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Biological sweetening of energy gases mimics in biotrickling filters

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Abstract

Removal of hydrogen sulfide from waste and energy-rich gases is required, not only because of environmental health and safety reasons, but also because of operational reasons if such gases have to be used for energy generation. A biotrickling filter for the removal of ultra-high concentrations of H_2S from oxygen-poor gases is proposed and studied in this work. Two laboratory-scale biotrickling filters were used to study the startup period and to determine the long-term performance of the gas sweetening process. The inlet H_2S concentration ranged from 900 to 12000 ppmv and two different packing materials were investigated. There was no toxicity effect observed even at a the highest H_2S concentration, and maximum elimination capacities of 280 and 250 g H_2S m⁻³ h⁻¹ were obtained at gas contact times of 167 and 180 s, respectively. Elemental sulfur and sulfate were found to be the most abundant end-products of the biological oxidation of sulfide when operated under microaerophilic conditions. The biotrickling filter was able to quickly recover its nominal performance after different load increases and system shutdowns simulating field operation. The results reported here show that biotreatment can be an interesting alternative to conventional gas sweetening systems normally used for such applications.

Keywords: Hydrogen sulfide; Gas sweetening; Biotrickling filter; Desulfurization; Fuel gas; Biogas

1. Introduction

Hydrogen sulfide is a common reduced sulfur compound found in several industrial waste gases. It is easily recognizable by its offensive rotten eggs odor. However, odor nuisance is not the main issue in energy-rich gases such as biogas from anaerobic digesters which may contain H_2S concentrations exceeding 500 ppmv and up to 20 000 ppmv (2% v/v) (Woodcock and Gottlieb, 2004). In such cases, H_2S removal, often called gas sweetening, is necessary to avoid corrosion of combustion engines and SO_x generation in the flue gases. Thus, removal of H_2S from waste and energy-rich gases is required, not only for

environmental health and safety reasons but also for operational reasons.

So far, the most commonly used treatment technology for H_2S removal is selective absorption in amines such as diglycolamine, monoethanolamine, methyldiethanolamine or other compounds that have a high affinity for H_2S (Woodcock and Gottlieb, 2004). Although these processes have been extensively and successfully applied, they have many drawbacks such as high energy and operating costs due to the regeneration of the absorbent phase. In this context, biological processes for air pollution control are gaining popularity (Deshusses, 1997; Devinny et al., 1999; Kennes and Veiga, 2001) but have not yet been generally applied to treatment of H_2S in energy-rich gases.

Biological H₂S utilization as energy source for lithoautotrophic organisms is a well-known process that can be described with the following overall reactions (Eqs. (2), (3)). Note that oxidation to elemental sulfur can only

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happen under oxygen limited conditions, and that excess oxygen is required for the formation of sulfate (Kuenen, 1975; Woodcock and Gottlieb, 2004).

$$H_2S \leftrightarrow H^+ + HS^-$$
 (dissociation) (1)

$$HS^- + 0.5O_2 \rightarrow S^0 + OH^-$$
 (2)

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$$
 (3)

Biofilters, bioscrubbers and biotrickling filters have been proven to be a suitable, environmentally friendly and costeffective alternative for waste gas treatment, especially for the treatment of low concentrations of H₂S (Yang and Allen, 1994; Devinny et al., 1999; Gabriel and Deshusses, 2003a; Kim and Deshusses, 2005). However, there has been limited success in dealing with high concentrations of H₂S (>1000 ppmv) using biofilters, biotrickling filters and bioscrubbers and only few industrial processes have been fully developed for such application. Among them, the Thiopaq® process (Paques, The Netherlands), and the Biopuprocess (Biothane, USA) are the only ones specifically developed for the removal of high concentrations of H₂S from biogas or fuel gas. The Thiopaq[®] process is a two-reactor system consisting of a conventional caustic scrubber followed by an expanded bed bioreactor for the recovery of the spent caustic and for elemental sulfur generation. The Biopuric® process is also a two-reactor system, which combines a conventional chemical scrubber followed by a biological treatment step. Little is publicly known about the latter process.

Alternative and sustainable processes need to be developed. Thus, the purpose of this study was to evaluate the technical feasibility of treating high concentrations of H₂S in laboratory-simulated biogas or fuel gas using a single biotrickling filter reactor, and attempt to produce mostly elemental sulfur which can be easily disposed or recovered. Unlike the above mentioned commercial systems, the treatment demonstrated in this paper relies on a single reactor system. Although H2S treatment had been widely reported in biofilters and biotrickling filters (Yang and Allen, 1994; Devinny et al., 1999; Gabriel and Deshusses, 2003a; Kim and Deshusses, 2005), the present study is different because it deals with ultra-high H₂S concentrations in gases that are initially oxygen-free. Operation at close-to-neutral pH was chosen in order to improve the H₂S absorption capacity of the liquid phase although many of the H₂S degrading organisms, like the genus Thiobacillus, have acidic optimum growing pH (Robertson and Kuenen, 1999, 2002). Also, absorption and oxidation of H₂S to elemental sulfur is pH neutral as shown by adding Eqs. (1) and (2).

Two laboratory-scale prototypes with different packing materials were used to evaluate the performance in terms of H_2S removal efficiency (RE = $(C_{in} - C_{out})/C_{in}$) and elimination capacity (EC = $(C_{in} - C_{out}) \times Q/V$, where Q is the gas flow and V is the bed volume). The ratio of SO_4^{2-}/S^0 produced under different operating conditions as

well as the robustness of the bioreactor when exposed to different perturbations were also assessed.

2. Materials and methods

Both experimental Reactors A and B (see Table 1) were based on the same design (Fig. 1) but with slightly different characteristics. They consisted of a biotrickling filter reactor operated in an upflow, counter-current mode, fed with a mimic of biogas or fuel gas containing mostly nitrogen, CO₂ and H₂S as needed. Although the gas did not contain any methane or gaseous hydrocarbon, it was a reasonable mimic of fuel gas or biogas for H₂S treatment purposes. This is because H₂S is degraded by lithoautotrophic organisms which have been shown not to be affected by the presence of organic carbon sources (Cox and Deshusses, 2002). Even so, the presence of heterotrophic methanotrophic bacteria would result in some competition for oxygen with the H₂S degraders. Since methane is only sparingly soluble in water (Sander, 1999) and not well degraded in biofilters or biotrickling filters (Nikiema et al., 2005), only a slight amount of extra oxygen would need to be supplied to compensate for oxygen consumption by heterotrophic organisms. During the experiments, a small metered stream of air (as required for the aerobic oxidation of H₂S) was added to the biogas or fuel gas mimic.

Mineral medium containing (g l⁻¹) KNO₃, 1; KH₂PO₄, 1; K₂HPO₄, 1; NaCl, 1; MgSO₄, 0.2; CaCl₂, 0.02; trace elements (Pfenning et al., 1981), 1 ml l⁻¹ for Reactor A and NH₄Cl, 1; KH₂PO₄, 1; K₂HPO₄, 1; MgSO₄ · 7H₂O, 0.5; CaCl₂, 0.25; trace elements (Pfenning et al., 1981), 1 ml l⁻¹ for Reactor B was also continuously fed to supply nutrients and wash out by-products. Inorganic carbon was supplied as CO₂ via the gas phase (Reactor A) or dissolved HCO₃ in the liquid phase (Reactor B).

Reactor A was packed with randomly dumped $2 \times 2 \times 2$ cm cubes of open pore polyurethane (PU) foam (EDT, Eckental, Germany). The PU foam packing was developed specifically for biotrickling filtration (Gabriel and Deshusses, 2003a; Philip and Deshusses, 2003; Kim and Deshusses, 2005). It has a high specific surface area (600 m² m⁻³) and a low density (35 kg m⁻³), a relatively

Table 1
Main characteristics of the laboratory prototypes bioreactors

	Reactor A	Reactor B
Packing material	PU foam	HD Q-PAC®
Specific surface area (m ² m ⁻³)	600	433
Bed height (m)	0.4	0.5
Reactor inner diameter (m)	0.04	0.071
Reactor volume (L)	0.5	2.15
Fresh liquid flow (L d ⁻¹)	2.4	2.9-5.7
Recirculation velocity (m h ⁻¹)	1-5	2.4
EBRT (s)	167	180
Inorganic carbon supply (g C d ⁻¹)	0.23-0.46	0.37 - 2.4
$C_{\rm in}$ (ppmv H ₂ S)	2500-12300	900-10000
Loading (g H_2S m ⁻³ h ⁻¹)	75–370	25–280

EBRT = empty bed gas residence time.

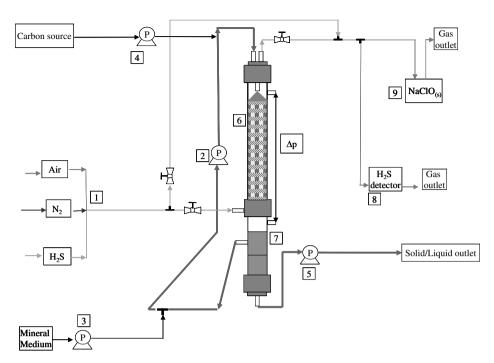


Fig. 1. Schematic of the experimental setup: 1. inlet gas; 2. recirculation pump; 3. mineral medium pump; 4. inorganic carbon pump (Reactor B only); 5. purge pump; 6. packed bed zone; 7. solid settling zone; 8. H₂S detector; 9. H₂S trap.

fine mesh (4–6 pores per cm), and a low compression strength (5–10 kPa). The PU foam bed had an initial porosity of about 0.97.

Reactor B was packed with polypropylene HD Q-PAC® (Lantec Products Inc., CA, USA) with a 4×4 mm grid opening. The HD Q-PAC® is a common wet scrubber structured packing with a slightly lower specific area $(430~\text{m}^2~\text{m}^{-3})$ than the foam and wider pores. A cylinder of structured packing was cut to tightly fit inside the biotrickling filter reactor. The initial bed porosity was 0.88. HD Q-PAC® was selected because of its structural strength and because its open structure may minimize the retention of sulfur expected from the proposed treatment.

Reactors were operated continuously for a period of 3 months (Reactor A) and 7 months (Reactor B) in order to test a range of operating conditions. Both reactors where inoculated with sulfur-oxidizing biomass in order to speed up the startup period. Reactor A was packed with PU foam cubes taken from a lab-scale biotrickling filter treating less than 100 ppmv H₂S, whereas Reactor B was packed with clean HD Q-PAC® and inoculated with an enriched sulfur-oxidizing culture. The enrichment was carried out in a 21 Biostat-B fermentor (Braun Biotech International, USA) with Na₂S as energy source, with an inoculum obtained from the liquid phase of a full-scale biogas desulfurization column, treating about 2000 ppmv H₂S at pH 1.6. Throughout the enrichment step, which was carried out over a 2-month period, pH was progressively increased to a value of 6 in order to acclimate the enriched culture to the desired operation pH.

Reactor A was monitored manually on a daily basis. Gas phase H_2S concentrations (inlet and outlet) were mea-

sured using a portable detector (Jerome 631X series, Arizona Instruments, USA) after dilution of grab samples. pH and sulfate were measured in the liquid purge using a pH electrode and a standard turbidimetric method (APHA, 1995), respectively.

Experimental Reactor B was equipped with automated monitoring of pH and oxidation–reduction potential (ORP) (PH 28, Crison Instruments, Spain), on-line monitoring of hydrogen sulfide inlet and outlet concentrations (H₂S L sensor, Sixth Sense, UK) and liquid phase dissolved oxygen (DO) (oxi340i, WTW, Germany). The data acquisition system also allowed for regulation and calculation of the inlet gas composition by adjusting the set-points of digital mass flow controllers (Bronkhorst, The Netherlands).

Sulfate, thiosulfate and sulfite concentrations in Reactor B were measured on a daily basis using an ICS-1000 Ion Chromatography system with an IonPac AS9-HC column (Dionex Corporation). Dissolved sulfur species ($H_2S/HS^-/S^2-$) concentrations were measured by flow injection analysis (Delgado et al., 2006) and elemental sulfur production was calculated by subtraction as previously reported (Janssen et al., 1997). Inorganic carbon concentration measurements in the liquid purge were carried out using a TOC 1020 analyzer (IO Analytical).

3. Results and discussion

3.1. Startup

During the startup phase, inlet H_2S concentration in Reactor A varied significantly (Fig. 2a) due to problems with the inlet gas generation system. The average concen-

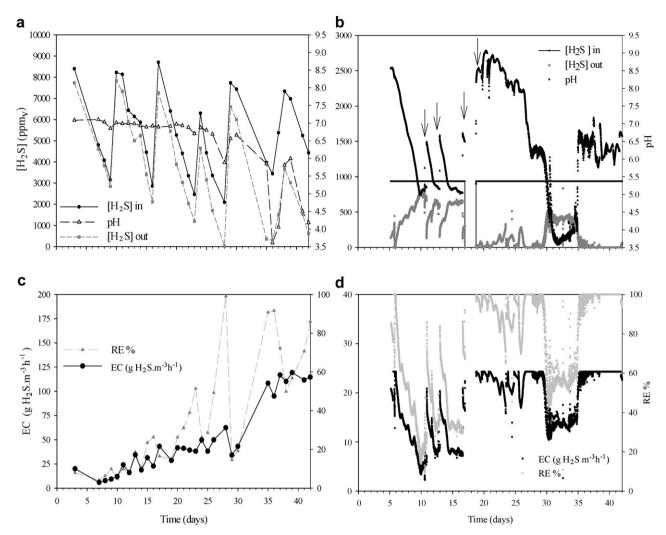


Fig. 2. Inlet and outlet H₂S concentrations and pH profiles during startup in (a) Reactor A and (b) Reactor B (the arrows show medium renewal). H₂S EC and RE during startup in (c) Reactor A and (d) Reactor B.

tration was 5000 ± 2000 ppmv H_2S corresponding to a loading of 150 ± 60 g H_2S m $^{-3}$ h $^{-1}$, whereas in Reactor B, the H_2S inlet concentration was initially kept constant at 930 ppmv H_2S , i.e. a loading of 26 g H_2S m $^{-3}$ h $^{-1}$. Initially, before an effective sulfide degrading biofilm is established, H_2S removal can be due to physical absorption into the trickling liquid. Hence, using H_2S outlet concentration alone to assess treatment performance is not adequate. Both the evolution of pH and the production of sulfur or sulfate should be considered.

Although a slow pH drop was observed in Reactor A from the very beginning, it was not until day 28 that significant acidification was observed (Fig. 2a). At this stage, pH control to a value between 6 and 7 was implemented by manually adjusting the mineral medium flow rate, as previously done in full-scale biotrickling filters treating low concentrations of H₂S (Gabriel and Deshusses, 2003a). However, as it can be seen in Fig. 2a, the rapid performance increase after day 30 made it difficult to manually keep the pH within the desired range. Thus, some pH fluctuations were observed between days 30 and 42, which

revealed that short term exposures to pH values between 3.5 and 5.5 did not significantly affect H_2S removal. The elimination capacity remained stable at values between 100 and 120 g H_2S m⁻³ h⁻¹ (Fig. 2c).

For Reactor B (Fig. 2b and d), the liquid phase was only renewed every 2-3 d during the startup phase after allowing suspended solids to settle in the sump of the biotrickling filter, which minimized washout of biomass. Before day 20, liquid phase acidification was probably due to absorption and dissociation of H₂S (Eq. (1)). As shown by arrows in Fig. 2b, each replenishment of mineral medium corresponded to pH and RE increase until about day 20 (Fig. 2d). After day 24, mineral medium was continuously supplied to the biotrickling filter and sulfate analyses revealed that the subsequent pH drops were not due to H₂S absorption, but rather to the biodegradation of H₂S and the associated production of sulfuric acid (Eq. (3)). pH control was carried out manually thereafter by adjusting the mineral medium flow rate. Between day 30 and 35, the pH was allowed to decrease to about 3.5, which resulted in a significant drop in the removal of H₂S. The

reasons for the different pH sensitivity between Reactor A and Reactor B were not fully elucidated. One possible reason is that Reactor B may have become carbon limited due to stripping of dissolved HCO_3^- as CO_2 gas at low pH. Another likely explanation may be that the progressive and controlled pH adaptation during the enrichment phase may have led to an irreversible change in the culture characteristics, hindering its capacity to degrade H_2S at low pH.

The long startup period of Reactor A compared to other reports on H₂S biotrickling filtration (Gabriel and Deshusses, 2003b; Duan et al., 2005) was a surprise since packing material with a fully developed sulfur-oxidizing biofilm was used. It is possible that the culture was not adapted to operation at high concentrations of H₂S and that additional biofilm growth was required in order to obtain a sufficiently high cell density to handle the high H₂S load.

Reactor B was started with a clean packing and the long startup time is clearly linked to the time required for the sulfur-oxidizing bacteria to colonize the packing, grow and form a dense biofilm. Therefore, if a fast startup time is desired, not only is a packing material with an established grown biofilm needed, but the biofilm should also be adapted to the specific conditions and have the required high cell density.

3.2. Long-term performance

Reactor A was operated for 95 d at concentrations ranging from 2500 and 12300 ppmv corresponding to loadings ranging from 75 to 370 g $\rm H_2S~m^{-3}~h^{-1}$ whereas Reactor B was operated for 205 d at six different inlet $\rm H_2S$ concentrations between 900 and 10000 ppmv corresponding to loadings between 25 and 280 g $\rm H_2S~m^{-3}~h^{-1}$. Results are shown in Fig. 3a and b. The highest ECs observed were 280 and 250 g $\rm H_2S~m^{-3}~h^{-1}$ for Reactors A and B, respectively. Such ECs are higher than many other previously reported $\rm H_2S$ removal rates, with the highest ones usually in the range of 110–140 g $\rm H_2S~m^{-3}~h^{-1}$ (see e.g. Yang and Allen,

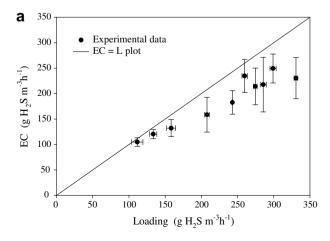
1994; Robertson and Kuenen, 1999; Gabriel and Deshusses, 2003b; Bailón, 2005; Duan et al., 2006) however the conditions (H₂S concentrations and nature of the gas treated) are not directly comparable. Both the high specific surface area of the packing materials used in this study, the high H₂S inlet concentrations and the controlled operating conditions (stable oxygen, nutrients and inorganic carbon supply) are probably responsible for such a high performance.

Monitoring of ionic sulfur species $(SO_4^{2-}, SO_3^{2-}, S_2O_3^{2-})$ and dissolved sulfide species (H₂S, HS⁻, S²⁻) in the liquid phase of Reactor B allowed to follow the fate of sulfur in the system. Although elemental sulfur was not directly measured, subsequent observation and analysis of the solid deposits by scanning electron microscopy with an attached analytical energy dispersive X-ray spectroscopy confirmed that they were mostly elemental sulfur with traces of Zn, Ca and Na. The predominant species detected in the liquid purge were sulfate and elemental sulfur (S⁰). These amounted for 98% of the H₂S removed, its distribution depending on the O₂/H₂S supplied ratio (Table 2), while less than 2% of the H₂S was removed as H₂S/HS⁻/S²⁻. This is consistent with Buisman et al. (1989) observations during the removal of dissolved sulfide in a continuously stirred tank bioreactor.

However, the SO_4^{2-}/S^0 produced ratio varied considerably depending on the O_2/H_2S supplied ratio. Since the amount of O_2 supplied to Reactor B was constant, the O_2/H_2S supplied decreased as the inlet H_2S concentration

Table 2 Sulfur and sulfate production in Reactor B as a function of the H_2S supplied

H ₂ S _{in} (ppmv)	Load (g H ₂ S m ⁻³ h ⁻¹)	O ₂ / H ₂ S _{supplied} (v/v)	S-SO ₄ ²⁻ /S- H ₂ S _{removed} (%)	S-S ⁰ /S- H ₂ S _{removed} (%)
3000	74	5.3	60–70	28-38
6000	155	2.6	20-30	68-78
10000	259	1.6	3–4	94–95



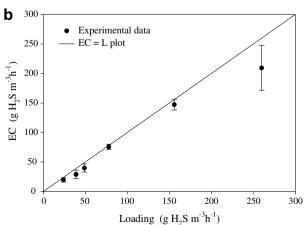


Fig. 3. Steady-state elimination capacity vs. loading in (a) Reactor A and (b) Reactor B.

was increased. As shown in Table 2, this resulted in a decrease of the SO_4^{2-}/S^0 produced ratio, with almost no sulfate production when the H₂S inlet concentration reached 10000 ppmv. Thus, the greater the oxygen limitation in the bioreactor, the more sulfur and the less sulfate were formed, as reported earlier by Janssen et al. (1995) for the treatment of dissolved sulfide in a fed-batch reactor. Thus, controlling the inlet oxygen content of the gas treated allowed tuning of the nature of the end-product. From a process design perspective, elemental sulfur may be preferred over sulfate, because sulfur formation does not lead to acidification of the trickling liquid. Further, sulfur can be a valuable raw material (Janssen et al., 1997). However, while sulfur is relatively easy to remove from liquid streams, excess sulfur production can lead to clogging of the packed bed if an effective bed washing procedure is not implemented. Here, pressure drop remained below 1-2 cm of water column during most of the experiment, in spite of the significant sulfur accumulation in the packing. This was possible because of the long gas residence time and open structure of the packing. However, differences were observed with respect to sulfur accumulation in the two bioreactors. Packing A was almost completely clogged with elemental sulfur after 3 months of operation (Fig. 4a and b) probably because its fine mesh and irregular structure hindered solid flushing. This resulted in pressure drop greater than 10 cm of water column and ultimately caused reactor shut down. Reactor B showed fewer sulfur accumulation, which occurred mainly at the bottom of the reactor, i.e. where the gas inlet is located. This is the location where the highest sulfide removal rate takes place and where the elemental sulfur washed from the upper reactor segment accumulates (Fig. 4c, d and e).

Both reactors investigated in this work showed similar maximum ECs even though their packings were markedly different both in structure and interfacial area. Examination of the packing of Reactor A after sulfur accumulation (Fig. 4b) revealed that the effective area was reduced by the accumulation of sulfur. This was not the case with packing B. Obviously, succeeding in high performance treatment of ultra-high H₂S concentrations requires a packing material that strikes a good compromise between a high interfacial area and an open mesh structure.

These observations suggest that a few key parameters must be taken into account when dealing with high loads of H₂S. First, the packing material and structure must facilitate solids flushing and have a firm, open and regular structure to avoid compaction. Even so, careful design of the make-up water sprinkling system and implementation of adequate solid flushing strategies are needed when dealing with solids formation. Second, an accurate control of the oxygen supply must be implemented in order to guarantee stable operation. Insufficient oxygen can lead to possible treatment limitation and increased clogging problems,

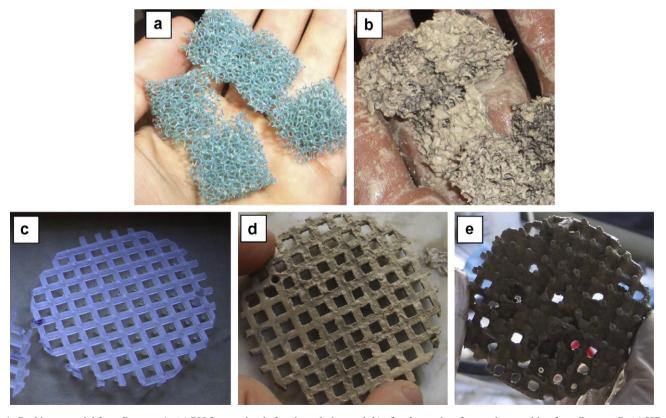


Fig. 4. Packing material from Reactor A: (a) PU foam cubes before inoculation and (b) after 3 months of operation; packing from Reactor B: (c) HD Q-PAC before inoculation, (d) after 160 d of operation, top of the reactor, (e) after 160 d of operation, bottom of the reactor. The foam cubes are $2 \times 2 \times 2$ cm, while the HD Q-PAC is 7.1 cm in diameter.

while an excess of oxygen can lead to undesired residual oxygen in the gas outlet and low pH. The amount of sulfur produced in both Reactors A and B indicated that both systems were operated with some degree of oxygen limitation as is necessary for elemental sulfur formation. This was confirmed by DO and ORP measurements (Reactor B only). DO of the trickling liquid of Reactor B was systematically below the probe's detection limit while ORP values remained between -250 and -400 mV (results not shown) which is within the range of ORP usually reported for dissolved sulfide oxidation to elemental sulfur (Janssen et al., 1998).

Controlling the pH is another key factor in such systems. Biological reactors dealing with low concentrations of H₂S usually do not need a sophisticated pH control (Koe and Yang, 2000; Gabriel and Deshusses, 2003a). Variations of H₂S inlet concentration will result in small proton production variations easily buffered by a constant make-up water flowrate. However, systems treating high H₂S concentrations may be exposed to wide inlet concentration variations, resulting in large proton production changes. This effect can be amplified if the oxygen supply is not adequately controlled and may lead to important pH swings that may cause system failure. Thus a tight pH control is strongly recommended.

Another parameter that must be considered is the availability of a carbon source for the autotrophic sulfide oxidizing culture. Inorganic carbon limitation should not be an issue for biogas treatment as biogas usually contains 30–50% CO₂. However, an external inorganic carbon source addition may be required when treating gases with little or no carbon dioxide, such as fuel gas or shale gas. Although carbon limitation was not investigated systematically, a low removal (20–30%) of H₂S was occasionally observed during operation of Reactor B (results not

shown). This was attributed to inorganic carbon limitation, as increasing the feeding rate of HCO_3^- resulted in a rapid recovery of the H_2S removal. The inorganic carbon requirement of the culture could not be determined since it was well below the detection and accuracy limits of the analytical methods. However, the threshold for carbon limitation occurred at C/H_2S (supplied) ratios lower than about 0.3–0.4 g C g S^{-1} .

3.3. System response to different perturbations

During the operation, both reactors were subjected to different perturbations, but little or no adverse effect on performance could be observed. Fig. 5 shows the response of Reactor B after an increase of the H2S inlet concentration from 1500 to 6000 ppmv (i.e. loading increase from 42 to 167 g H_2 S m⁻³ h⁻¹) in less than 24 h. This experiment was conducted before ever exposing the reactor to higher inlet concentrations. A drop of RE from 100% to values around 90% after 5 d operating at high inlet concentration was observed. It is relevant to notice that outlet H₂S concentration was continuously kept below 500 ppmv, which is the typical H₂S concentration that combustion engines may withstand without developing corrosion problems. Further, the reactor was able to rapidly recover its previous performance after two days of complete shutdown (Fig. 5 on day 148). After normal system operation was resumed, H₂S removal was initially close to 50% but it recovered its original value of over 90% in less than 48 h. Both experiments illustrate the capacity of the system to overcome operational setbacks typical of industrial settings.

Additionally, some minor RE and outlet H_2S concentration fluctuations were observed for Reactor B (Figs. 2b and 5). These were attributed to a few extreme temperature changes (15–30 °C) in the laboratory which was not

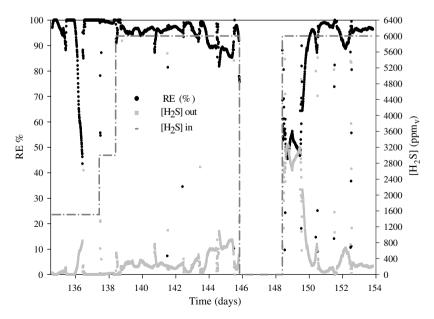


Fig. 5. System response to an inlet concentration peak (137-146 days) and to a two days shutdown (146-148 days).

thermostated. Thus, although biological systems have sometimes been labeled as being sensitive to variations and not suitable for the treatment of off-gasses with widely oscillating loadings, data shown in this work proves otherwise.

Overall, the results indicate that the proposed process can be an interesting alternative for the treatment of off-gases containing high concentrations of H_2S . The biotric-kling filters were able to effectively treat inlet H_2S concentrations up to 12000 ppmv, and reach elimination capacities of 250–280 g H_2S m⁻³ h⁻¹. The biotrickling filters proved to be very robust with sustained H_2S treatment with effluent concentrations usually below the typical limit of 500 ppmv for combustion engines, even under fluctuating H_2S inlet concentrations or fluctuating pH. Further research should address the influence of pH and optimize the packing and operating conditions to avoid reactor clogging with sulfur.

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References

- APHA, 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. American Public Health Association, New York.
- Bailón, L., 2005. Development of a biotrickling filter for the removal of H₂S from biogas. In: Proceedings of the 2005 International Congress Biotechniques for Air Pollution Control, La Coruña, Spain, pp. 143– 148.
- Buisman, C., Post, P., Ijspeert, S., Geraats, G., Lettinga, G., 1989. Biotechnological process for sulphide removal with sulphur reclamation. Acta Biotechnol. 9, 255–267.
- Cox, H.H.J., Deshusses, M.A., 2002. Co-treatment of H₂S and toluene in a biotrickling filter. Chem. Eng. J. 87, 101–110.
- Delgado, L., Masana, M., Baeza, M., Gabriel, D., Alonso, J., 2006. New approach for on-line simultaneous monitoring of hydrogen sulphide and sulphide in gas-phase bioreactors for biogas treatment. In: Proceedings of the Flow Analysis 10th International Conference, Porto, Portugal, p. 148.
- Deshusses, M.A., 1997. Biological waste air treatment in biofilters. Curr. Opin. Biotechnol. 8, 335–339.

- Devinny, J.S., Deshusses, M.A., Webster, T.S., 1999. Biofiltration for Air Pollution Control. CRC-Lewis Publishers, Boca Raton, Florida.
- Duan, H., Koe, L.C.C., Yan, R., 2005. Treatment of H₂S using a horizontal biotrickling filter based on biological activated carbon: reactor start-up and performance evaluation. Appl. Microbiol. Biotechnol. 67, 143–149.
- Duan, H., Koe, L.C.C., Yan, R., Chen, X., 2006. Biological treatment of H₂S using pellet activated carbon as a carrier of microorganisms in a biofilter. Water Res. 40, 2629–2636.
- Gabriel, D., Deshusses, M.A., 2003a. Performance of a full-scale biotrickling filter treating H₂S at a gas contact time of 1.6 to 2.2 seconds. Environ. Prog. 22, 111–118.
- Gabriel, D., Deshusses, M.A., 2003b. Retrofitting existing chemical scrubbers to biotrickling filters for H₂S emission control. Proc. Natl. Acad. Sci. USA 100 (11), 6308–6312.
- Janssen, A.J.H., Sleyster, R., van der Kaa, C., Jochemsen, A., Bontsema, J., Lettinga, G., 1995. Biological sulfide oxidation in a fed-batch reactor. Biotechnol. Bioeng. 47, 327–333.
- Janssen, A.J.H., Ma, S.C., Lens, P., Lettinga, G., 1997. Performance of a sulphide-oxidizing expanded-bed reactor supplied with dissolved oxygen. Biotechnol. Bioeng. 53, 32–40.
- Janssen, A.J.H., Meijer, S., Bontsema, J., Lettinga, G., 1998. Application of the redox potential for controlling a sulfide oxidizing bioreactor. Biotechnol. Bioeng. 60, 147–155.
- Kennes, C., Veiga, M.C., 2001. Bioreactors for Waste Gas Treatment. Kluwer Academic Publishers., Dordrecht, The Netherlands.
- Kim, S., Deshusses, M.A., 2005. Understanding the limits of H₂S degrading biotrickling filters using a differential biotrickling filter. Chem. Eng. J. 113, 119–126.
- Koe, L.C.C., Yang, F., 2000. A bioscrubber for hydrogen sulphide removal. Water Sci. Technol. 41 (6), 141–145.
- Kuenen, J.G., 1975. Colourless sulphur bacteria and their role in the sulphur cycle. Plant Soil 43, 49-76.
- Nikiema, J., Bibeau, L., Lavoie, J., Brzezinski, R., Vigneux, J., Heitz, M., 2005. Biofiltration of methane: an experimental study. Chem. Eng. J. 113, 111–117.
- Pfenning, N., Widdel, F., Trüper, H.G., 1981. The dissimilatory sulfatereducing bacteria. In: Starr, M.P., Stolp, H., Trüper, H.G., Balows, A., Schlegel, H.G. (Eds.), The Prokaryotes, vol. 1. Springer, Verlag, NY, USA, pp. 926–940.
- Philip, L., Deshusses, M.A., 2003. Sulfur dioxide treatment from flue gases using a biotrickling filter-bioreactor system. Environ. Sci. Technol. 37, 1978–1982.
- Robertson, L.A., Kuenen, J.G., 1999. The colorless sulfur bacteria. In: Dworkin, M. (Ed.), The Prokaryotes: An Evolving Electronic Resource for the Microbiological Community. Springer, Verlag, NY, USA http://www.springer.com/.
- Robertson, L.A., Kuenen, J.G., 2002. The genus *Thiobacillus*. In: Dworkin, M. (Ed.), The Prokaryotes: An Evolving Electronic Resource for the Microbiological Community. Springer, Verlag, NY, USA http://www.springer.com/.
- Sander, R., 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (Version 3). http://www.mpch-mainz.mpg.de/~sander/res/henry.html>.
- Woodcock, K.E., Gottlieb, M., 2004. Natural gas. In: Kirk-Othmer Encyclopedia of Chemical Technology, vol. 12. Wiley, pp. 377–386.
- Yang, Y., Allen, E.R., 1994. Biofiltration control of hydrogen sulfide.1. Design and operational parameters. J. Air Waste Manage. 44, 863–868.