322 s). During this first phase, the overall RE was always higher than $96 \pm 4\%$, with the outlet concentration always being lower than $28 \pm 1 \text{ mg m}^{-3}$. At low H_2S concentrations, 100% of the incoming H_2S was fully treated by the CCAF. For higher concentrations, RE_{CCAF} could drop to $60 \pm 3\%$, but the remaining H_2S in the gas leaving the CCAF was then removed by the BTF. The desulfurization process coupling the CCAF and the BTF thus ensured total H_2S removal. In terms of removal capacity, Figure 3 shows that RC_{CCAF} can reach values higher than $56 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$, while RC_{BTF} can therefore be nil since the loading rate was fully treated by the CCAF. These first findings were confirmed during phase 2, in which the overall EBRT was maintained at 120 s ($\text{EBRT}_{\text{CCAF}} + \text{EBRT}_{\text{BTF}}$) and the inlet H_2S concentration fluctuated between high ($>1000 \pm 20 \text{ mg m}^{-3}$) and low values (around $160 \pm 3 \text{ mg m}^{-3}$). For this EBRT, the amount of O_2 in the gas was around $1.2 \pm 0.1\%$ in volume. Similarly to phase 1, the H_2S loading rate was mainly treated by the CCAF ($\text{RE}_{\text{CCAF}} > 80\%$ and RC_{CCAF} usually higher than $56 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$), with the BTF thus acting as a refining system. Consequently, this hybrid desulfurization process in two steps was efficient and able to support sudden increases in concentration. It has to be noted that the maximum value of the overall removal capacity, RC, of the desulfurization process was around $35 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ (Figure 3), i.e., significantly lower than RC_{CCAF} , since volumes of both the CCAF and the BTF must be considered for the calculation. Nonetheless, for an EBRT of 120 s, an RC around $35 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ is in the range of the data from the literature reviewed by Almenglo et al. [5], dedicated to the biological technologies for anoxic biogas desulfurization.

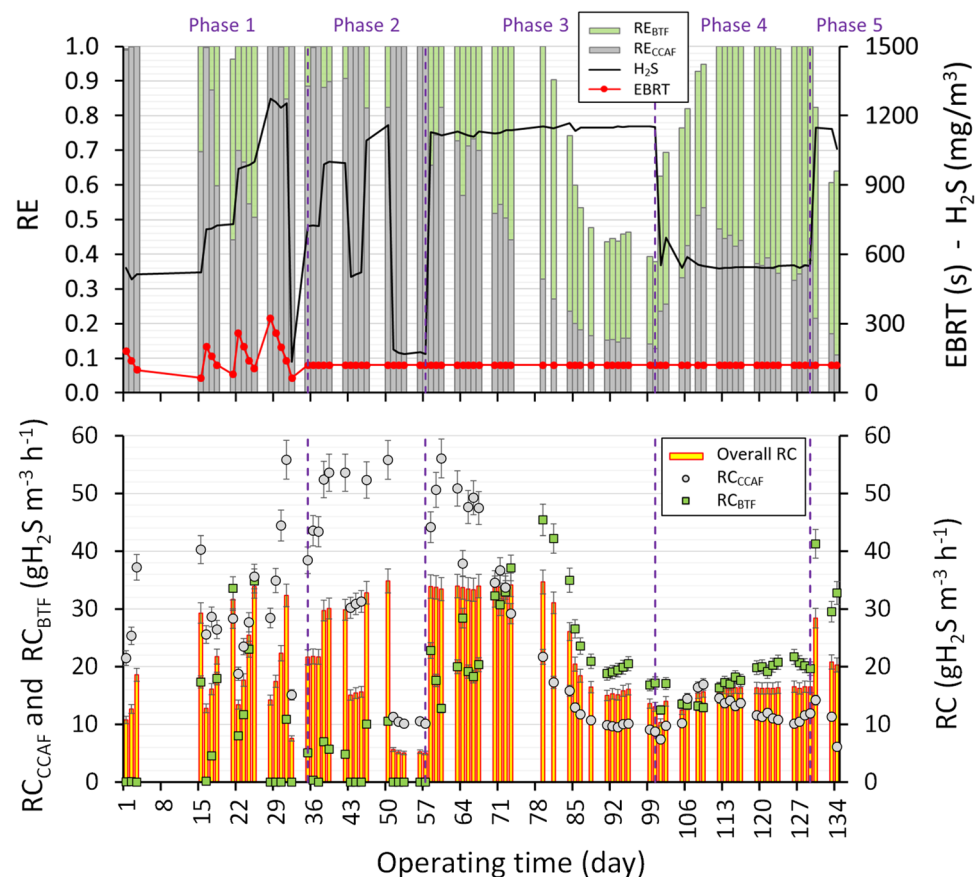


Figure 3. Performance of the desulfurization process (RE_{CCAF} and RE_{BTF} : part of the overall removal efficiency due to the CC abiotic filtration using cellular concrete and due to the BTF filled with expanded schist, respectively; RC_{CCAF} and RC_{BTF} : removal capacity of the CC abiotic filtration and the BTF, respectively; RC: overall removal capacity of the desulfurization process. Note that $\text{RC}_{\text{CCAF}} = Q(C_{\text{in,CCAF}} - C_{\text{out,CCAF}})/V_{\text{CCAF}}$; $\text{RC}_{\text{BTF}} = Q(C_{\text{in,BTF}} - C_{\text{out,BTF}})/V_{\text{BTF}}$; $\text{RC} = Q(C_{\text{in,CCAF}} - C_{\text{out,BTF}})/(V_{\text{CCAF}} + V_{\text{BTF}})$.

3.2. Resilience of the Process

To test the resilience of the desulfurization process, the H_2S inlet concentration was first abruptly increased from 160 ± 3 to $1150 \pm 20 \text{ mg m}^{-3}$ for $\text{EBRT} = 120 \text{ s}$ starting from day 57 and for 43 days ($\text{EBRT}_{\text{CCAF}} + \text{EBRT}_{\text{BTF}}$). During phase 3, the H_2S loading rate was $34 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ for the desulfurization process, i.e., $68 \pm 4 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ for the CCAF ($\text{EBRT}_{\text{CCAF}} = 60 \text{ s}$). Then, the H_2S inlet concentration was dropped from 1150 ± 20 to $550 \pm 10 \text{ mg m}^{-3}$ for $\text{EBRT} = 120 \text{ s}$ from day 100 and for 29 days (phase 4), corresponding to a H_2S loading rate of $16 \pm 1 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ for the desulfurization process, i.e., $32 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ for the CCAF. During phase 3, the overall removal efficiency of the desulfurization process was 100% for 22 days, but RE_{CCAF} gradually decreased from 100% at day 57 to $33 \pm 2\%$ at day 79 (Figure 3). The BTF was then able to compensate for this decrease by processing an increasing H_2S loading. This ability of the BTF to handle the loading left by the CCAF is clearly shown by the changes in the RC_{CCAF} and RC_{BTF} curves in Figure 3, which move in opposite directions (between day 60 and day 79), while the overall RC was kept constant at $34 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$. At day 79, RC_{BTF} reached a maximum value of $45 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$, which is a significant value for a BTF operating at $\text{EBRT}_{\text{BTF}} = 60 \text{ s}$. The increase in the ability of the BTF to treat high loading rates from the CCAF was visually observed from the colonization of the expanded schist by the biofilm (Figure 4). During phase 1, the BTF was colonized by biomass to a height of $43 \pm 1 \text{ cm}$, which remained stable during phase 2. But during phase 3, from day 71 onwards, the biomass grew and rapidly colonized the entire height of the packing material. This biomass development related to the increase in the loading rates to be treated led to an increase in the pressure drop of the BTF (ΔP_{BTF} around $234 \pm 8 \text{ Pa m}^{-1}$ at day 79; Figure 5). This increase in ΔP could also be partly due to the accumulation of elemental sulfur in the BTF since the sulfate production remained unchanged over this period. This value is far larger than pressure drops usually reported in BTF filled with expanded schist (some dozen of Pa m^{-1}) but significantly lower than those obtained using other packing materials, as reported in several studies [28]. From day 81, the performances of both the CCAF and the BTF decreased simultaneously, resulting in a decrease in the overall RE of the desulfurization process. At the end of phase 3, the RE was around $40 \pm 3\%$ (overall RC around $14 \pm 1 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$), with the part of the CCAF and the BTF being 13 and $27 \pm 2\%$, respectively. It can then be concluded that the BTF was no longer able to compensate for the significant decreases in the performance of the CCAF. Without ruling out a possible limitation due to nutrient depletion or low oxygen mass transfer, it is likely that the removal capacity of the BTF was limited by bacterial inhibitions due to the high loadings remaining to be treated after passing through the CCAF, of the order of $50 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ ($\text{EBRT}_{\text{BTF}} = 60 \text{ s}$). The pressure drop ΔP_{BTF} was then decreased to $45 \pm 3 \text{ Pa m}^{-1}$ at day 99. It has to be noted that for the CC abiotic filter, ΔP_{CCAF} was never higher than $10 \pm 2 \text{ Pa m}^{-1}$ during the whole experiment (Figure 6). At the end of phase 3, it was possible that the cellular concrete reached its lifetime. The reduction in the loading rate by a factor of 2, achieved by decreasing the H_2S concentration during phase 4 (constant overall $\text{EBRT} = 120 \text{ s}$), resulted in a temporary improvement in the efficiency of the CCAF (RE_{CCAF} up to $51 \pm 3\%$ at day 108) but without returning to the RE_{CCAF} measured during phase 2. After day 108, RE_{CCAF} progressively decreased to $35 \pm 3\%$, confirming that CC was losing its capacity to remove H_2S . At the same time, the reduction in the loading rate was beneficial to the BTF, confirming the resilience of the desulfurization process, which reached $\text{RE} = 100\%$ from day 112 to the end of phase 4 (RC_{BTF} around $20 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$; Figure 3). During this period, ΔP_{BTF} doubled (from 48 ± 3 to $109 \pm 5 \text{ Pa m}^{-1}$; Figure 5), indicating that the BTF runs well in terms of biomass development and H_2S removal. The last H_2S shock load due to the doubling in the H_2S concentration (phase 5) rapidly led to a decrease in the performance of the desulfurization process, similarly to phase 3. During phase 5, ΔP_{BTF} reached $210 \pm 7 \text{ Pa m}^{-1}$, close to the values recorded during phase 3.

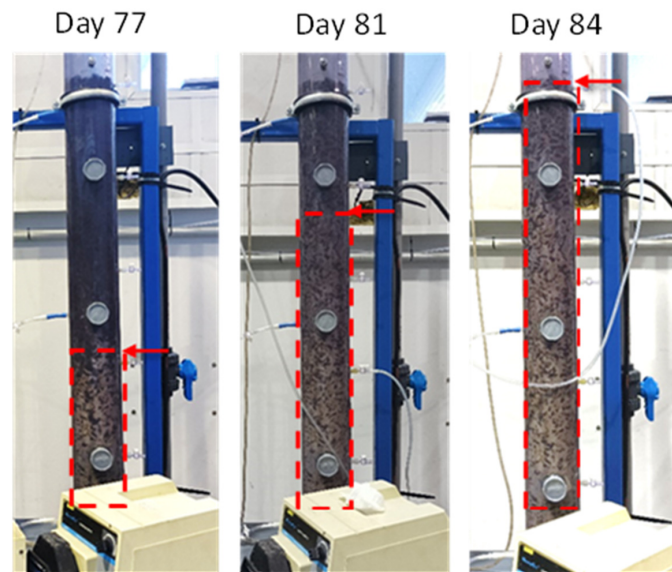


Figure 4. Progression of the microbial population front in the BTF during phase 3.

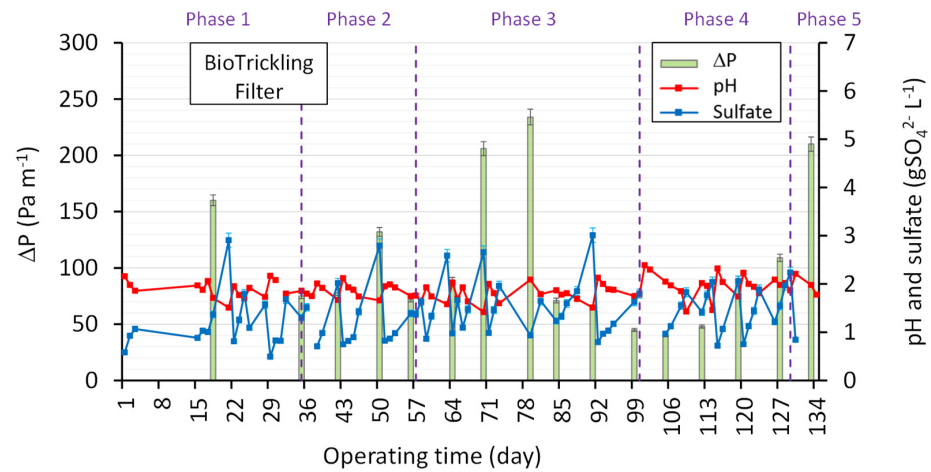


Figure 5. Pressure drops (ΔP) in the BTF measured between the top and the bottom of the column; pH and sulfate concentration measured in the liquid recirculating the BTF.

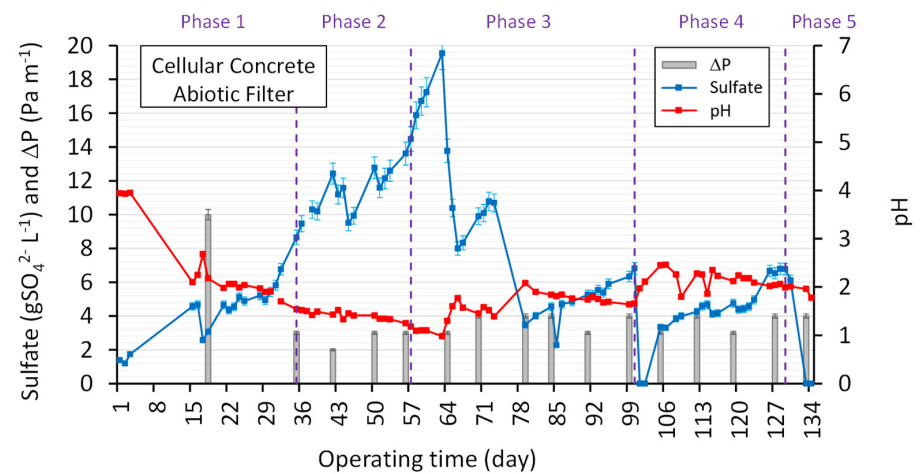


Figure 6. Pressure drops (ΔP) in the CCAF measured between the top and the bottom of the column; pH and sulfate concentration measured in the liquid recirculating the CCAF.

3.3. Microbial Community Analysis

In the presence of oxygen in the gas ($1.2 \pm 0.1\%$ in volume), the biological reaction products in the BTF are either elemental sulfur ($\text{H}_2\text{S} + 0.5\text{O}_2 \rightarrow \text{S}^0 + \text{H}_2\text{O}$) or sulfate ($\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$) according to the H_2S /electron acceptor ratio. Elemental sulfur production and biomass accumulation lead to an increase in the pressure drops, while sulfate formation lead to a pH decrease [29]. The biomass accumulation due to BTF performance was evidenced by the change in pressure drops, and the presence of sulfate was detected by monitoring the pH and quantified by the sulfate concentration measurement using high-pressure ion chromatography (Figure 5). During the operating period, the pH of the recirculating liquid was maintained at a value higher than 1.5 through regular water renewal (once a week) to avoid sulfate accumulation, which can have a negative impact on the microbial population and the BTF efficiency, as evidenced by Ben Jaber et al. [29]. Consequently, the sulfate concentration continuously ranged between 1 and $3 \text{ gSO}_4^{2-} \text{ L}^{-1}$, demonstrating the sulfate production and the fact that the BTF was not oxygen-limited, since the $\text{H}_2\text{S}/\text{O}_2$ molar ratio was significantly higher than 2. Regarding the biomass analysis of the microbial communities extracted from the BTF, Figure 7 reveals the enrichment of the biofilm by bacteria belonging to the genera *Acidithiobacillus*. The presence of these chemolithoautotrophic sulfur oxidizing bacteria (SOB) in large abundance is in agreement with the acidic conditions and consistent with the microbial community analysis reported in the literature dedicated to the desulfurization by BTF, both in aerobic or anoxic conditions [5,13,30]. Consequently, the ability of the BTF to efficiently remove H_2S due to the domination of chemolithoautotrophic *Acidithiobacillus* sp. all along the running of the experiment makes this desulfurization process very robust. Regarding the possible natural colonization of the cellular concrete by microorganisms (the CCAF had not been inoculated), all attempts to extract the biomass from the CCAF failed, and consequently, a biological H_2S removal was certainly insignificant in the apparatus.

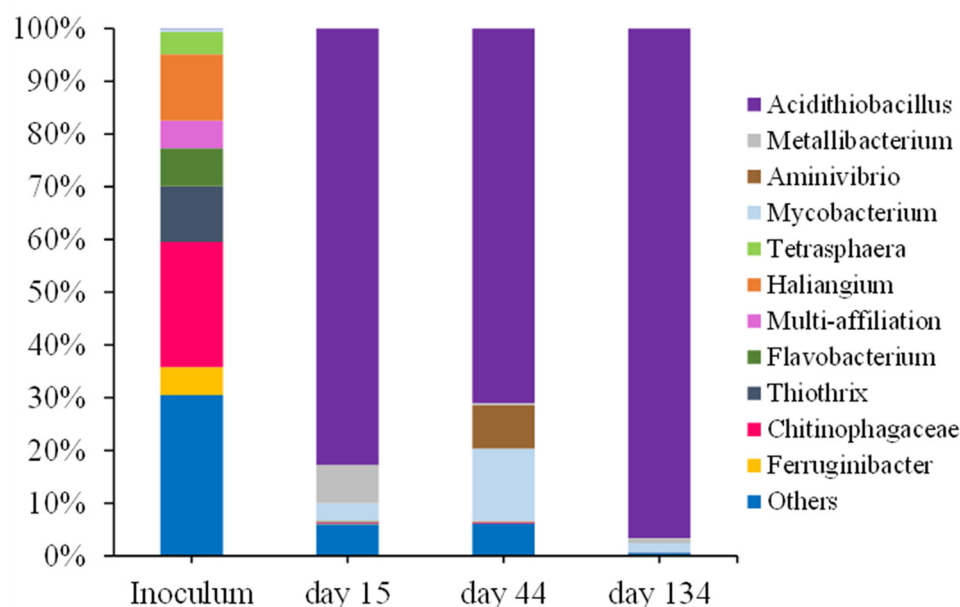


Figure 7. Bar charts of relative abundance of the microbial communities at the genus level extracted from the BTF. Comparison with microbial community of the inoculum.

3.4. Pro and Cons of the Hybrid Filtration Process

It was evidenced that a hybrid desulfurization process combining a physical filtration stage on cellular concrete (CCAF) and a biotrickling filter (BTF) filled with expanded schist as packing material can be successfully used to remove high H_2S concentrations from a gas phase, without the addition of a nutritive solution nor nitrogen salt input (nitrate or nitrite), provided that a small amount of oxygen is present in the gas ($1.2 \pm 0.1\%$ in

volume). This H₂S treatment solution therefore offers new prospects for the purification of biogas containing traces of oxygen. Indeed, this process will be cheaper than anoxic desulfurization biotrickling filters, which require nitrite or nitrate additions as electron acceptors [5]. In the configuration tested in this study (CCAF followed by BTF), the BTF reacted either as a refining system or as an efficient system able to treat significant H₂S loading rates when the performance of the CCAF declined over time. Since RC_{BTF} can reach up to $45 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ at EBRT = 60 s and low pressure drops, it is confirmed that expanded schist is a good material for H₂S removal due to its mechanical stability and porosity, providing a favorable environment for the development of microorganisms. Compared with the available biological desulfurization technologies such as biofilters, bioscrubbers and photobioreactors, BTF represents a good choice in terms of pressure drops and footprint [16], even if the role of pH is still discussed. For instance, neutral or alkaline pH values are preferable for a H₂S mass transfer point of view, but acidic pH values down to 2 are not detrimental for the biological activity of the microorganisms [29,31]. To date, for large-scale applications, adsorption is the most effective and mature technology for H₂S removal at the ppm level, while membrane separation processes, absorption and membrane contactors are adapted for the treatment of high H₂S concentrations (at % levels as in natural gases) [8]. Absorption using amines, alkaline salts and physical solvents is a mature technology for removing H₂S (and CO₂ simultaneously), but work is ongoing to find new environmentally friendly solvent mixtures that will reduce environmental impacts and the process operating costs. Concerning membrane separation, the polymeric type is most widely used for commercial applications with advantages of smaller capital and operating expenses in comparison with the absorption technology. The hybrid filtration process proposed in this study complements these proven technologies and will be suitable for alternative small individual installations such as aerobic digestion units installed on livestock farms. More importantly, it appeared that the use of the CCAF alone could be considered a very promising solution as a single desulfurization process since RC_{CCAF} can reach up to $56 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ at EBRT = 60 s and insignificant pressure drops. In this case, i.e., in the absence of BTF, the desulfurization process would be as simple as adsorption using activated carbon, but using a waste material rather than a functionalized material. Thus, a simple and cheap H₂S filtration through a bed of wet cellular concrete waste could be applied for many uses at different scales, such as the purification of industrial biogas produced by small units as well as household biogas. However, to date, there are only few sources of data on the ability of the cellular concrete to remove H₂S, and further investigations are still needed to improve knowledge on this process. The first findings on this topic [22,23] showed that reactions occurring between H₂S, O₂ and the components of the cellular concrete (mainly calcium oxides and ferric oxide) modify the structure of the material, leading to gypsum formation (CaSO₄ 2H₂O), which, consequently, limits its lifetime. The presence of large amounts of sulfate in water (Figure 6) confirmed the reaction mechanisms leading to gypsum formation due to reactions of calcium carbonate or calcium hydroxide with sulfuric acid (note that the decrease in the sulfate concentration observed after day 64 is due to water replacement to keep pH > 1). However, once all calcium species had reacted to form gypsum, CC lost its capacity to react with H₂S and had to be replaced, as observed during phase 3 of the experiment (Figure 3). The main challenge now is, consequently, to determine the CC lifetime in order to keep the desulfurization process efficient. A previous study determined that the CC lifetime is inversely proportional to RC_{CCAF} [22]. Considering the operating conditions applied during the experiment, and those applied during the preliminary phases of the experiment, it was assessed that the lifetime was around 137 days. Consequently, it can be assumed that the conversion of the cellular concrete in gypsum was virtually complete at the end of experiment. Thus, to be efficient, the desulfurization process requires careful monitoring of the CCAF in order to replace the material when needed. Considering that the lifetime is inversely proportional to RC_{CCAF} , the operating time will be shorter as the ability of the material to remove H₂S increases. In other words, the design of the CCAF should allow for some of the worn

CC to be replaced with raw material to avoid shutting down the filter for maintenance. Once transformed into gypsum, CC waste becomes a new waste whose usefulness must be considered. On the basis that the CC converted into gypsum is not toxic, it would eventually be recyclable as a soil amendment. Indeed, huge amounts of produced gypsum have applications in agriculture in relation to the ability of the CaSO_4 to improve the physical and chemical properties of soils and to stimulate the overall plant growth [32].

Finally, the role of oxygen should be investigated to quantify, in detail, the influences of oxygen concentrations on the performances of the CCAF, but also in the case of the BTF. For O_2 concentrations below 1% (i.e., 10,000 ppm), the limits of the desulfurization process, via the influence of the molar ratio $\text{H}_2\text{S}/\text{O}_2$, need to be highlighted in order to consider industrial applications.

4. Conclusions

The desulfurization process pairing a physical filtration stage on cellular concrete (CCAF) and a biotrickling filter (BTF) filled with expanded schist as packing material can be successfully used to removed high H_2S concentrations from a gas, without the addition of a nutritive solution nor nitrogen salt input (nitrate or nitrite), provided that a small amount of oxygen is present in the gas ($1.2 \pm 0.1\%$ in volume). For a total EBRT of 120 s ($\text{EBRT}_{\text{CCAF}} + \text{EBRT}_{\text{BTF}}$), the removal efficiency was 100%, and the removal capacity was $35 \pm 2 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$, with the CCAF protecting the BTF from high H_2S concentrations. According to the performance of the CCAF, which can decline over time, the BTF reacted either as a refining system or as an efficient system able to treat significant H_2S loading rates (up to $45 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ at $\text{EBRT}_{\text{BTF}} = 60 \text{ s}$). Thus, depending on the operating conditions of the BTF, the pressure drops varied from 45 ± 3 to $234 \pm 8 \text{ Pa m}^{-1}$, which are moderate values for gas treatment. Moreover, very severe variations in the H_2S concentration have demonstrated the resilience of the desulfurization process. Consequently, its ability to satisfactorily remove H_2S should be now validated in real conditions by using real biogas, for instance. According to the performance of the CCAF, a diminution of the total EBRT could be considered, thus reducing the operating costs. Moreover, a desulfurization process based on the use of a single CCAF without the BTF could also be considered since removal capacities of up to $56 \pm 3 \text{ gH}_2\text{S m}^{-3} \text{ h}^{-1}$ ($\text{EBRT}_{\text{CCAF}} = 60 \text{ s}$) were recorded. This simple and economical process, which does not have an impact on the environment, will be perfectly suited to the treatment of biogas from household digesters. However, the decrease in the performance of the CCAF over time, because of the modification in the CC composition after reactions with H_2S , should be investigated to address this issue.

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