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Removal of hydrogen sulfide in air using cellular concrete waste: biotic and abiotic filtrations

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Abstract

The objective of this study was to investigate the removal of hydrogen sulfide (H_2S) present in air using cellular concrete waste as the packing material. Air filtration was performed under biotic and abiotic conditions. Experiments were carried out in a laboratory-scale PVC column (internal diameter of 300 mm) filled with a volume of 70 L of cellular concrete (1 m height). The polluted air flow was generated at $4 \text{ m}^3 \text{ h}^{-1}$ corresponding to an Empty Bed Residence Time (EBRT) of 63 s. In dry conditions without biomass (abiotic conditions), cellular concrete can be an effective medium for the treatment of H_2S in air. For an H_2S concentration of 100 ppmv, the removal efficiency was around 70 % (Elimination Capacity (EC) of $5.6 \text{ g m}^{-3} \text{ h}^{-1}$). This finding can be explained by the physicochemical reactions that can take place between H_2S and the cellular concrete components (mainly CaO , CaCO_3 and Fe_2O_3). However, interactions between cellular concrete and H_2S are not yet fully understood. Used as a packing material for H_2S biofiltration (biotic conditions), cellular concrete waste efficiently

treated (Removal Efficiency = 100 %) high concentrations of H₂S (up to 133 ppmv corresponding to an EC of up to 10.5 g m⁻³ h⁻¹). Physicochemical and biological mechanisms explaining H₂S removal seem to occur simultaneously in the biofilter. At an EBRT of 63 s, the maximal elimination capacity (EC_{max}) was 17.8 g m⁻³ h⁻¹. A packed bed of cellular concrete also presents a satisfactory mechanical behavior with low pressure drops.

Keywords: Cellular concrete; Packing material; Biofiltration; H₂S; Calcium oxide; Iron oxide

1 Introduction

Hydrogen sulfide is an odorous, toxic, flammable and corrosive air pollutant. It is a colorless gas with the characteristic foul odor of rotten eggs. H₂S can cause death immediately when concentrations are over 500 - 1000 ppmv, while exposure to lower concentrations, such as 10 - 500 ppmv, can cause various respiratory symptoms. H₂S may also affect the nervous, cardiovascular, and hematological systems. H₂S is emitted from various industries, such as petroleum refining, rendering, wastewater treatment, paper manufacturing and food processing. H₂S also occurs in volcanic and natural gases. Several processes are available for the treatment of hydrogen sulfide, including absorption [1–5], adsorption [6–11], and membrane separation [12–16]. These methods generally entail high energy, chemical and disposal costs. Biofiltration appears to be a convenient alternative for treating gaseous emissions containing H₂S. This process uses microorganisms immobilized in the biofilm attached to a packing material. The contaminated gaseous stream flows through the filter bed. H₂S is transferred from the gas phase to the biofilm where chemical reactions occur (Eqs. 1-2). The bacteria most used in the biofiltration of hydrogen sulfide belong to the genus *Thiobacillus*, which uses H₂S as an energy source for growth.



The selection of the packing material is a key step in a successful biofiltration operation. Organic media, such as compost, peat, and pine bark, are widely used for H_2S treatment because they contain nutrients [17–20]. Inorganic media, such as expanded schist, pozzolan and lava, are also used due to their interesting mechanical behavior [21–24]. Currently, a combination of expanded schist and UP20 (a synthetic nutrient material) can be successfully used to treat gas with a high H_2S concentration (up to 360 ppmv). However, if the biofilter is continuously overloaded by H_2S , sulfate accumulation in the biofilter bed leads to a significant decrease in the process performances related to a pH decrease ($\text{pH} < 1$). As a result, the watering flow rate of the biofilter must be increased to avoid sulfate accumulation and maintain the $\text{pH} > 1$ [21]. In order to limit this fall in pH due to sulfate production, new packing materials, naturally basic and low-cost, have to be investigated for effective H_2S removal. The objective is clearly to find a material that could be used as a H_2S scavenger to treat high H_2S concentration in air as well as in biogas. In a first approach, the H_2S concentrations considered are ranged from 50 to 500 ppmv in order to compare the results obtained with data reported in the literature [17,19,25–27]. One such new material is cellular concrete waste. Cellular concrete is a material whose physical and chemical properties could be useful for the removal of H_2S . Moreover, the use of waste is an interesting and economic solution for the reduction of air pollution. To the best of our knowledge, this material has never been studied for H_2S treatment. Therefore, the objective of this study was to investigate the removal of hydrogen sulfide using cellular concrete by a physical technique and a bioprocess, *i.e.* biofiltration. The treatment of H_2S was first investigated by filtration of the polluted air through a packed bed of cellular concrete in the absence of biomass in dry conditions (*i.e.* an abiotic filtration). Second, a classic biofiltration was tested using cellular

concrete as the porous support for biomass attachment. In the latter case, the results could be directly compared with performances obtained using expanded schist in the same operating conditions [21].

2 Materials and methods

2.1 Cellular concrete

The properties of cellular concrete depend on its microstructure and composition, which are influenced by the type of binder used, methods of pore-formation and curing. The physical, chemical, mechanical and functional characteristics of different cellular concretes are given in the review paper by Narayanan and Ramamurthy [28].

2.1.1 Composition

The cellular concrete used in this study is a recycled mineral medium, distributed by the company Florentaise in Nantes, France (<http://www.florentaise.com>) (Figure 1). Its composition was determined using an Energy Dispersive X-ray Fluorescence Spectrometer (EDX-800HS, Shimadzu Company) (Table 1). Cellular concrete is mainly composed of calcium (Ca) and silicon (Si). A complementary analysis was carried out using X-Ray Diffraction (XRD) (Siemens Brüker D5000). From the XRD peaks (not shown), the following phases were identified: quartz (SiO_2), calcium carbonate (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), and calcium silicate hydroxide hydrate ($\text{Ca}_{45}\text{Si}_6\text{O}_{15}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$).

Figure 1: Picture of cellular concrete particles

Table 1. Composition (% weight) of cellular concrete and expanded schist as determined by energy dispersive X-ray (the main components are given).

2.1.2 Properties

Specific surface area was determined using a Micromeritics ASAP® 2020 gas adsorption analyzer. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method. Internal porosity and apparent density were measured using a mercury porosimeter, Micrometrics autopore IV 9500. 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).

The specific surface area S_{BET} for cellular concrete was $44 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$. This value is comparable to that of the synthetic material, Biosorbens™ ($41 \text{ m}^2 \text{ g}^{-1}$), used by Shareefdeen *et al.* [29] for the biofiltration of H_2S . However, other biofiltration packing materials have low surface areas ($< 1 \text{ m}^2 \text{ g}^{-1}$) such as sapwood, pine bark and pozzolan [24]. The density determined for cellular concrete was $547 \pm 5 \text{ kg m}^{-3}$. Some biofiltration packing materials have similar densities, such as peanut shells and bagasse (520 kg m^{-3}) [30]. Other media have lower densities, such as polypropylene Pall rings (110 kg m^{-3}) [31] and wood bark (96 kg m^{-3}) [32], whereas others present a high density, such as expanded schist (1248 kg m^{-3} ; Table 3) and pozzolan (1500 kg m^{-3}) [25]. The water retention capacity for cellular concrete was $56 \pm 2\%$. This high value can limit the watering rate in the biofilter and avoid compaction of the bed. Moreover, this value is comparable to those obtained for porous lava (47 %) [22], peat (64 %) [33] and UP20 (47 %) [34]. For the pH, cellular concrete was characterized by a value

of 9. Generally, the pH of the medium is close to neutrality, with a few exceptions such as peat (pH = 4.5) [35] and pine bark (pH = 4.5) [24]. During H₂S treatment by biofiltration, sulfuric acid is produced (Eq. 2) leading to an acidification of the packing material. Having a basic medium can be advantageous to limit the pH drop in the packed bed biofilter.

Table 2. Physical characteristics of the cellular concrete used in this study. Comparison with expanded schist [21].

2.2 Experimental set-up

The laboratory-scale system used for the treatment of H₂S by cellular concrete is shown in Figure 2. It consisted of a PVC column with an internal diameter of 300 mm. The column was filled with cellular concrete (1 m height; volume 70 L). The air flow was generated using a regulated fan (FMV frequency controller 2107, Leroy Somer, Angouleme, France). It passed through a humidification column (if necessary) with an internal diameter of 200 mm, packed with Hiflow rings (1.50 m height). A stream of H₂S (99.7 % purity), controlled by a mass flow controller (Model 5850S, Brooks Instruments, Hatfield, USA), was diluted in the atmospheric air at the outlet of the humidification column. The polluted air was then introduced at the bottom of the biofilter. The H₂S concentration was measured along the column, which was equipped with sampling ports located at the inlet and outlet, and at 10, 30, 50, 70, 90, and 100 cm from the bottom of the column (Figure 2). The H₂S analyzer was an Onyx 5220 device (measurement accuracy $\pm 1\%$) from the Cosma Environment SA Company (Passy, France).

Leachate samples were taken periodically from the bottom of the column. Their pH values were measured by a pH electrode (Consort). Sulfate concentration was determined by the

turbidimetric method as described in Standard Methods [36] for the examination of water and wastewater.

Figure 2. Schematic diagram of the experimental pilot-scale column used for H₂S removal.

2.3 Operating conditions

The parameters used in this paper to describe the operating conditions and for the determination of the removal performances were: (i) the inlet Loading Rate (LR, g m⁻³ h⁻¹); (ii) the Elimination Capacity (EC, g m⁻³ h⁻¹); (iii) the Empty Bed Residence Time (EBRT, s); (iv) the Removal Efficiency (RE, %). All parameters are defined in Table 3. During experiments, the polluted air flow rate was constant at 4 m³ h⁻¹ corresponding to an EBRT of 63 s.

Table 3. Parameters used in this study.

2.3.1 Abiotic experiments

The treatment of H₂S was first investigated by filtration of the polluted air through a packed bed of cellular concrete in the absence of biomass (Table 4). Dry material was used for phases 1 to 10. H₂S concentration was sequentially increased from 25 to 250 ppmv (phases 1 to 5). Then, for phases 6 to 10, the H₂S concentration level was changed in order to study the ability of the cellular concrete bed to respond to a significant change in the pollutant concentration, *i.e.* a change in the inlet loading rate (from 6.4 to 40.0 g m⁻³ h⁻¹).

Table 4. Operating conditions for the filtration of the polluted air through a bed packed with cellular concrete particles in the absence of biomass (air flow rate: $4 \text{ m}^3 \text{ h}^{-1}$ corresponding to an EBRT of 63 s).

2.3.2 Biofiltration experiments

The treatment of H_2S was also considered by classic biofiltration using cellular concrete as the packing material. The bed (Figure 2) was inoculated with 5 L of a diluted solution of activated sludge (about 50 mg of dry sewage sludge per liter) from a domestic wastewater treatment plant (Tougas, Nantes, France). The cellular concrete was topped with a layer of the synthetic material UP20 (2 cm corresponding to 1.4 L) in order to provide nutrients for the biomass. UP20 contained urea phosphate ($\text{CH}_4\text{N}_2\text{O}$, H_3PO_4), calcium carbonate (CaCO_3) (C/N/P molar ratio: 100/10/ 5) and an organic binder (ELOTEX ST2400; 20 % in mass) from the Elotex Company (Switzerland) [34]. In order to maintain the humidity of the bed material, the biofilter was watered periodically (12 L day^{-1} , once a day). During biofiltration experiments, an increase in H_2S concentration from 40 ppmv to 360 ppmv was applied at a constant EBRT = 63 s (Table 5).

Table 5. Operating conditions for the biofiltration experiments (EBRT = 63 s).

3 Results and discussion

3.1 Treatment of H₂S using cellular concrete in abiotic conditions

The effect of increasing the H₂S concentration on process performances is highlighted in Figure 3. For phases 1 to 5, the removal efficiency ranged from 90 % (25 ppmv; LR = 2.0 g m⁻³ h⁻¹) to 50 % (250 ppmv; LR = 20.0 g m⁻³ h⁻¹). This finding indicates that a simple filtration of the polluted air through a packed bed of cellular concrete removed a significant proportion of the hydrogen sulfide. Thus, for an H₂S concentration of 100 ppmv, which represents a level Immediately Dangerous to Life and Health (IDLH) according to the Occupational Safety and Health Administration (OSHA) [37], the removal efficiency was around 70 %, corresponding to an elimination capacity of around 5.6 g m⁻³ h⁻¹. This result means that gas filtration through a packed bed of cellular concrete could be used either to treat the pollution directly in the case of moderately polluted air or as a primary treatment for highly polluted air loaded with H₂S. The removal efficiencies recorded during phases 1 to 5 were similar to or better than those obtained by biofiltration using natural packing materials, such as sapwood, pine bark or pozzolan [18,24]. In order to confirm the ability of cellular concrete to treat the polluted air and respond to a significant change in pollutant load, the H₂S concentration was reduced from 250 ppmv to 80 ppmv (phase 6). Surprisingly, the removal efficiency remained constant at around 50 % (Figure 3). A similar procedure was tested again (phases 7 and 8). The increase in the H₂S concentration to 250 ppmv led to RE = 40 % (against 50 % for phase 5) while the return to an H₂S concentration of 80 ppmv led to the removal efficiency of 50 % being recovered. Such results revealed that reactions occurred between the cellular concrete and H₂S, but they could not be strictly related to the change in the loading rate. Two significant increases in H₂S concentration were then applied (phases 9 and 10). Whereas a significant drop in the removal efficiency could be expected, RE remained

surprisingly constant at around 30 %. As a result, for the last phase in dry conditions corresponding to an H₂S concentration of 500 ppmv, the elimination capacity was 12 g m⁻³ h⁻¹, which confirms the possible interest of using cellular concrete waste as a primary treatment for H₂S removal.

Figure 3. Removal efficiency of H₂S by cellular concrete in the absence of biomass (H₂S concentrations from 25 to 500 ppmv; EBRT = 63 s).

In the light of the results described in Figure 3, the ability of cellular concrete to remove H₂S physically in the absence of biomass had to be explained. Sorption mechanisms and chemical reactions between H₂S and the cellular concrete components were considered. Due to its specific surface area (44 m² g⁻¹), adsorption tests carried out at laboratory scale indicated that cellular concrete is not a good adsorbent for H₂S removal (data not shown). Chemical reactions between H₂S and the cellular concrete components are therefore probable. Calculating the mass balance of the H₂S pollutant between the column inlet and outlet showed that 0.9 kg of H₂S was captured by the material during the 100 days of operation, which corresponded to 42 g of H₂S per kg of cellular concrete during this period (*i.e.* 4.2 % w/w). An analysis of the elemental composition of the material using an EDX fluorescence spectrometer confirmed that the cellular concrete reacted with H₂S, leading to an increase in the percentage weight of the sulfur component in the medium after treatment (Table 6). Between day 0 and day 100, the amount of sulfur component doubled. Taking the volume of the packing material in the column, the porosity of the bed material and the density of the cellular concrete into account, it can be calculated that the increase in the percentage weight

of the sulfur component was consistent with the amount of H₂S calculated from the mass balance.

Table 6. Influence of H₂S treatment on cellular concrete composition.

The corrosion of concrete due to the presence of H₂S is well documented in the literature, especially in sewer systems [38]. However, there are no data suggesting a single-step reaction between H₂S and concrete [39]. There are indications of multi-step reactions leading to the formation of sulfate, gypsum, ettringite and pyrite [38,40,41]. Moreover, the interactions between H₂S and concrete depend on its composition, which is mainly influenced by the type of binder used. Considering the initial composition of the cellular concrete (Table 1), the removal of H₂S can be attributed to the following reactions:



The influence of iron was investigated because the addition of iron salts is widely used to control H₂S emissions in sewer systems [38] and several materials containing iron oxide, like sewage sludge, red mud, bottom ashes or steel slags, have been identified as possible iron sponges for H₂S removal [42]. An analysis by X-ray diffraction (XRD) was carried out before and after treatment. The appearance of two new phases (iron (II) sulfide (FeS) and FeS₂ (pyrite)) on the material after treatment was evidenced, confirming chemical reactions between iron and H₂S (Eqs. 3-4). A black precipitate of FeS formed on the cellular concrete

bed according to Eq. (3). However, the rate of FeS_2 formation is slow relative to the rate of dissociation of FeS [43]. Thus, FeS acts as a continuous source for pyrite formation (Eq. 4). These results are similar to those found by Sahu *et al.* [43] who reported the formation of FeS_2 and FeS during the treatment of H_2S using red mud. If the ability of cellular concrete to remove H_2S was mainly due to the presence of iron and taking into account the initial amount of Fe_2O_3 in the cellular concrete (1.3 % in weight; Table 1), it can be calculated that the amount of H_2S that could be treated by the whole packed bed is around 0.25 kg, *i.e.* around a quarter of the amount of H_2S removed from the air. In other words, even if the total amount of iron present in the packed bed probably reacted with H_2S , other reactions (Eq. 5-7) must be considered inside the packing material to satisfy the mass balance of the H_2S pollutant between the column inlet and outlet. It should be noted that the possible production of SO_2 due to H_2S oxidation was taken into consideration in the mass balance of H_2S . It is also possible that cellular concrete acts as an iron sponge, allowing the regeneration of iron and the production of elemental sulfur S^0 . The use of iron oxide for gas desulfurization is a well-known technology. The hydrated iron oxide reacts with H_2S forming iron sulfide, thus removing H_2S from the gas [44]. Commercial products, such as SulfaMasterTM, Sulfur-RiteTM, Media-G2TM and SulfaTreatTM, are major iron sponge systems in which iron oxides are coated onto different supports [45]. Iron oxides can remove H_2S by forming insoluble iron sulfides, which can be regenerated by oxidation with air to give elemental sulfur:



In such conditions, the packed bed can become clogged by the accumulation of elemental sulfur. However, the regeneration of iron oxide according to Eq. (9) was not evidenced and remains to be demonstrated.

The conversion of concrete to gypsum and ettringite could also explain the ability of this material to remove H₂S. According to Eqs. (5-6), calcium carbonate (CaCO₃) and calcium oxide (CaO) can also react with H₂S to form calcium sulfide (CaS) while according to Eq. (7), calcium sulfide could lead to the production of calcium sulfate (gypsum). The calcium sulfate formed can subsequently react, usually *via* the formation of monosulfoaluminate, to form ettringite [46]. Ettringite is known to be an expansive material that can cause the disintegration of concrete [39]. In the present case, this potential disintegration is not a problem because the purpose of the study is to use cellular concrete waste for gas treatment. Besides, as cellular concrete is mainly composed of calcium oxide, one can assume that large amounts of H₂S will be removed before its complete destruction. To date, and although interactions between cellular concrete and H₂S are not fully understood, it can be considered that each gram of the cellular concrete used in this study could remove at least 42 mg of H₂S. Such a finding will be useful to design a column filled with cellular concrete for the treatment of gas polluted by H₂S. For this purpose, further investigations will be needed to study the behavior of cellular concrete in order to treat H₂S in abiotic conditions over a long period.

3.2 Biofiltration of H₂S using cellular concrete as the packing material

As cellular concrete can remove H₂S in abiotic conditions, it can be expected to be an effective support for biofiltration. To check this assumption, the column was inoculated with 5 L of a diluted solution of activated sludge from a domestic wastewater treatment plant (Tougas, Nantes, France). Consequently, the cellular concrete was not changed between the abiotic and biotic experiments.

3.2.1 Effect of increasing concentrations on H₂S removal

The influence of an increasing concentration of H₂S on the performances of the process is

shown in Figure 4. Hydrogen sulfide was totally eliminated from the 5th day. A high removal efficiency of H₂S (> 99 %) was observed for concentrations up to 133 ppmv. The performances of the process started to decrease from the 43rd day, and this decrease was clearly highlighted from the 60th day when the H₂S concentration increased from 250 to 360 ppmv (LR from 20.0 to 28.8 g m⁻³ h⁻¹). For an EBRT of 63 s, the maximal elimination capacity (EC_{max}) obtained with cellular concrete was 17.8 g m⁻³ h⁻¹. This value is higher than some data reported with other packing materials used for H₂S biofiltration. For instance, at an EBRT of 57 s, a maximal elimination capacity of 8 g m⁻³ h⁻¹ was achieved in a biofilter filled with sapwood [24]. At EBRT = 51 s, an EC_{max} of 8 g m⁻³ h⁻¹ was obtained with Pall rings by Kim *et al.* [47]. At an EBRT of 30 s, Shareefdeen *et al.* did not exceed an EC_{max} of 8 g m⁻³ h⁻¹ using a synthetic medium BIOSORBENSTM as packing material [29]. The comparison with recent biofiltration results reported in the literature at an EBRT close to 63 s (Table 7) indicates that the removal performances of cellular concrete, although less than those of packing materials such as peat or polyurethane foam, are satisfactory. As a result, cellular concrete waste could be an effective and cheap material for the treatment of gas polluted by H₂S, especially as the mechanical behavior of the packed bed is suitable as shown below.

Table 7. Examples of recent biofiltration results reported in the literature on the treatment of gas polluted by H₂S at an EBRT close to 63 s.

Increasing H₂S concentrations led to a decrease in pH (Figure 4). This can be explained by the accumulation of sulfuric acid as a by-product of the biological oxidation of H₂S (Eq. 2). However, even for a high H₂S concentration (360 ppmv), the pH remained greater than 2, whereas the use of expanded schist as the packing material to remove the same H₂S

concentration involved a decrease in pH to values lower than 1, leading to a significant fall in the biofilter performances [21]. The initial pH of cellular concrete (pH = 9) highlights the potential positive effect of this new medium as a packing material for H₂S biofiltration.

Figure 4. Removal efficiency of H₂S and pH changes in a biofilter packed with cellular concrete (concentrations of H₂S from 40 to 360 ppmv; EBRT = 63 s).

Figure 5 shows a picture of the column filled with cellular concrete some days after the end of the biofiltration experiment. One can observe that the column was stratified into two different layers. At the bottom, in a layer of around 20 cm, the cellular concrete kept its original color but a slight orange color also appeared, whereas above, the whole packing material became black. Such coloration underlines the probable presence of ferric oxide Fe³⁺ and iron (II) sulfide FeS. The presence of Fe³⁺ can be related to the original composition of the cellular concrete (presence of Fe₂O₃, Table 1) and the regeneration of Fe³⁺ in the biofilter can be explained by the following reactions:



According to Eq. (10), Fe³⁺ reacts with H₂S to form elemental sulfur. Then, the Fe²⁺ produced can be converted into Fe³⁺ by oxidation with air (Eq. 11). Fe²⁺ can also be biologically oxidized into Fe³⁺ using *Thiobacillus ferrooxidans*. According to Pagella and De Faveri [48], the optimum pH for the growth of *T. ferrooxidans* is around 2.2, which corresponds to the pH values recorded at the end of the experiment (Figure 4). At these low pH values, ferric ion precipitation is avoided. It should be noted that the combined action of a chemical reaction

step (Eq. 10) and a biological oxidation step exploiting the ability of *T. ferrooxidans* was considered by Pagella and De Faveri [48] for H₂S gas treatment using two distinct columns. This coupled process was first studied under the name of BIO-SR [49] and is close to the commercial SulFerox® process (a Shell Iron Redox process), in which Fe²⁺ is converted to Fe³⁺ by oxidation with air. It is interesting to note that, in the presence of biomass, cellular concrete can probably regenerate ferric ion. Finally, the stratification shows that different removal mechanisms (physicochemical and biological) occurred simultaneously in the biofilter. The change in pH along the height of the column could explain this stratification. Further experiments are necessary to confirm this interpretation.

Figure 5. Picture of the column filled with cellular concrete at the end of the biofiltration experiment.

3.2.2 Effect of sulfate accumulation on H₂S removal

Sulfuric acid is produced during H₂S treatment by biofiltration (Eq. 2). Figure 6 illustrates the influence of sulfate accumulation on the performances of the process. For a sulfate concentration lower than 21 mg_{S-sulfate/g_{dry medium}}, H₂S was completely removed in the biofilter. These results suggest that a sulfate content of around 21 mg S-SO₄²⁻/g is a critical level for the removal of the pollutant. Above this concentration, the removal efficiency decreased. Thus, a significant drop in the removal efficiency, up to 60 %, was observed for a concentration of 360 ppmv corresponding to a sulfate concentration of 30 mg_{S-sulfate/g_{dry medium}} (Figure 6). Such a decrease could be due to a drop in the microbial activity in relation to a biomass inhibition as well as an H₂S mass transfer limitation related to the low pH. Therefore, to maintain a high H₂S removal efficiency, it is preferable to work at sulfate concentrations lower than 21 mg_{S-sulfate/g_{dry medium}}. This critical value is close to that found by Yang and Allen [20] (25 mg_{S-sulfate/g_{dry medium}}).

sulfate/g_{dry medium}) and greater than those found for expanded schist (12 mg_{S-sulfate}/g_{dry medium}) [21] and compost (12 mg_{S-sulfate}/g_{dry medium}) [50]. To avoid sulfate accumulation in the biofilter, Ramirez-Saenz *et al.*[51] suggested a periodical recirculation of water in the packed bed to limit the concentration to about 8 mg_{S-sulfate}/g_{dry medium}.

Figure 6. Effect of sulfate accumulation on H₂S degradation.

3.2.3 Pressure drops

The pressure drops (ΔP) were measured between the ports located at 10 and 100 cm from the bottom of the biofilter. Pressure drops in biofilters depend mainly on the superficial gas velocity and particle size [52]. At the beginning of the operation, ΔP varied between 2 Pa m⁻¹ and 62 Pa m⁻¹ for gas velocities varying between 56 and 565 m h⁻¹ (Figure 7). After 110 days of operation, the pressure drops slightly increased, to reach values between 2 and 74 Pa m⁻¹ for the same range of gas velocities. This increase in pressure drop (around 20 %) during H₂S biofiltration can be explained by: (i) the growth of the biofilm; (ii) a possible deposit of elemental sulfur [52–54]; and (iii) a possible formation of gypsum and ettringite (as described in Section 3.1) leading to a degradation of the cellular concrete. In this case, monitoring the ΔP change over a long period will give useful information about the change in the mechanical behavior of the packed bed. Nonetheless, it should be highlighted that these ΔP values are mostly lower than those found using other packing materials in different studies, which confirms the interest of using cellular concrete for biofiltration. For instance, using pine bark, ΔP varied from 15 to 370 Pa m⁻¹ at gas velocities varying between 65 and 520 m h⁻¹ [25] while for pig manure and sawdust, Elias *et al.* [54] measured pressure drops between 15 and 460 Pa m⁻¹ at gas velocities ranging between 100 and 200 m h⁻¹. Moreover, the ΔP values

recorded for the cellular concrete bed are even lower than those found using expanded schist whose mechanical behavior has been identified as excellent for long operation periods (no attrition, no bed compaction) [21]. In fact, for the same range of gas velocities, ΔP varied from 4 to 105 Pa m⁻¹ (Figure 7), namely 40 % more for a gas velocity of 565 m h⁻¹.

Figure 7. Pressure drop measurements in the biofilter for gas velocities varying between 56 and 565 m h⁻¹ (symbols: experimental data; dashed line: Ergun's model [55]). Comparison with data recorded in the same biofilter filled with expanded schist [21].

3.2.4 Comparative study: cellular concrete versus expanded schist particles

The comparison between cellular concrete and expanded schist particles is useful because the latter is recognized as an excellent material for H₂S removal in terms of removal efficiency and mechanical behavior [23,26]. As indicated above, the pressure drops in the biofilter filled with cellular concrete were lower than those obtained with expanded schist during 110 days of operation at a gas velocity of 565 m h⁻¹ (Figure 7). Nonetheless, this interesting finding remains to be confirmed by studying the behavior of cellular concrete over a long period (> 1 year in operating conditions). By comparing the removal efficiencies of H₂S obtained by cellular concrete to those reported in Ben Jaber *et al.* [21] using expanded schist, one can observe that expanded schist showed better performances (Figure 8). Although both materials are efficient for concentrations lower than 133 ppmv (LR = 10.6 g m⁻³ h⁻¹), differences can be observed for concentrations higher than 250 ppmv (corresponding to LR > 20.0 g m⁻³ h⁻¹). For a loading rate of 28.8 g m⁻³ h⁻¹ (360 ppmv), the removal efficiencies obtained for expanded schist and cellular concrete were 87 % and 63 %, respectively (Figure 8). The physical

characteristics of the two materials given in Table 1 could explain this difference. For example, the amount of iron oxide Fe_2O_3 in expanded schist is ten times higher than in cellular concrete. Moreover, the amount of calcium oxide CaO in expanded schist is very low whereas it is a major component of cellular concrete. Assuming that the overall H_2S removal was due to both a physical removal caused by the presence of iron oxide and a biodegradation by the biomass, expanded schist should have better properties for H_2S treatment than cellular concrete. A packed bed of expanded schist was previously tested for H_2S removal in abiotic conditions; the results are extensively described in Dumont *et al.* [53]. Removal efficiencies from 30 to 50 % were recorded. However, the experiments were not carried out in dry conditions. Moreover, the EBRTs applied (14 to 35 s) were significantly lower than that used in the present study, which prevents a direct comparison. As a result, further experiments need to be carried out to evaluate and compare the performances of both packing materials to remove H_2S without biomass in dry conditions. Such an investigation should provide valuable information about the possible mechanisms of H_2S removal due to the presence of calcium and iron in both materials, respectively.

Figure 8. Comparison of the removal efficiencies of H_2S using cellular concrete and expanded schist as packing materials (EBRT = 63 s; pH > 1).

4 Conclusion

The removal of H_2S by cellular concrete waste as a new packing material was evaluated. At a constant EBRT of 63 s, the results are promising in terms of removal efficiency and pressure drops. This packing material thus presents several advantages, summarized below.

In dry conditions without biomass, cellular concrete can be an effective medium for the treatment of H₂S in air. This finding can be explained by chemical reactions that can take place between H₂S, CaO, CaCO₃ and Fe₂O₃. The large amount of H₂S removed suggests that multiple reactions occur in cellular concrete. Gypsum and ettringite are probably formed. Moreover, cellular concrete could act as an iron sponge with iron regeneration. However, the interactions between cellular concrete components and H₂S are not yet fully understood. Consequently, further studies are needed to identify the chemical mechanisms between H₂S and this material.

Used as a packing material for H₂S biofiltration, cellular concrete waste efficiently treated (RE = 100 %) high concentrations of H₂S in air up to 133 ppmv (loading rate up to 10.5 g m⁻³ h⁻¹). Physicochemical and biological mechanisms explaining H₂S removal seem to occur simultaneously in the biofilter. At an EBRT of 63 s, the maximal elimination capacity (EC_{max}) calculated was 17.8 g m⁻³ h⁻¹. The packed bed of cellular concrete also presents a satisfactory mechanical behavior with low pressure drops (30 % lower than those found with expanded schist in the same conditions).

This study is the first experimental evidence that the gaseous pollutant H₂S can be removed using cellular concrete waste. Further investigations are necessary (i) to identify the precise chemical and biological mechanisms involved in both abiotic and biofiltration conditions; (ii) to determine the ability of the material to be used over a long period. Investigations could also be performed for the treatment of H₂S in biogas with high values of EBRT.

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Table 4. Composition (% weight) of cellular concrete and expanded schist as determined by energy dispersive X-ray (the main components are given).

Elemental composition of cellular concrete (%)		Comparison of composition of cellular concrete and expanded schist		
		Composition (%)	Cellular concrete	Expanded schist
Ca	44.8	SiO₂	50.5	56.4
Si	41.8	CaO	24.6	0.9
S	6.8	SO₃	19.7	1.6
Fe	2.7	Al₂O₃	2.2	20.5
Al	2.0	P₂O₅	1.4	1.6
P	1.3	Fe₂O₃	1.3	12.4
K	0.4	K₂O	0.2	5.0

Table 5. Physical characteristics of the cellular concrete used in this study. Comparison with expanded schist [13].

Physical characteristics	Cellular concrete	Expanded schist
Density (kg m ⁻³)	547	1248
Median diameter (mm)	11	12
Specific surface area S _{BET} (m ² g ⁻¹)	44	-
Internal porosity (%)	64	47
Initial pH	9	7
Water retention capacity (%)	56 %	-

Table 6. Parameters used in this study.

Parameter	Definition	Nomenclature
Loading Rate (LR)	$LR \left(g \text{ m}^{-3} \text{ h}^{-1} \right) = \frac{Q}{V} C_G^{\text{in}}$	C_G^{in} : inlet concentration (g m^{-3}) C_G^{out} : outlet concentration (g m^{-3}) Q: gas flow rate ($\text{m}^3 \text{ h}^{-1}$) V: bed volume (m^3)
Elimination Capacity (EC)	$EC \left(g \text{ m}^{-3} \text{ h}^{-1} \right) = \left(C_G^{\text{in}} - C_G^{\text{out}} \right) \frac{Q}{V}$	
Empty Bed Residence Time (EBRT)	$EBRT \left(s \right) = \frac{V}{Q}$	
Removal Efficiency (RE)	$RE \left(\% \right) = \frac{\left(C_G^{\text{in}} - C_G^{\text{out}} \right)}{C_G^{\text{in}}} 100$	

Table 4. Operating conditions for the filtration of the polluted air through a bed packed with cellular concrete particles in the absence of biomass (air flow rate: $4 \text{ m}^3 \text{ h}^{-1}$ corresponding to an EBRT of 63 s; $[\text{H}_2\text{S}]$ concentrations $\pm 1\%$; LR $\pm 5\%$).

Phase	Duration (days)	$[\text{H}_2\text{S}]$ (ppmv)	LR ($\text{g m}^{-3} \text{ h}^{-1}$)
Dry conditions			
1	13	25	2.0
2	13	50	4.0
3	13	100	8.0
4	12	150	12.0
5	10	250	20.0
6	5	80	6.4
7	8	250	20.0
8	6	80	6.4
9	5	350	28.0
10	6	500	40.0

Table 5. Operating conditions for the biofiltration experiments (EBRT = 63 s; [H₂S] concentrations ± 1 %; LR ± 5 %).

Phase	Duration (days)	[H ₂ S] (ppmv)	LR (g m ⁻³ h ⁻¹)
1	7	40	3.2
2	7	60	4.8
3	13	80	6.4
4	16	133	10.6
5	16	250	20.0
6	15	360	28.8

Table 6. Influence of H₂S treatment on cellular concrete composition.

Composition	Before H ₂ S treatment (% weight)	After 100 days of H ₂ S treatment (% weight)
Ca	44.8	42.0
Si	41.8	36.5
S	6.8	15.6
Fe	2.7	2.5
Al	2.0	1.6
P	1.3	1.2
K	0.4	0.4

Table 7. Examples of recent biofiltration results reported in the literature on the treatment of gas polluted by H₂S at an EBRT close to 63 s.

Packing material	EBRT (s)	Elimination Capacity EC (g m ⁻³ h ⁻¹)	Removal Efficiency RE (%)	Reference
Peat	60	65.9	90	[38]
Peat	57	25.5	50	[16]
Sugarcane bagasse	49	73		[39]
Coconut fiber	49	68		[39]
Pine bark	57	10	69	[22]
Sapwood	57	8	50	[16]
Synthetic medium (UP20)	57	10	93	[22]
Peat + UP20 (mixed)	57	25.5	80	[16]
Pozzolan + UP20 (layers)	57	10	74	[22]
Polyurethane foam	80	56.6	95	[40]
Polyurethane foam	49	66		[39]
Biomedium encapsulated by Na-alginate and polyvinyl alcohol	51	6	99	[37]
Cellular concrete	63	10.5 17.8	100 63	This study

Figure 2: Picture of cellular concrete particles

Figure 2. Schematic diagram of the experimental pilot-scale column used for H₂S removal.

Figure 3. Removal efficiency of H₂S by cellular concrete in the absence of biomass (H₂S concentrations from 25 to 500 ppmv; EBRT = 63 s; RE values \pm 2%).

Figure 4. Removal efficiency of H₂S and pH changes in a biofilter packed with cellular concrete (concentrations of H₂S from 40 to 360 ppmv; EBRT = 63 s; RE values \pm 2%; pH values \pm 0.2).

Figure 5. Picture of the column filled with cellular concrete at the end of the biofiltration experiment.

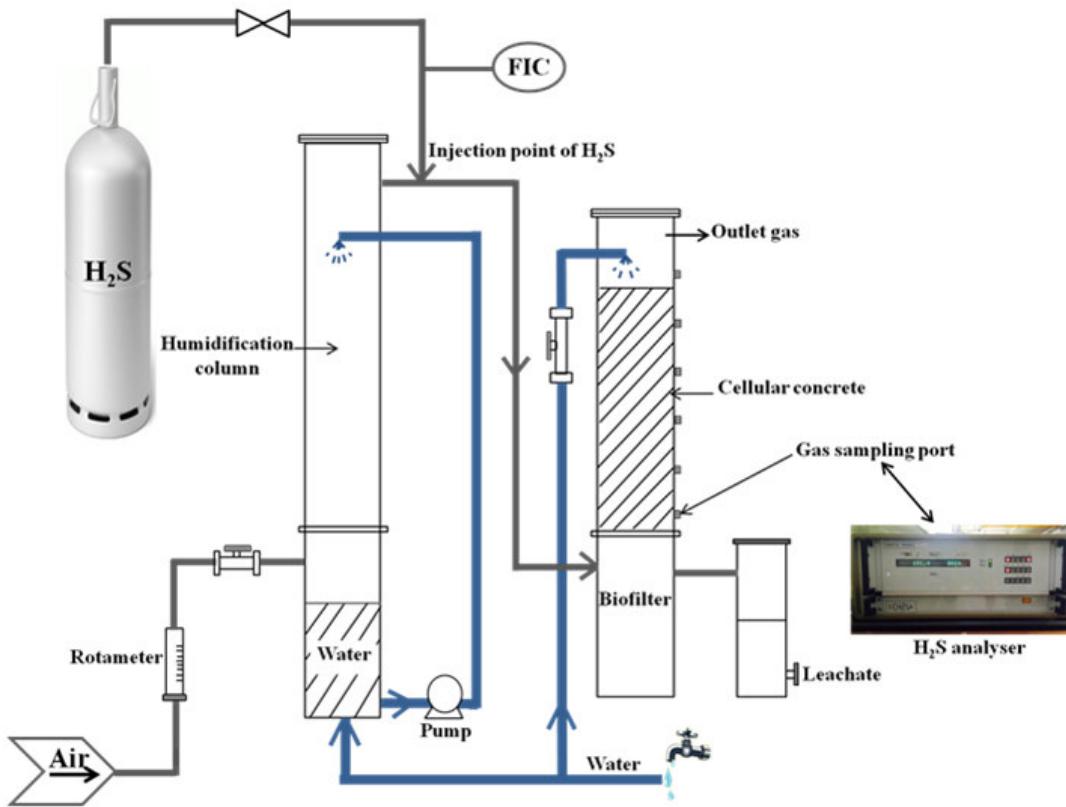
Figure 6. Effect of sulfate accumulation on H₂S degradation (RE values \pm 2%; pH values \pm 0.2).

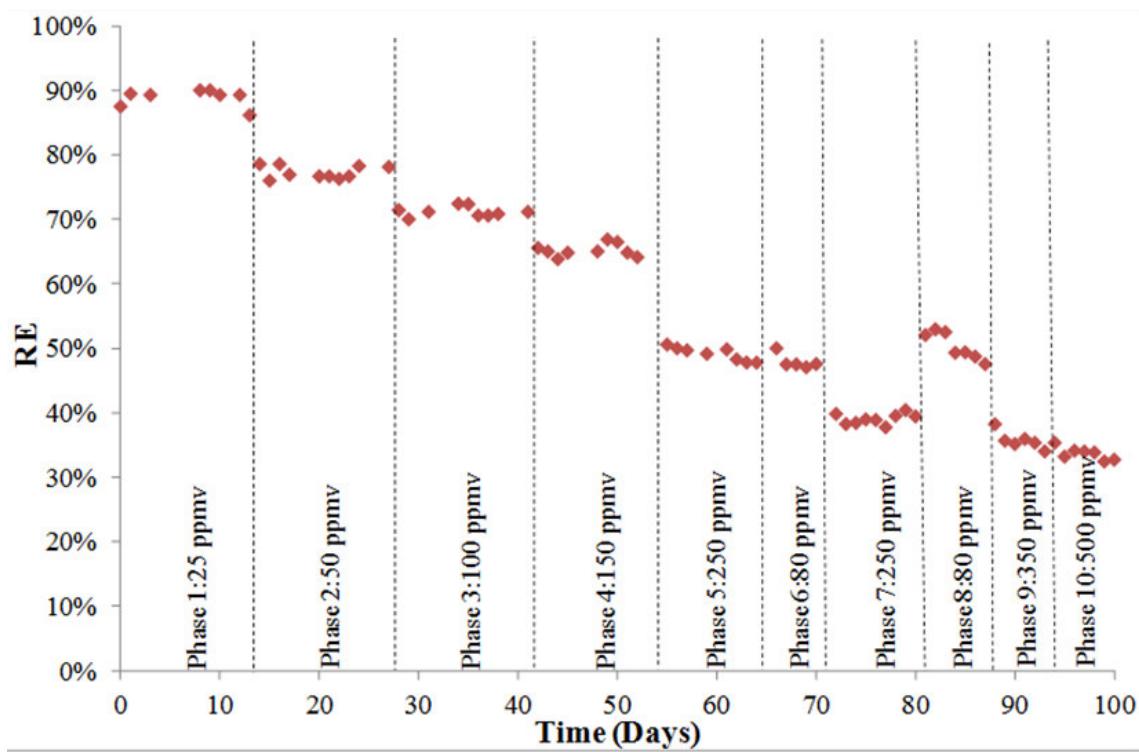
Figure 7. Pressure drop measurements in the biofilter for gas velocities varying between 56 and 565 m h⁻¹ (symbols: experimental data; dashed line: Ergun's model [48]). Comparison with data recorded in the same biofilter filled with expanded schist [13].

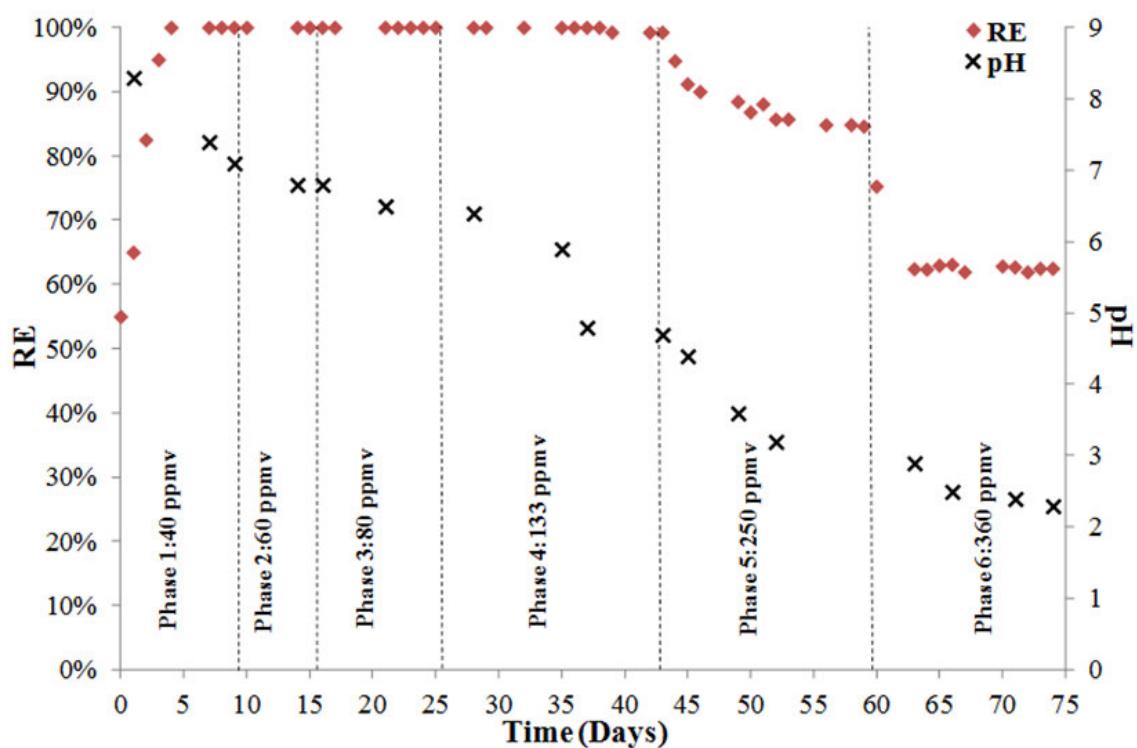
Figure 8. Comparison of the removal efficiencies of H₂S using cellular concrete and expanded schist as packing materials (EBRT = 63 s; pH > 1).

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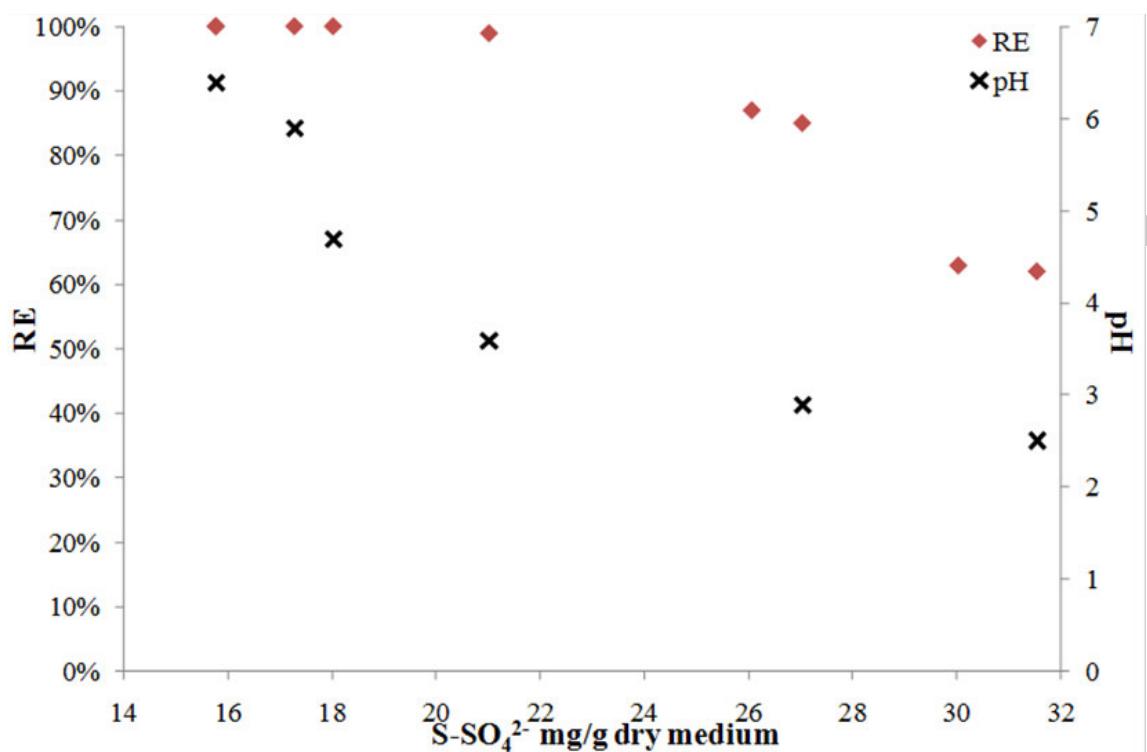


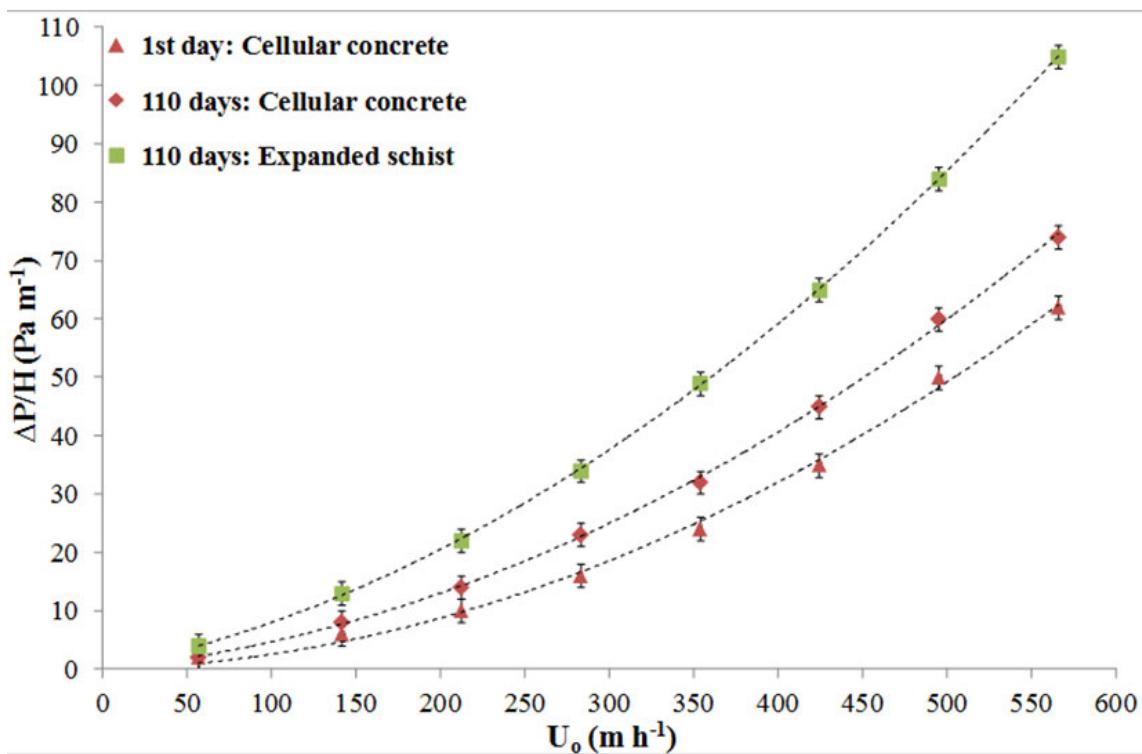


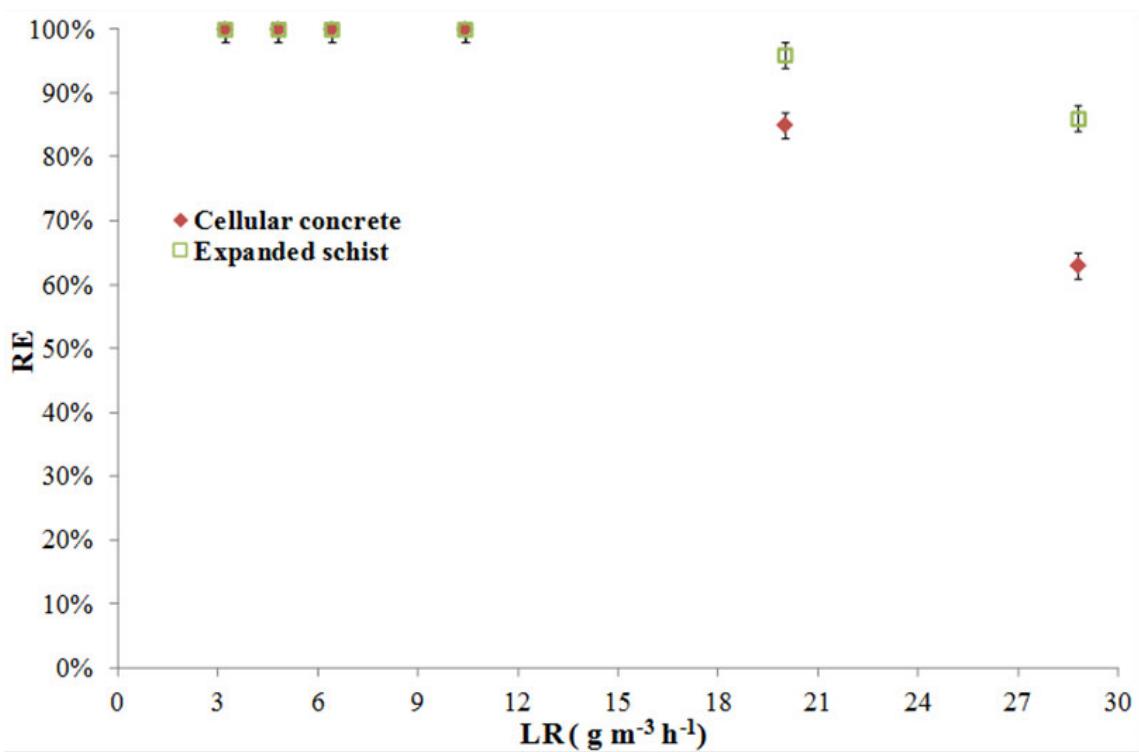


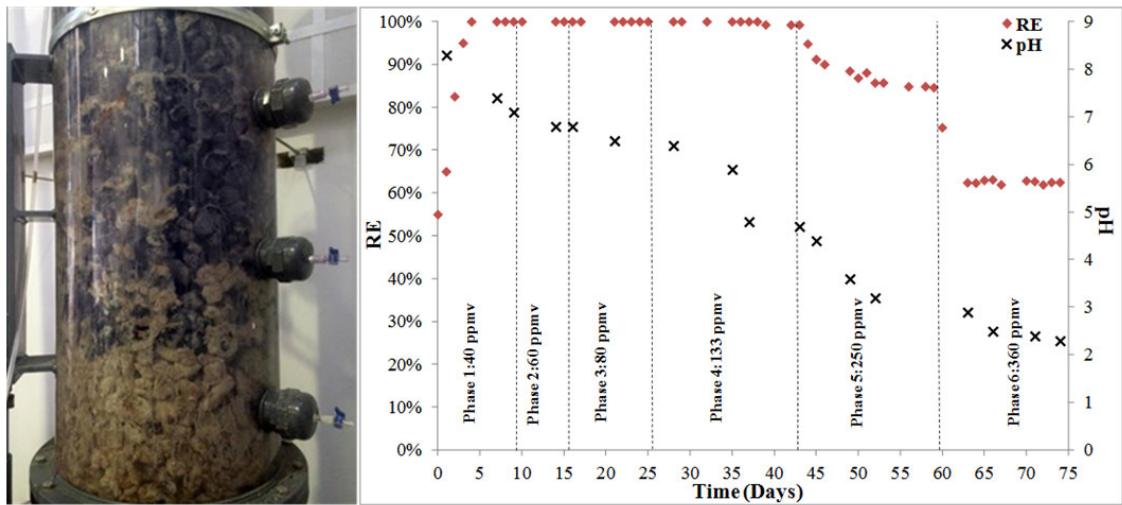


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Graphical abstract

Highlights

H₂S removal using cellular concrete waste was investigated

Cellular concrete is efficient for removing H₂S under dry conditions without biomass

Under abiotic conditions, each gram of concrete could remove at least 42 mg of H₂S

Cellular concrete waste is also efficient as a packing material for biofiltration

At EBRT = 63 s, the EC_{max} of the biofilter was found to be 17.8 g m⁻³ h⁻¹