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Biogas biodesulfurization in an anoxic biotrickling filter packed with open-pore polyurethane foam

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HIGHLIGHTS

- The use of different nitrate sources did not affect the RE.
- Programmed nitrate feeding is feasible for biogas at constant H_2S IL.
- A high EC_{CRIT} of 130 gS-H_2S m^{-3} h^{-1} can be achieved using OPUF.

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ABSTRACT

Biogas biodesulfurization by an anoxic biotrickling filter packed with open pore polyurethane foam at the laboratory scale (packed volume 2.4 L) has been studied. The biotrickling system was operated for 620 days with biogas supplied continuously and two nitrate feeding regimes were tested (manual and programmed). Biomass immobilization was carried out under the manual nitrate feeding regime and a study was then carried out on the effects on removal efficiency of the following parameters: nitrate source, H_2S inlet load, nitrate concentration, sulfate accumulation, temperature, pH and trickling liquid velocity. The effect of increased H_2S inlet load was studied under the programmed nitrate feeding regime. The results show that a removal efficiency of 99% can be obtained when working under the following conditions: inlet loads below 130 gS m^{-3} h^{-1}, a programmed nitrate feeding system, temperature of 30 °C, sulfate concentration below 33 g L^{-1}, a pH between 7.3 and 7.5, and a trickling liquid velocity higher than 4.6 m h^{-1}.

1. Introduction

The production and use of biogas have recently increased as this fuel represents a valuable renewable energy source. Biogas utilization produces an indirect reduction of greenhouse gas emissions through the replacement of fossil fuel [1]. However, the use of biogas is limited by the presence of hydrogen sulfide (H_2S) at high concentrations (0.1–2%). H_2S is a corrosive and toxic compound that has an adverse environmental effect due to the sulfur oxides generated during combustion.

The main approaches employed for gas desulfurization are physicochemical methods. However, physicochemical methods are characterized by high consumption of energy and/or chemicals, and these methods can lead to other pollution problems such as the generation of large amounts of carbon dioxide (CO_2), nitrogen oxides or exhausted adsorbents that require disposal [2].

One of the most widely used biological methods for the purification or treatment of gas streams is biofiltration. Biofiltration is a safer and cleaner technology. The development of biofiltration has been rapid in recent years because it is less expensive than other technologies, has good performance at the pilot scale and in industrial applications, and is feasible for the treatment of a wide variety of gaseous effluents [3,4]. A biotrickling filter (BTF) is a packed bed bioreactor with biomass immobilized. The gas flows through a fixed bed usually counter-currently to a mobile liquid phase. Synthetic carriers are usually used such plastic, ceramic, lava rocks, polyurethane foam, etc. First of all, the pollutant compound must be transfer from the gas to liquid phase and finally the degradation is carried out in the biofilm. Fresh medium is fed to provide nutrients and remove the oxidation products [2].

The biological removal of H_2S from biogas has been mainly studied under aerobic conditions [5–8], with very few studies carried out under anoxic conditions [9–14]. One advantage of anoxic BTFs over aerobic BTFs is that the biogas is not diluted with air and therefore the methane (CH_4) concentration is not reduced [6,13]. Furthermore, the electron acceptor mass transfer limitation is negligible because the nitrate solubility is very high [91.2 g (100 g)$^{-1}$

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at 25 °C] [15]. Thus, for the production of pipeline grade methane anoxic biofiltration is a more feasible technology as a pretreatment for H_2S removal than the more commonly used aerobic BTFs [14].

The aim of work described here was to study the anoxic biofiltration process for H_2S removal from biogas using a BTF packed with open-pore polyurethane foam (OPUF) to increase the elimination capacity (EC) and to acquire a deeper understanding of the influence of the operating variables.

2. Materials and methods

2.1. Experimental setup

The biofiltration system used in this study was previously described by Montebello et al. [13]. Experiments were carried out during 620 days (Table 1) with the biogas supplied continuously (68 ± 3%, v/v CH_4; 26 ± 2%, v/v CO_2). A BTF with a volume of 2.4 L (working volume bed) was packed with OPUF cubes (26 g, 600 $m^2\ m^{-3}$, cube size 8 cm^3) (Filter TM25450, Recticel, Spain) (Fig. 1). The volume of the liquid phase under recirculation was 2.25 L. The biogas was produced by two Upflow Anaerobic Sludge Bed reactors (UASB) of 200 L (biogas flow rate up to 1 L min^{-1}). In order to increase and set different H_2S concentrations, the biogas was passed through an H_2S generating column. A digital Multimeter 44 (CRISON, Spain) was used for pH control, which was achieved by the addition of NaOH (2 N). Temperature was controlled using a thermostatted bath (Lauda RM6, Germany) and an Allihn refrigerant (length 300 mm) (Fig. 1).

2.2. Inoculum and medium preparation

The inoculum was obtained from an experimental bioreactor (stirred tank reactor) installed at the 'Guadalete' Wastewater Treatment Plant (WWTP), located in Jerez de la Frontera (Cádiz), Spain. This experimental bioreactor (174 L of volume; 3 h of hydraulic retention time) was fed with the primary effluent [16].

Calcium nitrate [15 g of $Ca(NO_3)_2{\cdot}4H_2O$] was dissolved in the inoculum (6 L) and this was stored at 4 °C (inoculum solution). Three nitrate mineral media were used to test three types of nitrate source: $Ca(NO_3)_2{\cdot}4H_2O$ (NMCa medium), $NaNO_3$ (NMNa medium) and KNO_3 (NMK medium). The nitrate sources were diluted in modified mineral medium (M3). M3 was adapted from ATCC-1255 *Thiomicrospira denitrificans* medium. The M3 composition was (g L^{-1}): KH_2PO_4, 2; NH_4Cl, 1; $MgSO_4{\cdot}7H_2O$, 0.8; iron solution, 1 mL; trace element solution (SL-4), 2 mL. The iron solution was prepared by dissolving 0.2 g of $FeSO_4{\cdot}7H_2O$ in 100 mL of H_2SO_4 solution (0.1 N). The SL-4 composition was (g L^{-1}): EDTA, 0.5; $FeSO_4{\cdot}7H_2O$, 0.2; trace element solution (SL-6), 100 mL. The SL-6 composition was (g L^{-1}): $ZnSO_4{\cdot}7H_2O$, 0.1; $MnCl_2{\cdot}4H_2O$, 0.03; H_3BO_3, 0.3; $CoCl_2{\cdot}6H_2O$, 0.2; $CuCl_2{\cdot}2H_2O$, 0.01; $NiCl_2{\cdot}6H_2O$, 0.02; $Na_2MoO_4{\cdot}2H_2O$, 0.03. The pH values of the mineral media were adjusted to 7.0 with NaOH (2 N).

2.3. Biomass immobilization procedure

Biofilm formation was performed in situ in the BTF (day 1–35). The BTF was filled with 2.25 L of inoculum solution. Half (50%, v/v) of the recirculation medium was replaced with inoculum solution before the nitrate was exhausted ([$N{-}NO_3^-$] < 20 mg L^{-1}) to ensure the presence of bacteria and to improve the biofilm formation. On day 15, after three cycles, NMCa medium (1.125 L) was used as a fresh medium in the immobilization procedure (final nitrate concentration in the recirculation medium of 0.38 g $N{-}NO_3^-\ L^{-1}$).

2.4. Influence of the main operational variables

The inlet load (IL), elimination capacity (EC), removal efficiency (RE) and trickling liquid velocity were described with:

$$\mathrm{IL}(\mathrm{gS\ m^{-3}\ h^{-1}}) = C_0 \times \frac{Q}{V} \quad (1)$$

$$\mathrm{EC}(\mathrm{gS\ m^{-3}\ h^{-1}}) = (C_0 - C_e) \times \frac{Q}{V} \quad (2)$$

$$\mathrm{RE}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

$$\mathrm{TLV}(\mathrm{m\ h^{-1}}) = \frac{Q}{A} \quad (4)$$

where C_0 and C_e are the inlet and outlet concentration (g m^{-3}) of H_2S, respectively, Q is the biogas volumetric flow ($m^3\ h^{-1}$), V is the packed volume (m^3) and A the cross section area of the column (m^2).

The operational conditions are shown in Table 1. Two nitrate feeding regime methods were performed: manual (day 1–413) and programmed (day 414–620). In the manual method, before the nitrate was exhausted ([$NaNO_3^-$] < 20 mg $N{-}NO_3^-\ L^{-1}$), 50% (v/v) of the recirculation medium was replaced by fresh medium (NMCa, NMNa or NMK mediums). In the programmed method, NMNa medium was fed in by a peristaltic pump. The running time of the peristaltic pump was controlled by a logic module (Logo! 12/24RC, Siemens, Spain). The time was switched on for 1 s and the off time was fixed manually between 10 and 30 s for an IL up to 60 gS $m^{-3}\ h^{-1}$ (NMNa medium concentration of 5 g L^{-1} of $NaNO_3$) and between 20 and 50 s for IL higher than 60 gS $m^{-3}\ h^{-1}$ (NMNa medium concentration of 10 g L^{-1} of $NaNO_3$). The biomass immobilization was carried out under the manual nitrate feeding regime and the effects of the following variables on the H_2S RE were studied: nitrate source, H_2S IL, nitrate concentration, sulfate accumulation, temperature, pH and TLV. The effect of increased IL was studied under the programmed nitrate feeding regime (Table 1).

2.5. Analytical methods

The quantity of immobilized biomass was measured according to the counting method described by Gómez et al. [17]. The concentrations of sulfate, nitrate and nitrite were determined in the liquid medium by spectrophotometric methods [18]. The sulfide concentration was determined using the 1-88 NANOCOLOR® kit (Macharey-Nagel, Germany).

A specific digital sensor (GasBadge® Pro, Industrial Scientific, UK) was used to measure the H_2S concentration from 0 to 500 ppmv (accuracy 0.1 ppmv). A GA2000Plus gas analyzer (Fonotest Instruments S.L., Spain) equipped with an external electrochemical H_2S gas sensor was used to measure the following: H_2S concentration from 500 to 5000 ppmv (accuracy 10%) and CH_4 and CO_2 concentration by infrared absorption (accuracy 0.5%). H_2S concentrations greater than 5000 ppmv were measured by a gas chromatograph with TCD (450-GC, Bruker, Spain).

A Quanta FIE 200 electron microscope (Philips) coupled to qualitative Energy Disperse X-ray analyzer (EDX) was used to obtain a scanning electron microscopy image (SEM) and elemental analysis of the biofilm was performed at the end of the experiment (day 619). The samples were fixed with glutaraldehyde and dehydrated by immersion in increasing concentrations of acetone solution (50–100%). The samples were dried with CO_2 to a critical point to remove the acetone and were metallized with gold (at 15 mA, 120 s, and a distance of 35 mm).