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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).

Table 1
Variables studied and operational conditions.

Nitrate feeding regime	Variable studied	t (d)	pH	T^a (°C)	TLV ($m\,h^{-1}$)	IL ($gS\,m^{-3}\,h^{-1}$)	SO_4^{2-} ($g\,L^{-1}$)	EBTR (min)
Manual	Immobilization	1–35	6.8–7.0	30	7	6–38	0.2–10	4.3 ± 1.5
	$Ca(NO_3)_2\,4H_2O$	35–43	6.8–7.0	30	7	11–35	6–12	2.4 ± 0.2
	KNO_3	44–60	6.8–7.0	30	7	8–74	5–14	2.9 ± 0.1
	$NaNO_3$	61–96	6.8–7.0	30	7	22–100	10–33	3.7 ± 0.4
	IL/SO_4^{2-}	1–131	6.8–7.0	30	7	6–186	0.2–40	3.7 ± 1.1
	T[a]	332–350	6.8–7.0	15–36	7	54 ± 3.5	17 ± 4	4.3 ± 0.8
	pH	351–383	6.1–7.5	30	7	54 ± 3.9	1.5–18	4.0 ± 0.7
	TLV	384–398	7.3–7.5	30	2.3–21	93–201	2.4 ± 0.3	2.4 ± 0.2
Programmed	IL	414–620	7.3–7.5	30	7–9	11–201	0.3–9.8	2.4–6.0

The biofilter remained in optimal conditions with loads less than 60 $gS\,m^{-3}\,h^{-1}$ on the days not shown.

3. Results and discussion

3.1. Study under the manual nitrate feeding regime

3.1.1. Biomass immobilization

The first 35 days of operation were considered to be the stage for the development and adaptation of the biofilm. The biomass concentration obtained was $2.79 \times 10^{10} \pm 0.28$ cells $(g\,dry\,carrier)^{-1}$. The image obtained by SEM (Fig. 2a) shows a predominance of rod-shaped bacteria in the biofilm. The accumulation of elemental sulfur in the carrier was confirmed by a qualitative EDX analysis (Fig. 2b), where it was found that elemental sulfur was the main component in the sample. Elemental sulfur has been used under anoxic conditions as an electron donor and as a carrier to grow denitrifying culture [19]. Thus, the elemental sulfur formation on the carrier, obtained by incomplete oxidation of H_2S, can be considered as an interesting strategy for the immobilization of biomass during biofilter start-up.

OPUF has been used for the removal of H_2S from air [20] and for the removal of VOCs [21]. OPUF has also been employed in aerobic BTFs for H_2S removal at high concentrations (10 000 ppmv) from synthetic biogas [22]. Fernández et al. [14] worked with an anoxic BTF inoculated with biomass immobilized in OPUF units from the BTF of this study and it was reached a similar biomass concentration of $1.23 \times 10^{10} \pm 0.21$ cells $(g\,dry\,carrier)^{-1}$ using polypropylene pall rings as packing material.

3.1.2. Effect of different nitrate sources

The bioreactor containing the inoculum was fed with Nutriox™ (solution of calcium nitrate concentrate) [16]. Therefore, in the immobilization stage, the BTF was fed with calcium nitrate as the nitrate source (NMCa medium). The addition of calcium nitrate might produce an accumulation of precipitate in the support due to the low solubility of calcium salts that can be formed by reaction with other components present in the recirculation medium, e.g., $CaCO_3$ and $Ca_3(PO_4)_2$ from CO_3^{2-} and PO_4^{3-}, respectively. Precipitate accumulation could cause clogging problems after long operating times. To avoid this problem, we tested other nitrate sources, specifically KNO_3 (NMK medium, day 44–60) and $NaNO_3$ (NMNa medium, day 61–96). The use of different nitrate sources did not affect the RE (Fig. 3a). In all cases, the RE achieved was between 98.0 and 99.9% while nitrate was not exhausted. When the nitrate concentration decreased to values below 20 mg $N\text{–}NO_3^-\,L^{-1}$ the RE dropped (Fig. 3a). The lowest RE values, in the first 70 days, were 63% (day 4) and 83% (days 34 and 66). However, the system showed a rapid RE recovery when nitrate was added to the recirculation medium. Soreanu et al. [10] found that the minimum required nitrate concentration to maintain the maximum RE (99%), with an IL of 4.9 $gS\,m^{-3}\,h^{-1}$, was 20 mg $N\text{–}NO_3^-\,L^{-1}$. Fernández et al. [14] also found that the lower limit value for nitrate concentration was 20 mg $N\text{–}NO_3^-\,L^{-1}$ before replacing the medium under a manual dosage supply method.

Although the different nitrate sources did not affect the H_2S RE, the use of $NaNO_3$ is recommended because $NaNO_3$ does not suffer from the drawbacks associated with $Ca(NO_3)_2$ and provides a greater mass of nitrogen per gram of compound compared to KNO_3. $NaNO_3$ also has a lower cost than KNO_3.

In the first 104 days, the nitrite concentration in the recirculation medium was less than 300 mg $N\text{–}NO_2^-\,L^{-1}$ and from day 106 to 108 it was in the range 797–453 mg $N\text{–}NO_2^-\,L^{-1}$ without showing an inhibitory effect on the process. Nitrate is reduced faster than nitrite and nitrite therefore accumulates as an intermediate in the reduction to elemental nitrogen. This phenomenon is very common in denitrification processes and it has been recognized

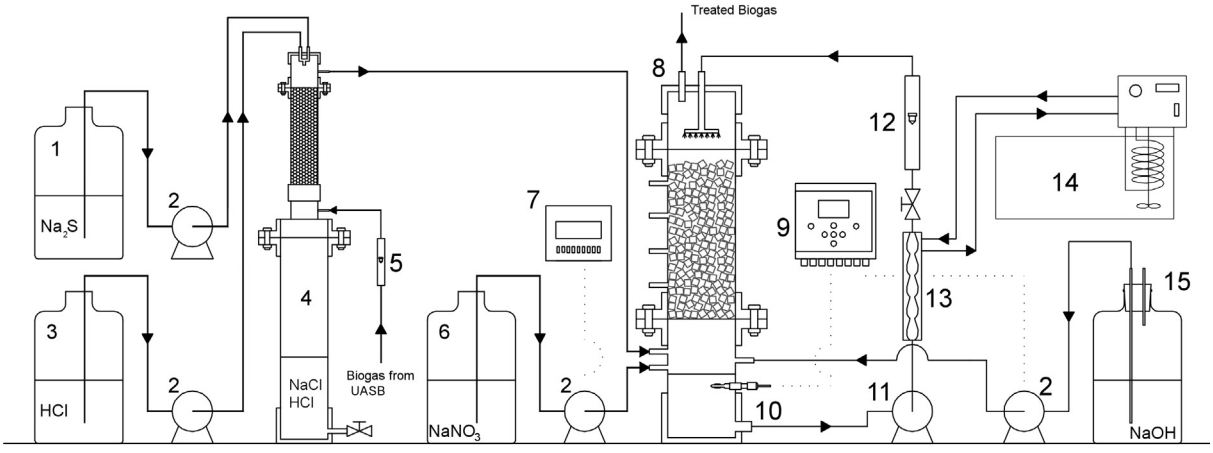

Fig. 1. Experimental biofiltration system. 1. Na_2S container, 2. peristaltic pumps, 3. HCl container, 4. H_2S generation tower, 5. gas rotameter, 6. nitrate stock solution, 7. logic module, 8. biotrickling filter, 9. pH controller, 10. pH electrode, 11. centrifugal pump, 12. liquid rotamter, 13. Ahllin refrigerant, 14. thermostatic bath, 15. NaOH container.

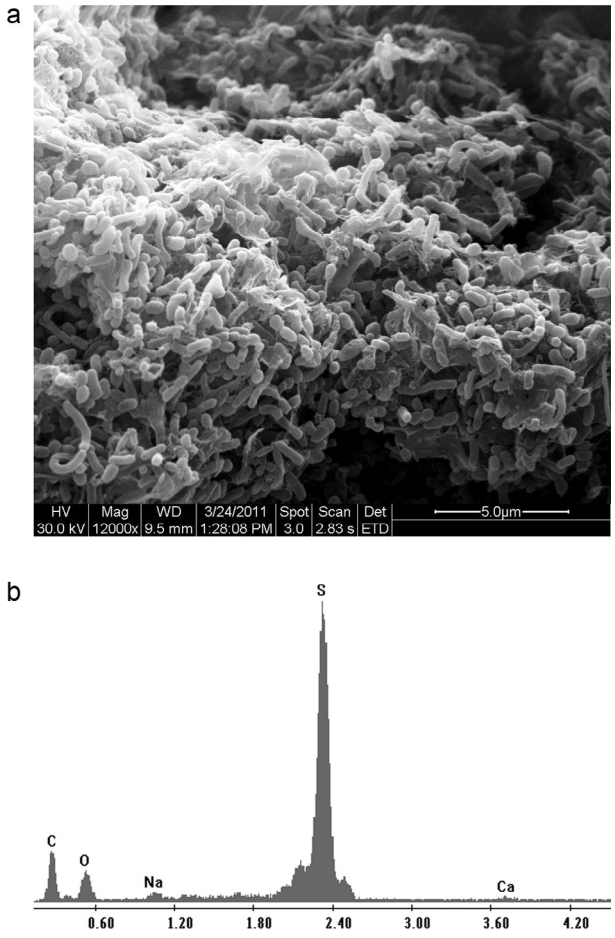

Fig. 2. (a) Scanning electron microscopy image. (b) EDX analysis.

as one of the causes of inhibition. Krishnakumar and Manilal [23] observed that above 100 mg $N–NO_2^-$ L^{-1}, the sulfide oxidation rate declined and at 500 mg $N–NO_2^-$ L^{-1} it was completely arrested. However, Soreanu et al. [9,10] worked with nitrite concentrations up to 300 mg $N–NO_2^-$ L^{-1} without observing inhibition of an anoxic biofiltration process. Similar behavior was found in this study. The lack of inhibition by nitrite is a great advantage because nitrite could be used instead of nitrate as an electron acceptor source. Nitrite production from ammonia requires a lower oxygen supply and thus lower energy consumption [24], although further study is required to confirm this behavior.

The establishment of high RE values from the first moments after the inoculation is an advantage for any eventual industrial application because the biological activity in the biofilter starts up immediately after inoculation. Nevertheless the IL must be increased slowly (Fig. 3b). It was concluded that the nitrate-reducing and sulfide-oxidizing bacteria (NR-SOB) were immobilized on the carrier very quickly because the RE remained constant after replacement of the recirculation medium. The biomass population was characterized by PCR-DGGE and the banding patterns showed several bands (data not published). So, it is very likely the existence of several NR-SOB species.

3.1.3. *Effect of IL*

The mean nitrate reduction rates were 0.154 ± 0.044 (day 6–62), 0.329 ± 0.091 (day 62–82), 0.401 ± 0.004 (day 82–108) and 1.02 ± 0.2 g $N–NO_3^-$ L^{-1} d^{-1} (day 122–129) for initial nitrate concentrations of 0.43 ± 0.08, 1.11 ± 0.14, 2.31 ± 0.07 and 1.7 ± 0.5 g $N–NO_3^-$ L^{-1}, respectively. Treatment of high nitrate concentrations in wastewater has led to high denitrification rates: 5.64 g $N–NO_3^-$ L^{-1} d^{-1} for complete denitrification using thiosulfate [25], 3.9 g $N–NO_3^-$ L^{-1} d^{-1} (denitrification 84%) using elemental sulfur [26] and 1.45 g $N–NO_3^-$ L^{-1} d^{-1} (denitrification > 99%) using sulfide [27]. Soreanu et al. [10] used an anoxic BTF and obtained lower values (0.02 g $N–NO_3^-$ L^{-1} d^{-1}) with a mass flow rate of 1.5g H_2S d^{-1} (IL of 4.9 gS m^{-3} h^{-1}). These differences could be attributed to the lower nitrate concentration and H_2S IL.

It is known that the $N–NO_3^-/S–H_2S$ ratio affects the $S–SO_4^{-2}/S^0$ ratio obtained [13,28]. Nitrite was not accumulated, so partial denitrification was not considered. Complete denitrification kinetic can by describe by the following equations [10]:

$$5H_2S + 2NO_3^- \rightarrow 5S^0 + N_2 + 4H_2 + 2OH^- \text{ (complete } H_2S \text{ oxidation)} \quad (5)$$

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{-2} + 4N_2 + 4H_2O + 2H^+ \text{ (partial } H_2S \text{ oxidation)} \quad (6)$$

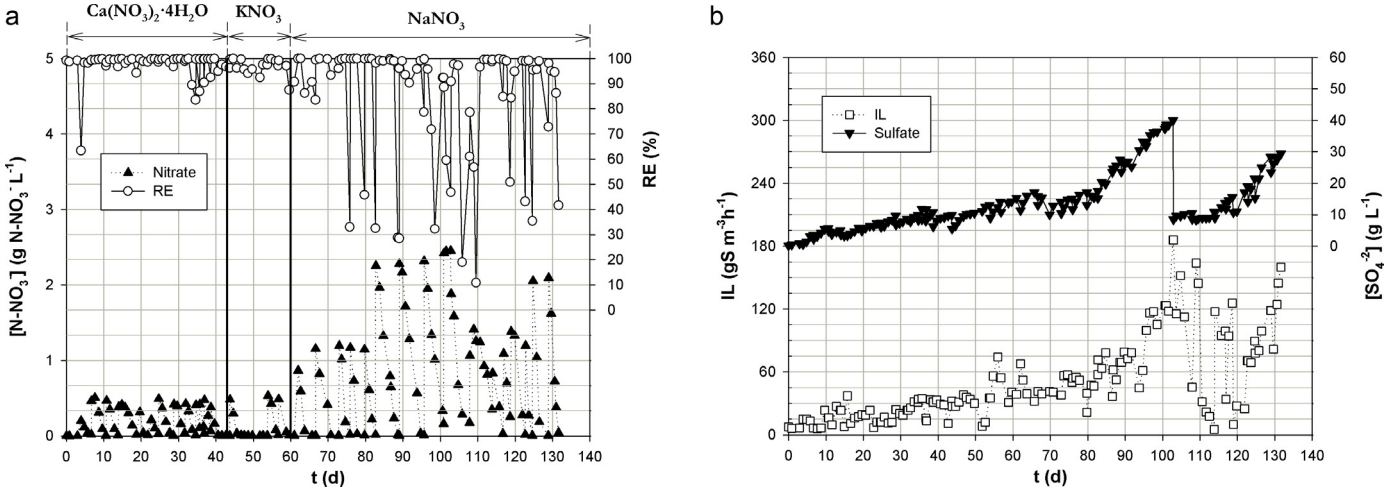

Fig. 3. (a) Evolution of nitrate concentration and removal efficiency under manual nitrate feeding regime, (b) evolution of sulfate concentration and H_2S inlet load under manual nitrate feeding regime.

According Eq. (5) if the N/S ratio is 0.4 mol mol^{-1} the sulfide can be oxidized mainly into sulfur and sulfide can be completely oxidized into sulfate when there is excess nitrate (Eq. (6), N/S ratio of 1.6 mol mol^{-1}) [10]. Under the manual nitrate feeding regime (day 1–413) the molar N/S ratio was between 0.29 and 2.26 mol mol^{-1} (average 0.77 ± 0.42 mol mol^{-1}). However, in 81% of the cycles the molar N/S ratio was below 1 mol mol^{-1}. For each cycle (period between nitrate dosage) the nitrate concentration decreased rapidly and therefore the N/S ratio also decreased. As a result, the S–SO_4^{-2}/S^0 ratio produced was not constant for each cycle under this nitrate feeding regime (manual). The resulting S–SO_4^{-2}/S^0 ratio was calculated under the programmed nitrate feeding regime as the nitrate concentration can be kept constant and therefore the mass balance can be achieved with great accuracy.

Similar N/S ratios were reported by Manconi et al. [29], who achieved complete oxidation of sulfide to sulfate with an N/S ratio of 0.89 mol mol^{-1}. Wang et al. [28] worked at an N/S ratio between 0.4 and 0.6 mol mol^{-1} for the oxidation of sulfide to elemental sulfur at a high sulfide concentration (300 mg L^{-1}) and Soreanu et al. [10] used an N/S ratio of 0.78 mol mol^{-1}.

Sulfate could have an inhibitory effect on RE and the effect of sulfate accumulation was therefore evaluated. The sulfate concentration was progressively increased from 15.2 g L^{-1} (day 82) to 40 g L^{-1} on day 103 (Fig. 3b). The critical EC was 99.8 gS m^{-3} h^{-1} (RE > 99%, Empty bed residence time (EBRT) 3.4 min) and this value was obtained while the sulfate concentration was less than 33 g L^{-1} and the nitrate was not exhausted. For sulfate concentrations higher than 33 g L^{-1} (day 96–103) the RE fluctuated in the range 32.3–95.8%. This behavior could be due to the high sulfate concentration or the high IL (from 105 to 186 gS m^{-3} h^{-1}) during this period. However, the RE increased from 46.9 to 90.9% for an IL of 186 gS m^{-3} h^{-1} (day 103), with the maximum EC (169 gS m^{-3} h^{-1}, EBRT 3.4 min) reached when the sulfate concentration decreased from 40 to 8.5 g L^{-1} on day 103. At low sulfate concentrations (<15 g L^{-1}, from day 103 to day 118) a decrease in RE was observed at high IL, indicating that the BTF shows instability at high IL (>115 gS m^{-3} h^{-1}), even at low sulfate concentrations. At IL values greater than 115 gS m^{-3} h^{-1} the BTF did not reach steady-state conditions and the sulfide concentration in the recirculation medium increased (the color of the recirculation medium became yellow when the sulfide concentration in the recirculation medium was higher than 45 mg S^{-2} L^{-1}). Under non-steady state conditions the RE was constant for a period not longer than 24 h and, in this case, the NR–SOB activity was seriously affected by the increased sulfide concentration in the medium and the RE dropped. After overloading, the H_2S IL was reduced to 30 gS m^{-3} h^{-1} and the system was restored to normal operation within 24 h. Thus, under the manual regime an IL greater than 99.8 gS m^{-3} h^{-1} and sulfate concentration greater than 33 g L^{-1} must been avoided.

3.1.4. Effect of temperature

It was observed that the optimum temperature for anoxic H_2S removal from biogas was 30 °C. This value is in agreement with the values reported in the literature for most denitrifying autotrophic microorganisms [30]. The temperature was fixed at 30 °C until day 131 and an RE of 100% was reached for an IL of 57.4 gS m^{-3} h^{-1} (day 74). When the temperature was increased up to 36 °C the RE decreased slowly and then remained constant at 88 ± 2% at an IL of 55 ± 2 gS m^{-3} h^{-1}. However, when the temperature was decreased to below 30 °C, a linear RE decrease to values of 65 ± 2% at 15 °C was observed. This finding shows that the NR-SOB population was more sensitive to inhibition at temperatures below 30 °C.

Table 2
Removal efficiency versus trickling liquid velocity at several inlet load.

TLV (m h^{-1})	IL (gS m^{-3} h^{-1})		
	93	157	201
2.3	89.6	82.9	78.7
4.6	98.0	93.0	85.1
9.1	99.0	94.9	88.8
13.7	99.2	96.0	91.8
18.3	99.6	96.4	92.2
20.6	99.8	96.1	92.9

3.1.5. Effect of pH

A high stability of RE (99.0 ± 1%) was observed when the pH was increased up to 7.3–7.5. A slightly alkaline pH favored the conversion of nitrate to nitrogen without the accumulation of intermediates (Eq. (7)) [31] and an increase in the H_2S solubility was observed.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (7)$$

The H_2S acid dissociation constants are 7.04 and 11.95 [32], so at pH values higher than 7.04 the HS^- concentration increased greatly. In this situation a slightly alkaline pH contributes to a higher RE because it improves the H_2S mass transfer from the gas phase to the liquid phase [33]. At pH values in the range 6.8–7.0 the RE values showed some instability, with RE values from 90.9 to 99.9% obtained, and when the pH was decreased to 6.5 the RE fell to 70%. The pH always decreased so that acid addition was not needed. The main oxidation product was elemental sulfur at low N/S ratio. However proton production was higher than hydroxide anion production. Hence, the kinetic must be more complex, although Eqs. (5) and (6) could be a good approximation.

Thomsen et al. [31] observed that the reduction of nitrous oxide is the slowest step in the reduction of NO_3^- to N_2. This stage can be affected when working at acidic pH due to progressive inhibition of the nitrous oxide reductase activity, which causes an accumulation of N_2O that is very toxic to denitrifying bacteria. The percentages of the flux reducing equivalents to reduction of nitrate to nitrogen obtained by Thomsen et al. [31] were 38, 87, 63, 30, 26 and 6 at pH values of 8.5, 7.5, 7.0, 6.5, 6.0 and 5.5, respectively. An optimum working pH between 7.3 and 7.5 is therefore proposed. The pH in this study was not increased above 7.5 because the system becomes more sensitive to H_2S overload due to the increase in H_2S solubility with pH.

3.1.6. Effect of TLV

Six TLV values were studied: 2.3, 4.6, 9.1, 13.7, 18.3 and 20.6 m h^{-1} at IL of 93, 157 and 201 gS m^{-3} h^{-1}. The gas velocity was 4.18 ± 0.7 m h^{-1} and therefore the liquid/gas velocity ratios were in the range 0.54–4.9. The RE was constant for TLV values higher than 13.7 m h^{-1} for the three IL tested (Table 2). RE decreased slightly for a TLV of 18.3 up to 4.6 m h^{-1} at IL values below 157 gS m^{-3} h^{-1} from 99.6 to 98.0% and from 96.4 to 93.0% for 93 and 157 gS m^{-3} h^{-1}, respectively. This reduction was more marked for an IL of 201 gS m^{-3} h^{-1}, with the RE decreasing from 92.2 to 85.1%. In all cases the RE fell quickly on decreasing TLV from 4.6 to 2.3 m h^{-1}; 98.0 to 89.6%, 93.0 to 82.9% and 85.1 to 78.7% for IL values of 93, 157 and 201 gS m^{-3} h^{-1}, respectively. It is clear that TLV has a significant effect on the H_2S mass transfer between the gas and liquid phases and this therefore influences RE. It is recommended to work with a TLV higher than 4.6 m h^{-1} to prevent RE reduction, with a maximum value of 15.0 m h^{-1}. The effect of TLV has been studied with polypropylene pall rings as a carrier under anoxic conditions, with an optimal TLV of 15 m h^{-1} [14]. The use of OPUF therefore allows a better mass transfer due its higher specific surface area.

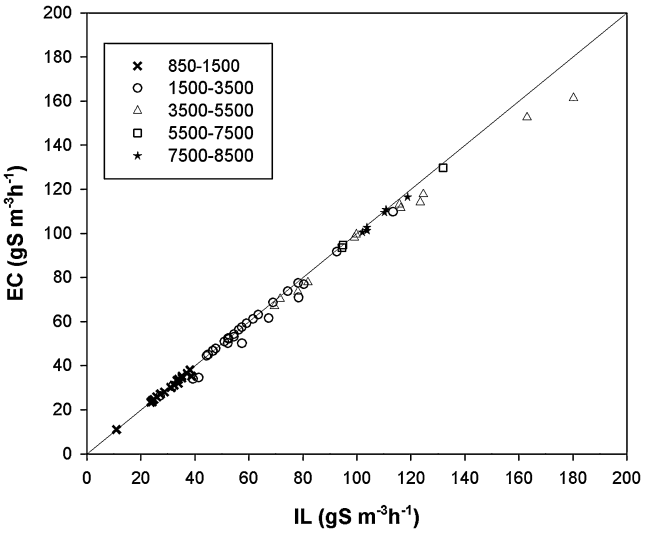

Fig. 4. Elimination capacity versus inlet load under programmed nitrate feeding regime. Icons show the range of inlet H_2S concentration (ppmv).

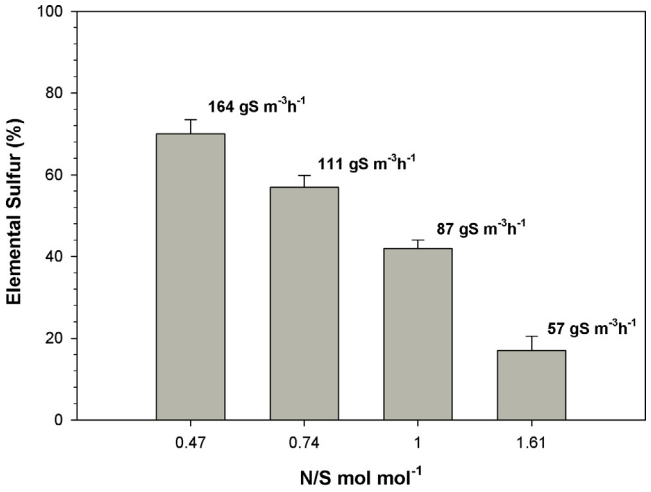

Fig. 5. Sulfur mass balance.

Gabriel and Deshusses [20] employed OPUF in an aerobic BTF for the removal of H_2S from air with a TLV of 1.7 m h^{-1} and RE values of 97% were achieved for IL between 14.1 and 89.4 gS m^{-3} h^{-1} and with low inlet concentrations of H_2S (<30 ppmv). Fortuny et al. [8,22] used aerobic BTFs with OPUF and polypropylene grids [HD Q-PAC® (0.16 × 0.16″)] to remove H_2S from synthetic biogas, working with TLVs between 1 and 5 m h^{-1} for OPUF and 2.4 and 3.8 m h^{-1} for HD Q-PAC®. Both studies involved high H_2S IL and values of 370 gS m^{-3} h^{-1} and a maximum EC of 270 gS m^{-3} h^{-1} were achieved.

3.2. Study of programmed nitrate feeding regime

3.2.1. Effect of IL

The critical EC was 130 gS m^{-3} h^{-1} (RE 99%, EBRT 2.4 min) (Fig. 4) and this is higher than the critical EC obtained under the manual feeding regime (99.8 gS m^{-3} h^{-1}, RE < 99%, EBRT 3.4 min). However, the maximum EC had the same value (170 gS m^{-3} h^{-1}, EBRT 2.4 min) under both nitrate feeding regimes. Similar results were also obtained on using polypropylene Pall rings, with a critical EC of 120 gS m^{-3} h^{-1} (RE 99%, EBRT 2.4 min) and a maximum EC of 171 gS m^{-3} h^{-1} (RE 85%, EBRT 2.4 min) [14].

At constant H_2S IL the programmed nitrate feeding regime can achieve steady-state conditions characterized by constant RE without nitrate exhaustion, nitrite accumulation (less than 80 mg L^{-1}) and sulfate accumulation (less than 10 g L^{-1}).

The N/S ratio can be easily calculated under the programmed nitrate feeding regime due to the stability of nitrate and product concentrations. A sulfur mass balance was performed by subtraction [34]. Sulfur mass balances showed a linear increase in sulfur production versus the ratio of supplied nitrate (mol N–NO_3^-) and sulfide removed (mol S–H_2S) (Fig. 5).

Therefore, on working at a high IL (>164 gS m^{-3} h^{-1}) elemental sulfur was the main product (70%) because the system was under nitrate-limited conditions. Similar results were obtained by Soreanu et al. [9] and Fortuny et al. [22], who observed that 65% of the H_2S degraded was oxidized to elemental sulfur. Fernández et al. [14] also obtained a similar level of elemental sulfur production (68%) on working under nitrate-limiting conditions (N/S ratio of 0.7 ± 0.32 mol mol^{-1}).

Comparison of these results with those reported in studies on the anoxic removal of H_2S in biogas through denitrification processes shows that the critical EC values achieved in this study are higher than those obtained by Soreanu et al. [10,11], who reported values between 9.0 and 11.8 gS m^{-3} h^{-1} on using anoxic BTFs packed with plastic fibers and volcanic rock (RE between 95 and 99% with EBRTs between 10.3 and 16.0 min). Another study on anoxic biofiltration by Soreanu et al. [35] gave a maximum EC value of 50 gS m^{-3} h^{-1} with an EBRT of 6 min. The higher EC values obtained in this study may be due to the use of OPUF as a carrier and the prior stimulation of inoculum by nitrate addition – a combination of factors that was able to improve RE.

Fortuny et al. [8] carried out a study on H_2S removal from biogas using an aerobic BTF and they found a lower critical EC of 79 gS m^{-3} h^{-1} and a maximum EC of 144 gS m^{-3} h^{-1} on using HD Q-PAC® as a carrier and an EBRT lower than that employed in the present study. However, in another study by the same authors [22], using HD Q-PAC® and OPUF, maximum EC values greater than those found in this study (250 and 280 gS m^{-3} h^{-1}) were obtained with EBRTs of 2.8 and 3 min. In a previous study on the simultaneous removal of methylmercaptan and H_2S from biogas on the biofilter used in this work, EC values similar to those in this experiment were obtained, i.e. critical EC of 84.7 gS m^{-3} h^{-1} (RE 98%) and maximum EC of 142 gS m^{-3} h^{-1} (RE 47%) [13]. It can be concluded that the anoxic BTF used in this study is capable of degrading high H_2S IL to a similar extent as those achieved with aerobic BTFs used for removal of this compound from biogas.

Programmed nitrate feeding is feasible for biogas treatment without a change in the H_2S IL because the nitrate supply system cannot detect the change in H_2S IL. Therefore, on increasing the H_2S IL, nitrate is exhausted and RE decreases; however, on decreasing the H_2S IL, nitrate was accumulated in the medium. This problem could be solved by applying a feed forward control for the measurement of the H_2S inlet concentration and biogas flow rate, or by measuring the nitrate with an ion-selective electrode (ISE). However, commercial ISE suffer from interference or inhibition by nitrite, sulfate and/or sulfide. Recently, Fernández et al. [14] developed another simple method for nitrate addition in an anoxic BTF. These authors employed an oxide reduction potential (ORP) measurement in the recirculation medium in order to detect H_2S accumulation and therefore avoid nitrate depletion. However, it was impossible to ascertain whether H_2S accumulation was due to nitrate depletion or to H_2S overload.

The cost per cubic meter of biogas treated by aerobic BTF, $FeCl_3$ addition and chemical-oxidative scrubbing are 0.013, 0.024 and 0.30 € m^{-3} of biogas respectively [36,37]. For anoxic BTF the investment cost compared to aerobic BTF is very similar. However, there is an additional operative cost related with nitrate consumption. In order to remove 1 kg of H_2S it is necessary 1.85 kg of $NaNO_3$ (at

N/S ratio of 0.74 mol mol^{-1}). Considering the previously study published by Tòmas et al. the cost will be of 0.016 € m^{-3} of biogas at $NaNO_3$ price of 0.45 € kg^{-1} (price buying 1 Tm, 2009). Hence, anoxic BTF could be considering a promising technology.

4. Conclusion

Our experimental results confirmed that the use of different nitrate sources did not affect the RE, although $NaNO_3$ is recommended. The maximum EC of 170 g S m^{-3} h^{-1} (EBRT 2.4 min) under both regimes. The optimal conditions were: temperature of 30 °C, sulfate concentration below 33 g L, pH between 7.3 and 7.5 and TLV higher than 4.6 m h^{-1}. In regard to nitrite concentration, high concentrations were reached without showing an inhibitory effect on the process, so nitrite could be used instead nitrate as an electron acceptor source. To sum up, OPUF has great properties as carrier for anoxic biofiltration and it can be reached critical EC of 130 g S m^{-3} h^{-1} (RE 99%, EBRT 2.4 min) under programmed nitrate feeding regime.

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