Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 71 (2008) 10–17
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Biological sweetening of energy gases mimics in biotrickling filters

Marc Fortuny [a,c], Juan A. Baeza [a], Xavier Gamisans [b], Carles Casas [a], Javier Lafuente [a], Marc A. Deshusses [c,*], David Gabriel [a,1]

[a] Department of Chemical Engineering, Universitat Autònoma de Barcelona, Edifici Q, Campus de Bellaterra, 08193 Bellaterra, Barcelona, Spain
[b] Department of Mining Engineering and Natural Resources, Universitat Politècnica de Catalunya, Manresa, Spain
[c] Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92520, United States

Received 25 July 2007; received in revised form 27 October 2007; accepted 29 October 2007
Available online 21 December 2007

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 12 000 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 H_2S 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

* Corresponding authors. Tel.: +1 951 827 2477; fax: +1 951 827 5696.
E-mail addresses: mdeshuss@engr.ucr.edu (M.A. Deshusses), david.gabriel@uab.cat (D. Gabriel).
[1] Tel.: +34 93 581 1587; fax: +34 93 581 2013.

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.10.072

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

$$H_2S \leftrightarrow H^+ + HS^- \text{(dissociation)} \quad (1)$$

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

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

Biofilters, bioscrubbers and biotrickling filters have been proven to be a suitable, environmentally friendly and cost-effective alternative for waste gas treatment, especially for the treatment of low concentrations of H_2S (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 H_2S (>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 Biopuric® process (Biothane, USA) are the only ones specifically developed for the removal of high concentrations of H_2S 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 H_2S 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 H_2S 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 H_2S concentrations in gases that are initially oxygen-free. Operation at close-to-neutral pH was chosen in order to improve the H_2S absorption capacity of the liquid phase although many of the H_2S degrading organisms, like the genus *Thiobacillus*, have acidic optimum growing pH (Robertson and Kuenen, 1999, 2002). Also, absorption and oxidation of H_2S 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, CO_2 and H_2S as needed. Although the gas did not contain any methane or gaseous hydrocarbon, it was a reasonable mimic of fuel gas or biogas for H_2S treatment purposes. This is because H_2S 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 H_2S 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 H_2S) was added to the biogas or fuel gas mimic.

Mineral medium containing (g l^{-1}) KNO_3, 1; KH_2PO_4, 1; K_2HPO_4, 1; NaCl, 1; $MgSO_4$, 0.2; $CaCl_2$, 0.02; trace elements (Pfenning et al., 1981), 1 ml l^{-1} for Reactor A and NH_4Cl, 1; KH_2PO_4, 1; K_2HPO_4, 1; $MgSO_4 \cdot 7H_2O$, 0.5; $CaCl_2$, 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 CO_2 via the gas phase (Reactor A) or dissolved HCO_3^- 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 m^2 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_{in} (ppmv H_2S)	2500–12 300	900–10 000
Loading (g H_2S m^{-3} h^{-1})	75–370	25–280

EBRT = empty bed gas residence time.