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Simultaneous methylmercaptan and hydrogen sulfide removal in the desulfurization of biogas in aerobic and anoxic biotrickling filters

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HIGHLIGHTS

- Co-treatment of H_2S and CH_3SH is effective in aerobic and anoxic bioreactors.
- Chemical reaction of CH_3SH and biosulfur enhances reactor performance.
- Loads of 100 gS-H_2S m^{-3} h^{-1} produce a negative effect on the removal of CH_3SH.
- CH_3SH mass transfer is the limiting step at reduced gas contact times.
- A similar performance was obtained with metallic Pall rings and PU foam.

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ABSTRACT

Hydrogen sulfide (H_2S) and methylmercaptan (CH_3SH) are the most common sulfur compounds found in biogas. The simultaneous removal of H_2S and CH_3SH was tested at neutral pH in two biotrickling filters, one operated under aerobic conditions and the other one under anoxic conditions. Both reactors were run for several months treating a H_2S concentration of around 2000 ppm_v. Then, the effect of CH_3SH loading rate (LR) on H_2S and CH_3SH removal was investigated in both reactors maintaining a constant H_2S LR of 53–63 gS-H_2S m^{-3} h^{-1}, depending on the reactor. Initially, CH_3SH concentration was stepwise increased from 0 to 75–90 ppm_v. Maximum elimination capacities (ECs) of around 1.8 gS-CH_3SH m^{-3} h^{-1} were found. After that, the CH_3SH LR was increased by testing different empty bed residence times (EBRTs) between 180 and 30 s. Significantly lower ECs were found at short EBRTs, indicating that the systems were mostly mass transfer limited. Finally, EBRT was stepwise reduced from 180 to 30 s at variable CH_3SH and H_2S loads. Maximum H_2S ECs found for both reactors were between 100 and 140 gS-H_2S m^{-3} h^{-1}. A negative influence was found in the ECs of CH_3SH by the presence of high H_2S LR in both biotrickling filters. However, sulfur mass balances in both reactors and batch tests under aerobic and anoxic conditions showed that CH_3SH chemically reacts with elemental sulfur at neutral pH, enhancing the overall reactors performance by reducing the impact of sulfur accumulation. Also, both reactors were able to treat CH_3SH without prior inoculation because of the already existing sulfide-oxidizing microorganisms grown in the reactors during H_2S treatment. Co-treatment of H_2S and CH_3SH under aerobic and anoxic conditions was considered as a feasible operation for concentrations commonly found in biogas (2000 ppm_v of H_2S and below 20 ppm_v of CH_3SH).

1. Introduction

Biogas is a typical energy-rich gas, which requires the removal of sulfur compounds for avoiding problems of corrosion in the combustion engines, as well as for human health and environmental protection. Most common reduced sulfur compounds found in biogas and in petrochemical industry waste gases are hydrogen sulfide (H_2S) and methylmercaptan (CH_3SH). Also ethylmercaptan,

Abbreviations: BTF1, aerobic biotrickling filter; BTF2, anoxic biotrickling filter; DMDS, dimethyl disulfide; DMS, dimethyl sulfide; DMTS, dimethyl trisulfide; DO, dissolved oxygen; E1, E2, E3, experiments 1, 2, 3; EBRT, empty bed residence time; EC, elimination capacity; HRT, hydraulic retention time; LR, loading rate; ORP, oxidation–reduction potential; PU, polyurethane; RE, removal efficiency; TDS, total dissolved sulfide; TLV, trickling liquid velocity.

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dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are found [1]. Typically, H_2S content in biogas ranges from 0.1% to 2% (1000–20000 ppm_v), while CH_3SH is normally present at trace levels of around 1–20 ppm_v; with maximum values reported around 100 ppm_v [2–4]. The importance of the removal of CH_3SH is related to the potential impact on the biological desulfurization process of biogas and, to a lesser extent, because of the formation of SO_x during biogas combustion in combustion engines. Besides that, the low odor threshold, high toxicity and potential carcinogenic effect are important reasons to study the CH_3SH removal from biogas. In terms of process performance impact, Van den Bosch et al. [2] reported that CH_3SH severely inhibits biological sulfide oxidation (50% reduction of the biological oxidation rate) at concentrations above 0.05 mM under natron-alkaline-aerobic conditions. Complete inhibition was found at CH_3SH concentrations of 0.65 mM. However, no previous studies of simultaneous H_2S and CH_3SH are available at high H_2S loads in bioreactors operating at neutral pH, neither under aerobic nor anoxic conditions. Thus, potential accumulation of CH_3SH in aerobic and anoxic biotrickling filters may hinder H_2S removal to a certain extent.

Biotrickling filters work by passing a stream of contaminated air through a chemically inert packing material, over which an aqueous phase is continuously trickled. Microorganisms grow as biofilms on the surface of the packing material by using pollutants transferred from the gas to the biofilm phase as energy and/or carbon sources. Removal of high loads of H_2S in biotrickling filters under aerobic and anoxic conditions has been reported as a viable and economical technique with several advantages in comparison with classical physical–chemical processes [5,6]. However the effect of CH_3SH in the removal of H_2S in biogas in biotrickling filters has not been explored yet, although there are few references in the co-treatment of low loads of CH_3SH and H_2S for odour removal [7,8].

The biological oxidation of H_2S in aerobic (Eqs. (1) and (2)) and anoxic (Eq. (3)) biotrickling filters occurs according to the following reaction scheme [5,9]:

$$H_2S + 1/2\ O_2 \rightarrow S^0 + H_2O \quad (1)$$

$$H_2S + 2O_2 \rightarrow SO_4^{-2} + 2H^+ \quad (2)$$

$$15NO_3^- + 12H_2S \rightarrow 9H_2O + 6S^0 + 6SO_4^{-2} + 5NO_2^- + 5N_2 + 2OH^- + 4H^+ \quad (3)$$

Eq. (3) involves both complete and partial denitrification coupled to complete and partial H_2S oxidation [10]. In both cases the principal products are sulfate and elemental sulfur (biosulfur) particles. The risk of clogging by elemental sulfur formation is the most important bottleneck for stable, long-term operation in biotrickling filters. The ratios between the available electron acceptor and H_2S, i.e. O_2/H_2S and NO_3^-/H_2S in an aerobic and anoxic biotrickling filter, respectively, are the key parameters to end up with a certain SO_4^{-2}/S^0 produced ratio [5,11].

The biological oxidation of CH_3SH under aerobic conditions produces formaldehyde and H_2S as intermediary products [12]. The overall reaction can be expressed by Eq. (4) [13]:

$$2CH_3SH + 7O_2 \rightarrow 2CO_2 + 2H_2SO_4 + 2H_2O \quad (4)$$

To our knowledge the stoichiometry of the anoxic biological reaction has not been described previously. Even if the oxidation of CH_3SH with molecular oxygen has been described to happen in strongly alkaline solutions in the presence of metal ion catalysts, the oxidation rates in the absence of catalytic materials are extremely low [14]. Chemical oxidation of CH_3SH to DMDS in an aerobic reactor has been reported to occur according to Eq. (5) [15]:

$$2CH_3SH + 0.5O_2 \rightarrow CH_3SSCH_3 + H_2O \quad (5)$$

Recently, van Leerdam et al. [15,16] have found that CH_3SH also reacts chemically with biosulfur particles at pH 8.7 to form DMDS and other polysulfides according to:

$$2CH_3S^- + H^+ + 1/8S_8 \leftrightarrows HS^- + CH_3SSCH_3 \quad (6)$$

$$2CH_3S^- + S_8 \leftrightarrows S_y^{2-} + CH_3S_xCH_3 (\text{with } x + y = 10) \quad (7)$$

These reactions depend on the CH_3SH and biosulfur concentration, temperature and nature of biosulfur particles [16]. The main products of these reactions are dimethyl polysulfides [DMDS, and dimethyl trisulfide (DMTS)] and some longer-chain dimethyl polysulfides [$(CH_3)_2S_{4-7}$]. DMDS and DMTS are less inhibitory than CH_3SH on biological (poly)sulfide oxidation [2].

The aim of this work was to investigate the impact of the pollutant load and the gas contact time in the performance of two well-established biotrickling filters operated under aerobic and anoxic conditions at neutral pH during the co-treatment of typical loads of H_2S and CH_3SH in biogas.

2. Materials and methods

2.1. Aerobic biotrickling filter setup

The aerobic biotrickling filter (BTF1) is a conventional counter-current biotrickling filter, in which the gas phase circulates upstream, counter-currently with the liquid phase. BTF1 was operated for more than 1 year under steady-state conditions, treating a reference synthetic biogas containing 2000 ppm_v of H_2S at an EBRT of 180 s (LR of 52.5 gS-H_2S m^{-3} h^{-1}). Unspecific inoculation was carried out with aerobic sludge from a local municipal wastewater treatment plant located in Manresa, Spain. BTF1 was located at the Universitat Autonoma de Barcelona, Spain. The schematic of the reactor is shown in Fig. 1. Reactor diameter is 7.14 cm and the packed bed volume is 2 L; metallic Pall rings (AISI 316), 10 mm diameter were used as packing material.

The synthetic biogas consisted of a mixture of H_2S, N_2 and CH_3SH, which was prepared by mixing metered amounts of pure gases by mass flow controllers (Bronkhorst, The Netherlands). Since methane is only sparingly soluble in water [17] and not well-degraded in biofilters or biotrickling filters [18], the potential impact of an extra amount of electron acceptor consumption due to methanotrophs growth was considered not significant. Dry air was fed by a digital mass flow controller into the bottom of the aeration tank and bubbled by means of a fine bubble diffuser; outlet air is then fed to the bottom of the packed bed. During normal operation, a flow of 250 mL min^{-1} of air was supplied to the aeration tank, corresponding to a maximum dilution factor of biogas inside the reactor of 27%. During experiments, depending on the total gas flow, the dilution factor was varied from 6% to 32%. It is worth noticing that calculations presented in this work already consider the corresponding dilution factor. The aeration tank acts as a recirculation sump and is also equipped with high and low control level gauges. Acid (HCl, 1 M) and base (NaOH, 1 M) are dosed by an on/off pH control system, directly into the referred oxygenation unit, in order to control the pH between 6.0 and 6.5. A solution of 21 g L^{-1} of $NaHCO_3$ was fed at a flowrate of 0.4 L day^{-1} to the biotrickling filter. Automated pumping of bicarbonate, mineral medium and purge was performed to warrant the continuous renewal of the liquid phase. Mineral medium contained (g L^{-1}): NH_4Cl, 1; KH_2PO_4, 0.12; K_2HPO_4, 0.15; $CaCl_2$, 0.02; $MgSO_4.7H_2O$, 0.2; and trace elements [19], 1 mL L^{-1}. During the present experiments, a trickling liquid velocity (TLV) of 7 m h^{-1} and a hydraulic retention time (HRT) of 9 h were maintained.

Previous studies in the same experimental setup as in BTF1 and under comparable operational conditions during the desulfuriza-

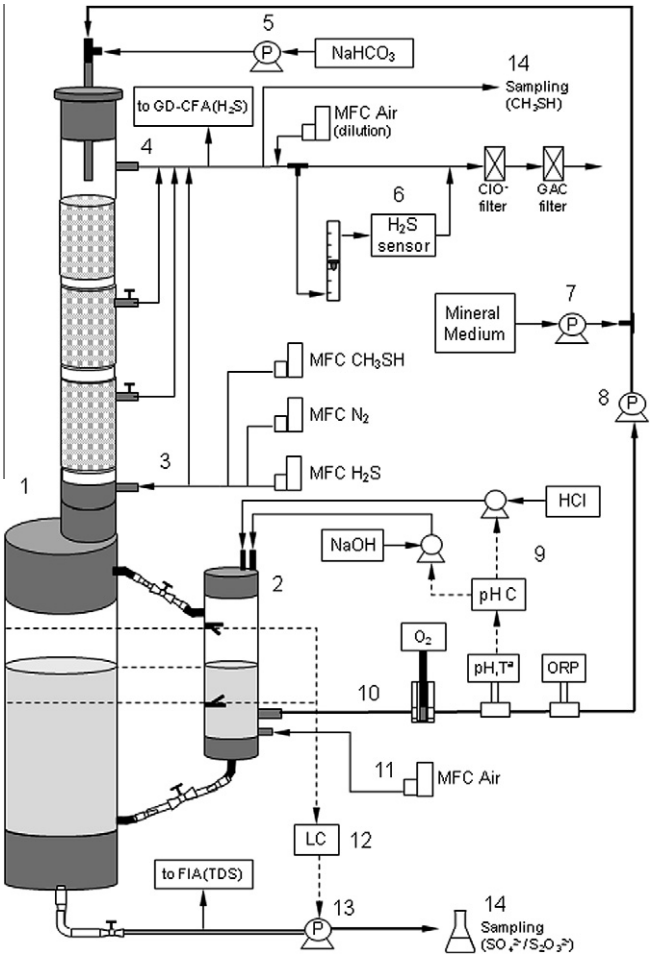

Fig. 1. Schematic of experimental set-up (BTF1): (1) main reactor, (2) air supply reactor, (3) gas inlet, (4) gas outlet, (5) bicarbonate supply, (6) gas monitoring, (7) mineral medium supply, (8) recirculation pump, (9) pH control, (10) liquid monitoring, (11) air supply, (12) level control, (13) liquid purge, (14) sampling points.

tion of H_2S as the sole contaminant can be found elsewhere [5,20,21]. Maximum ECs of 280 and 250 g S-H_2S m^{-3} h^{-1} at REs of 80–85% were encountered for PU foam and HD-QPac as packing materials in Fortuny et al. [5] treating H_2S concentrations up to 12000 ppm_v. Air was directly supplied to the biogas flow in both cases. Maximum ECs of 201 g S-H_2S m^{-3} h^{-1} at a RE of around 90% was found by Montebello et al. [20] treating H_2S concentrations up to 8000 ppm_v. Air was supplied both to the biogas flow and to the liquid phase through an aeration device. Maximum ECs of 130–145 g S-H_2S m^{-3} h^{-1} were found in Fortuny et al. [21] by decreasing the gas contact time down to 30 s. Except in the latter case, in which the system was mass transfer limited due to a reduced EBRT, the system was biologically limited and the production of elemental sulfur was found as the main process bottleneck at H_2S inlet concentrations above 6000 ppm_v.

2.2. Anoxic biotrickling filter setup

The anoxic biotrickling filter (BTF2), located at the Universidad de Cadiz, Spain, is also a conventional counter-current biotrickling filter. In the long-run, the reactor was fed with biogas produced on-site from two UASB (Upflow Anaerobic Sludge Blanket) reactors treating synthetic organic matter. BTF2 was run for several months under steady-state conditions at an EBRT of 163 s treating biogas containing around 2000 ppm_v of H_2S (63.2 g S-H_2S m^{-3} h^{-1}). Details about the biogas production system and BTF2 performance can be found elsewhere [6]. A schematic of the experimental set-up for the laboratory-scale anoxic biotrickling filter is shown in Fig. 2.

The BTF2 was made of transparent PVC (id. 105 mm, packed bed volume of 2.375 L) and packed with open pore polyurethane (PU) foam cubes of 8 cm^3 as packing material (Filtren TM25450, Recticel Iberica, Spain). The liquid phase was recirculated from the sump volume (2.25 L) to the packed bed by a magnetic centrifugal pump (MP-15R, Selecta, Spain). The water phase was renewed by adding a constant flow of 6 L d^{-1} of mineral medium fed through a peristaltic pump (EW-07540-30, Masterflex, USA) and controlled by a logic module (time switch-on 1 s; off time 14 s) (Logo 12/24RC, Siemens, Spain). The mineral medium was the ATCC-1255 *Thiomicrospira denitrificans* medium without $Na_2S_2O_3{\cdot}5H_2O$ (energy source) and $NaHCO_3$ (carbon source).

For a more reliable comparative between aerobic and anoxic reactors during the specific tests with CH_3SH, biogas mimics and CH_3SH were supplied to the BTF2 from three compressed gas cylinders: CH_4 (quality 2.5), CO_2 dry (quality 3.0), mixture (0.5 vol% CH_3SH, balance N_2), from Abelló Linde S.A (Spain). The biogas mimics was prepared by mass flow controllers (Brooks Instruments, USA), then the biogas passed through a H_2S generation system for adjustment of the required H_2S concentration as described by Ramírez et al. [22]. During the present experiments, TLV and HRT were maintained at 7 m h^{-1} and 9.0 h, respectively. The pH was maintained at 7.4–7.5 by on/off pH controller (multimeter 44, Crison instruments, Spain) and NaOH (2 M) or HCl (2 M) addition.

During the desulfurization of H_2S as the sole contaminant [6], the critical EC was 60 gS-H_2S m^{-3} h^{-1} at an EBRT of 240 s. A maximum EC of 169 gS-H_2S m^{-3} h^{-1} was encountered under non steady-state operation (period of time less than 24 h) while a sustained maximum EC of 92 gS-H_2S m^{-3} h^{-1} was found for steady-state conditions.

2.3. Analytical methods

The BTF1 is suited with on-line monitoring of pH, oxidation–reduction potential (ORP) (Crison Instruments, Spain) and dissolved oxygen (DO) (oxi340i, WTW, Germany). Also, total dissolved sulfide (TDS = $H_2S_{(aq)}$ + HS^- + S^{2-}) was on-line monitored during experiments by an integrated flow-based system with an ion-selective electrode for sulfide/hydrogen sulfide measurements [20]. Sulfate and thiosulfate were off-line analysed using an ICS-1000 Ion Chromatography system with an IonPac AS9-HC column (Dionex Corporation, USA). Gas phase in BTF1 was on-line monitored with an electrochemical $H_2S_{(g)}$ sensor (Sure-cell, Euro-Gas Management Services Ltd., UK). CH_3SH in BTF1 was analysed using a Hewlett Packard (Palo Alto, USA) 6890 N gas chromatograph equipped with a Supelco (Bellefonte, USA) Supel-Q PLOT column (length 30 m, inner diameter 0.53 mm, film thickness 0.40 mm) and a flame ionization detector (FID).

In the BTF2, ORP and conductivity were monitored in the liquid phase (MultiMeter 44, Crison Instruments, Spain). Also, sulfate, nitrite and nitrate were measured according to standard methods [23]. CH_3SH in BTF2 was analysed using a gas chromatograph Bruker 450 GC (Bruker Daltonik GmbH, Germany) equipped with a pulsed flame photometric detector (PFPD) and a Wcot Fused Silica column (30 m × 0.32 mm id, coating: cp-sil 5CB for sulfur, film thickness = 4.0 μm). $H_2S_{(g)}$ was analysed using an electrochemical H_2S sensor GA2000Plus (Fonotest S.L. Instruments, Spain), which accuracy is +/−10% of the measuring range (0–500 ppm_v). H_2S and CH_3SH were monitored at the inlet and outlet ports of both reactors during experiments.

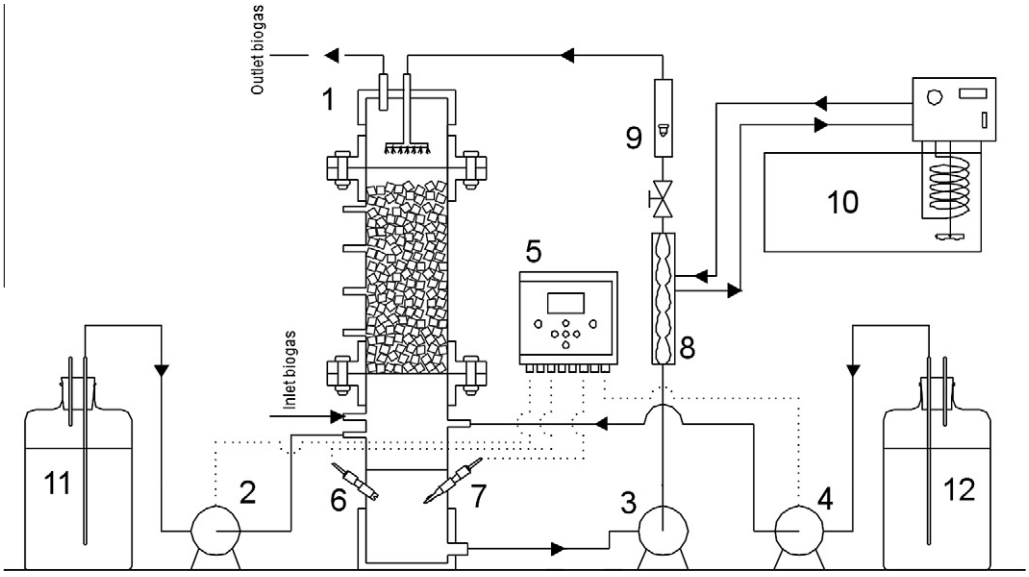

Fig. 2. Schematic of experimental set-up (BTF2): (1) anoxic biotrickling filter; (2) nitrate pump; (3) recirculation pump; (4) NaOH pump; (5) pH controller; (6) ORP electrode; (7) pH electrode; (8) heat exchanger (allihn condenser); (9) flowmeter; (10) thermostatic bath; (11) nitrate solution; (12) NaOH solution.

Table 1
Experimental conditions for the aerobic biotrickling filter (BTF1) and anoxic biotrickling filter (BTF2).

Experiment	$[H_2S]$ (ppm_v)		H_2S LR ($gS\text{-}H_2S\ m^{-3}\ h^{-1}$)		$[CH_3SH]$ (ppm_v)		CH_3SH LR ($gS\text{-}CH_3SH\ m^{-3}\ h^{-1}$)		EBRT (s)	
	BTF1	BTF2	BTF1	BTF2	BTF1	BTF2	BTF1	BTF2	BTF1	BTF2
E1					10	2	0.26	0.05		
					20	7	0.53	0.19		
	2000	2088	52.5	60	40	15	1.05	0.44	180	163
					60	22	1.58	0.62		
					75	50	2.00	1.46		
E2	2000	2594					0.34	0.34	180	181
	1001	1611					0.68	0.50	90	121
	666	1294	52.4	66	13	12.1	1.02	0.63	60	91
	501	862					1.36	0.91	45	61
	342	426					1.99	1.70	30	30
E3			52	57			0.34	0.24	180	181
			105	87			0.68	0.35	90	121
	2000	2144	158	111	13	9.1	1.02	0.49	60	91
			207	163			1.36	0.67	45	60
			306	301			1.99	1.33	30	30

2.4. CH_3SH and elemental sulfur microcosms

Sets of batch tests were performed to assess the chemical reaction between biosulfur particles and CH_3SH. Tests were performed in 12 mL bottles, sealed with aluminim caps (20 mm, butyl gray). Liquid from the recirculation line of each reactor (3 mL) containing a biosulfur concentration of 0.86 g S L^{-1}were incubated at 30 °C and 150 rpm under aerobic and anoxic conditions. The CH_3SH concentration in the gas phase was set to 83 ± 4 ppm_v. In the anoxic microcosms, N_2 was used instead of air to fill the bottles headspace. CH_3SH concentration in the gas phase was hourly measured, as described in Section 2.3 (GC-PFPD), until the initial gas concentration was reduced by a 90%. Three replicates and a blank without the addition of biosulfur were run per test. Bottles and medium were sterilized at 121 °C for 20 min and biosulfur particles were dried (105 °C until constant weight) and ground until a fine powder was obtained. In addition gas was filtered (0.22 μm, Millipore Filter SLG05010) to avoid contaminations.

2.5. Biofiltration experimental conditions

Three experiments were performed in parallel in each reactor to find out potential crossed effects during pollutants treatment (Table 1). First, a CH_3SH inlet concentration increase experiment (E1) was performed at constant H_2S LR in order to verify the possible effect of CH_3SH over the already existing H_2S desulfurization capacity in each reactor. Secondly, an EBRT decreasing experiment at constant H_2S LR (E2) was performed and, finally, an EBRT decreasing experiment at variable H_2S LR (E3). Experiments E2 and E3 were designed to investigate the operational limit and potential mass transfer limitations of each system and pollutant.

In E1, the H_2S inlet concentration was kept constant at around 2000 ppm_v while the CH_3SH concentration was stepwise increased in both reactors. Concentration steps were kept constant during 24 h that corresponded to almost three liquid residence times compared to an HRT of 9 h of the liquid phase. Then, pseudo-steady-state conditions after each concentration step were reached.

The EBRT was kept unaltered at the reference value for each reactor.

In E2, a constant H_2S LR was maintained to verify the single effect of the increasing CH_3SH LR produced by the reduction in the gas contact time. The EBRT was stepwise decreased, being each EBRT step kept for 1.5 h in both reactors. In E3, both H_2S and CH_3SH concentrations were kept constant, leading to an increase in both pollutants loading rates (LRs) due to the reduction in the gas contact time. Similarly to E2, the EBRT was stepwise decreased, being each EBRT step kept for 1.5 h in both reactors. In all cases, liquid and gas samples were analysed at the end of each step to assess the EC and RE as well as the sulfur mass balance in both reactors.

The concentration of the nitrate source was calculated according to a specific demand of nitrate of 0.85 mol $N-NO_3^-$ mol^{-1} S-H_2S removed [6] in the experiments at constant H_2S LR (E1 and E2), and from 1.46 to 0.6 mol $N-NO_3^-$ mol^{-1} S-H_2S removed in the experiments at variable H_2S LR (E3). The oxygen supplied to the aeration unit in the aerobic reactor corresponded to a 43 mol O_2 mol^{-1} S-H_2S removed ratio in E1 and E2, and from 43 to 7.4 mol O_2 mol^{-1} S-H_2S removed ratio in E3. The efficiency of the oxygen transfer unit was calculated to be around 5% according to previously reported data [5,20].

3. Results and discussion

3.1. CH_3SH and biosulfur reaction

A set of batch tests were performed to assess the chemical reaction between biosulfur particles and CH_3SH at neutral pH in the presence of O_2 or nitrate in the mineral medium. The rate of heterogeneous reactions between CH_3SH and biosulfur particles was approximated to a pseudo-first-order reaction according to:

$$-d[CH_3SH]/dt = k[CH_3SH]_x^m[S]^n = k'[CH_3SH]\ (m=1) \quad (8)$$

A constant biosulfur concentration was assumed since its concentration was approximately three orders of magnitude higher than that of CH_3SH. After data linearization, the pseudo-first order kinetic constants (k') were 0.56 and 0.66 h^{-1} for the BTF1 medium under aerobic conditions and for the BTF2 medium under anoxic conditions, respectively. In all cases, the regression coefficients were above 0.99. Therefore, kinetics were adjusted to a pseudo-first-order reaction. A quantitative comprehensive study has been carried out by van Leerdam et al. [16] on the reactions between CH_3SH and biologically produced sulfur particles at natron-alkaline conditions. They observed that the sulfur particles size affected the order constant rate (1.38–2.1 for CH_3SH) and constant kinetics (K at 30 °C between $10^{-5}\,(mol\,L^{-1})^{-1.1}\,m^{0.76}\,s^{-1}$ and $10^{-6}\,(mol\,L^{-1})^{-0.38}\,m^{1.11}\,s^{-1}$).

Although other authors that described the chemical oxidation of H_2S under aerobic conditions found that the intermediates can be further oxidized chemically [24], they also found that the abiotic chemical sulfide oxidation by oxygen can attain relatively high rates under alkaline conditions (pH > 9). Under aerobic and slightly acidic conditions (pH < 6) the rate of intermediate sulfur compounds formation is very low and it begins to increase at pH 7 [25]. Since the aerobic biotrickling filter operated at pH 6.0–6.5, the production of intermediate compounds from H_2S should not be relevant. To the authors' knowledge, there are not studies about the H_2S chemical oxidation under anoxic conditions and some research is warranted, even if such study was out of the scope of the present work. Results indicate that no significant differences existed between the aerobic and anoxic rates since the electron acceptors do not necessarily play a role in the chemical reaction between CH_3SH and elemental sulfur particles, according to Eqs. (6) and (7). In between 200 and 300 min more than 90% of CH_3SH was consumed, while the formation of an additional sulfur compound was detected by GC-PFPD (data not shown), confirming the chemical reaction between the biosulfur formed in the biotrickling filters and CH_3SH. According to Fortuny et al. [26] and van Leerdam et al. [16], no polysulfides other than DMDS were produced at neutral pH under aerobic and anoxic conditions. Since the reaction depends on others parameters such as particles size distribution, specific surface area of the biosulfur particles and biosulfur concentration [16], a deeper study is warranted to fully understand the interactions between biosulfur particles and CH_3SH at neutral pH.

3.2. Effect of CH_3SH concentration in biogas desulfurization

Elimination capacities calculated at the end of each pseudo steady-state period (Fig. 3) during stepwise concentration increases along E1 show that the critical CH_3SH EC under aerobic conditions (around 0.5 gS-CH_3SH m^{-3} h^{-1}) was significantly higher than that under anoxic conditions (around 0.2 gS-CH_3SH m^{-3} h^{-1}). Maximum ECs of around 1.5 and 1.0 gS-CH_3SH m^{-3} h^{-1} were reached in the aerobic and anoxic reactor, respectively. Although no previous ECs have been reported on CH_3SH removal by biofiltration under anoxic conditions, maximum ECs in the range of 3–25.6 gS-CH_3SH m^{-3} h^{-1} previously reported under aerobic conditions [27–29] indicated that a larger activity of the microbial populations in the biofilm with a greater adaptation to CH_3SH degradation could still be developed in both biotrickling filters. No detrimental effect over the desulfurization of H_2S was observed by the presence of CH_3SH at the studied conditions in none of the two processes since the RE of H_2S was kept around 99% during E1. Furthermore, a beneficial effect on H_2S desulfurization was found by the presence of CH_3SH that lead to a reduction of accumulated elemental sulfur, as discussed later on.

A sulfur mass balance was performed by substraction [30], allowing estimating the quantity of biosulfur produced in each reactor. For mass balances calculation, it was assumed that the only final products were elemental sulfur and sulfate, since DMDS, the sole by-product formed by the chemical reaction between CH_3SH and biosulfur particles at neutral pH, is further biologically oxidized to sulfate. Results for BTF1 (Fig. 4a) show that the production of biosulfur was kept at a constant rate during the first three CH_3SH concentration steps (around 0.031 g h^{-1}), resulting in a sulfate selectivity ($SO^{2-}_{4\,produced}/H_2S_{removed}$) of around 80%. Interestingly, the biosulfur production rate was reduced to 0.014 g h^{-1} during the last steps, leading to an increase in the sulfate selectivity up to 90%.

Results indicate that, particularly in BTF1, during the higher CH_3SH LR periods the consumption of biosulfur by chemical reaction with CH_3SH probably occurred according to the batch tests performed under neutral pH (6.8–7.0) (see Section 3.1). Similar results were found in BTF2 (Fig. 4b). In this case, a sulfur mass balance showed a decrease of the biosulfur production rate from 0.075 to 0.055 g h^{-1} in the last experimental period. The ORP was constant at -168.7 ± 13.75 mV, indicating that sulfide did not accumulate in the liquid phase. Sulfate selectivity of BTF2 during CH_3SH LR experiments was kept around 60–64% during the complete experiment.

The biological oxidation of the DMDS produced from the CH_3SH-biosulfur reaction was, consequently, the reason for the increase of the sulfate production observed in BTF1 at the end of the experiment. After the experimental period, the production rate of biosulfur was restored to the initial values. Visual evidence of the reduction of accumulated biosulfur inside BTF1 confirmed the consumption of biosulfur by reaction with CH_3SH.

Such observations indicate that the presence of CH_3SH favors the reduction of the amount of biosulfur that generally accumu-

lates in highly-loaded H_2S desulfurizing systems, even if artificial feeding of CH_3SH cannot be considered as an economically viable alternative to prevent clogging of the filter bed. Results for a full-scale biotrickling filter [31] treating a biogas flowrate of around 80 $m^3\ h^{-1}$ under the same aerobic conditions studied herein, indicate that the annual cost of externally added CH_3SH is as high as three times the initial investment cost of the biotrickling filter. However, the natural presence of CH_3SH in biogas could be considered as a technical advantage during the biogas desulfurization in biotrickling filters.

Finally, it is worth noticing that no CH_3SH or other mercaptans and polysulfides were fed to any of the reactors prior to the experiment, which confirms that sulfide-oxidizing bacteria developed in aerobic and anoxic biotrickling filters degrading H_2S at neutral pH are capable of degrading CH_3SH or any of the chemical reaction by-products and that no further inoculation of the system is needed.

Overall, results indicate that simultaneous treatment of H_2S and CH_3SH is feasible in the range of concentrations tested without any loss of performance of the desulfurization unit in terms of H_2S removal.

3.3. Effect of EBRT in the simultaneous treatment of CH_3SH and H_2S

The effect of EBRT was studied at constant (E2) and variable (E3) H_2S LR. Results of both experiments showed a larger impact in the RE of CH_3SH in both reactors in comparison with E1 results.

During E2, the RE of CH_3SH gradually decreased from 100% to 47% under aerobic conditions, and from 82% to 25% under anoxic conditions (Fig. 5a). No significant differences were found in terms of loss of efficiency between the aerobic and the anoxic process. Instead, large differences were encountered in terms of elimination capacity between both reactors. Maximum ECs of 1.0 gS-$CH_3SH\ m^{-3}\ h^{-1}$ in BTF1 and 0.43 gS-$CH_3SH\ m^{-3}\ h^{-1}$ in BTF2 were obtained. In comparison to E1, results in E2 indicate that the significant reduction in the RE and EC of CH_3SH was probably caused by mass transfer limitation under the experimental conditions tested.

Although PU foam is a well-known packing material in biofiltration with large surface areas that may help reducing mass transfer limitations [32], clogging problems have been also reported to occur due to biosulfur build-up and accumulation into the packed bed [5]. In addition, high gas velocities of 6480 m h^{-1} were found to contribute to reduce H_2S mass transfer limitations [32]. In this sense, Kim and Deshusses [33] studied, among other parameters, the trickling liquid velocity in a biotrickling filter packed with polyurethane foam and concluded that under low gas flow rates (4000 m h^{-1}), mass transfer from the gas phase to the liquid phase was the limiting factor and the recirculation rate had no effect on H_2S EC. In the present work, the lower gas velocity applied (14–62 m h^{-1} in the aerobic reactor; 6.9–41.6 m h^{-1} in the anoxic reactor) coupled to a reduced solubility of CH_3SH compared to H_2S [17] might have limited CH_3SH removal by mass transfer. Thus, results in E2 indicate that no special advantage was found for PU foam in the anoxic reactor in front of Pall rings used in the aerobic reactor in terms of mass transfer improvement for CH_3SH removal, confirming that the specific surface area of the packing is not that important in terms of mass transfer in desulfurizing biotrickling filters because they are commonly operated at much larger gas contact times compared to biotrickling filters for odor removal.

During E2, the H_2S EC was less affected than the CH_3SH EC by the reduction of EBRT in both reactors (Fig. 5b), because of the progressive decrease of the H_2S inlet concentration and the reduced solubility reported for CH_3SH in comparison to H_2S [17]. In BTF1, H_2S RE decreased from 100% to 95% and from 100% to 86% in BTF2. It is interesting to notice that such H_2S RE above 85% achieved at the lowest EBRT studied (30 s) corresponded to inlet H_2S concentrations between 400 and 500 ppm_v. These results are outstanding, and especially for anoxic degradation, compared to previous works that recommended a minimum EBRTs of 10 min to achieve H_2S RE greater than 95% [34,35]. In addition, critical EBRT were found at around 60 s for the aerobic reactor and at 90 s for the anoxic one. Therefore, 666 and 1294 ppm_v of H_2S can

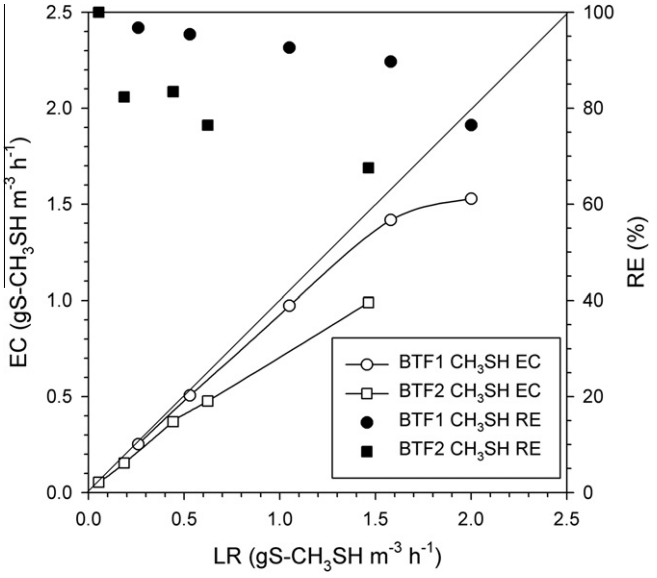

Fig. 3. Elimination capacity and removal efficiency in front of the load of CH_3SH for BTF 1 and BTF2 during E1.

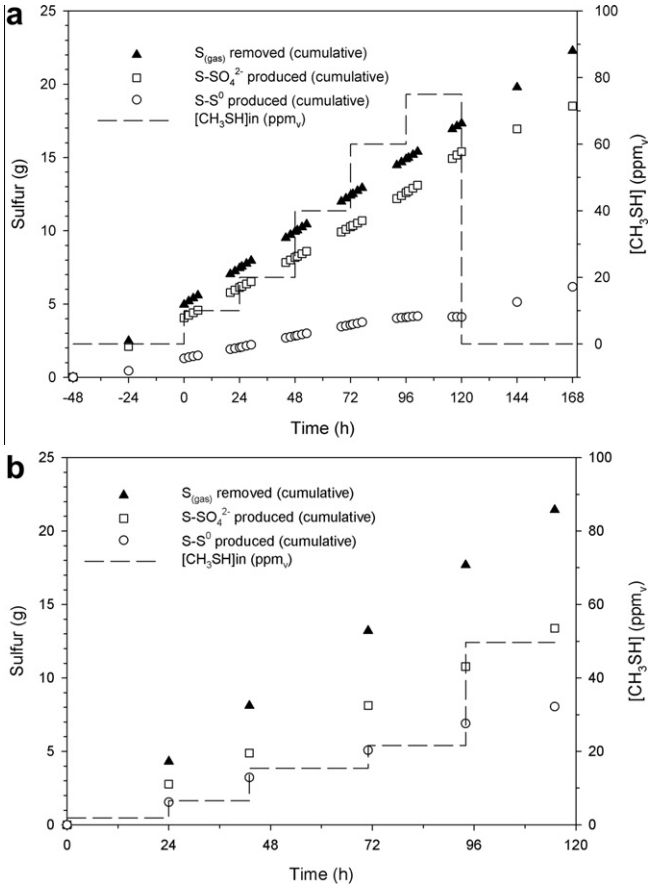

Fig. 4. Sulfur mass balance during E1 for (a) BTF1 and (b) BTF2.

be treated efficiently (RE > 98%) in aerobic and anoxic biofilters at 60 s and 90 s, respectively.

Few references exist on the co-treatment of H_2S and CH_3SH in biotrickling filters. All of them are aerobic biotrickling filters. To the authors' knowledge, there are no previous studies about treatment of H_2S and CH_3SH in biogas in anoxic biotrickling filters. Co-treatment of these compounds has been carried out for odor treatment (low-loads, 65–220 ppm_v H_2S and 26–47 ppm_v CH_3SH) in two-stage biotrickling filters connected in series [29,7]. Generally, the first stage at acidic pH removes most of the H_2S, small amounts of the CH_3SH and organic sulfur compounds. The second step, at neutral pH, removes the rest of organic sulfur compounds. Maximum ECs reached were 47.9 g$S\text{-}H_2S$ m^{-3} h^{-1} and 2.75 g$S\text{-}CH_3SH$ m^{-3} h^{-1} by Ruokojarvi et al. [29] at 61 and 118 s EBRT per stage, while 70.6 g$S\text{-}H_2S$ m^{-3} h^{-1} and 9.8 g $S\text{-}CH_3SH$ m^{-3} h^{-1} were obtained by Ramírez et al. [7] at 60 s EBRT per reactor.

During E3, the effect of a variable H_2S LR due to the decrease of the EBRT was clearly noticed by the impact on the elimination capacity of CH_3SH encountered, if compared to E2 (Fig. 6a). The RE of CH_3SH was reduced from 100% to 16% under aerobic conditions, and from 75% to 18% under anoxic conditions (Fig. 6a). Interestingly, the ECs-LR profile did not follow the profile typically reported in which the EC reaches a plateau at high pollutant loads [36]. Instead, a maximum is observed close to the critical EC value. Later, a progressive decrease of the EC was found as the H_2S and CH_3SH LRs increased. A similar behavior was observed by Ramírez et al. [7] who tested the co-treatment of H_2S, CH_3SH and other mercaptans at neutral pH and found a decrease in the RE of CH_3SH from 83% to 33% when the H_2S inlet concentration was increased from 23 to 376 ppm_v for a CH_3SH inlet load of 2.4 g$S\text{-}CH_3SH$ m^{-3} h^{-1}. It is known that H_2S is removed preferentially than other reduced sulfur compounds under aerobic conditions [37]. Thus, the high H_2S LR produced a crossed, negative effect in the removal of CH_3SH under both aerobic and anoxic conditions. It is worth noting that during the last EBRT period (at 30 s EBRT), the DO concentration measured in BTF1 dropped down to values close to zero, thus indicating that the system was under oxygen limiting conditions for complete H_2S oxidation to sulfate. Instead, partial oxidation to elemental sulfur occurred, which could not be verified through mass balances because of the dynamics of the HRT and the duration of the experiment. At this point, the air supply was increased from 250 mL min^{-1} to 313 mL min^{-1} in an attempt to improve the H_2S removal efficiency, but no significant changes were observed, probably because of the different dynamics between the gas and the liquid phase in E3.

As expected, the effect of EBRT during E3 on the RE of H_2S was considerably significant in both reactors (Fig. 7). In BTF1, the H_2S RE was sharply reduced from 100% to 31%. Despite of the differences between the HRT and the duration of the experiment, data obtained from ORP monitoring indicated a reduction in ORP from 30 mV (at 180 s, LR of 53 g$S\text{-}H_2S$ m^{-3} h^{-1}) to −80 mV (at 30 s, LR of 318 g$S\text{-}H_2S$ m^{-3} h^{-1}). According to Montebello et al. [20] and Fortuny et al. [21], such final ORP value suggests almost no TDS accumulation in the liquid phase and, thus, that mass transfer was the main limiting process. Monitoring of TDS indicated TDS concentrations below the detection limit ($1.5 \times 10^{-5} \pm 0.9 \times 10^{-5}$ M S^{2-}; 0.48 ± 0.29 mg S^{2-} L^{-1}). The critical and maximum EC of H_2S for BTF1 during E3 was found around 100 g$S\text{-}H_2S$ m^{-3} h^{-1}. The EC and RE of H_2S for BTF1 are comparable to the results obtained previously by Fortuny et al. [21] under similar experimental conditions with a different packing material, confirming that CH_3SH did not have any effect in the H_2S removal under the range of conditions tested. After the experimental period, normal operating conditions were resumed and the H_2S RE quickly recovered normal values (around 99%), confirming the high recovery capacity of the system.

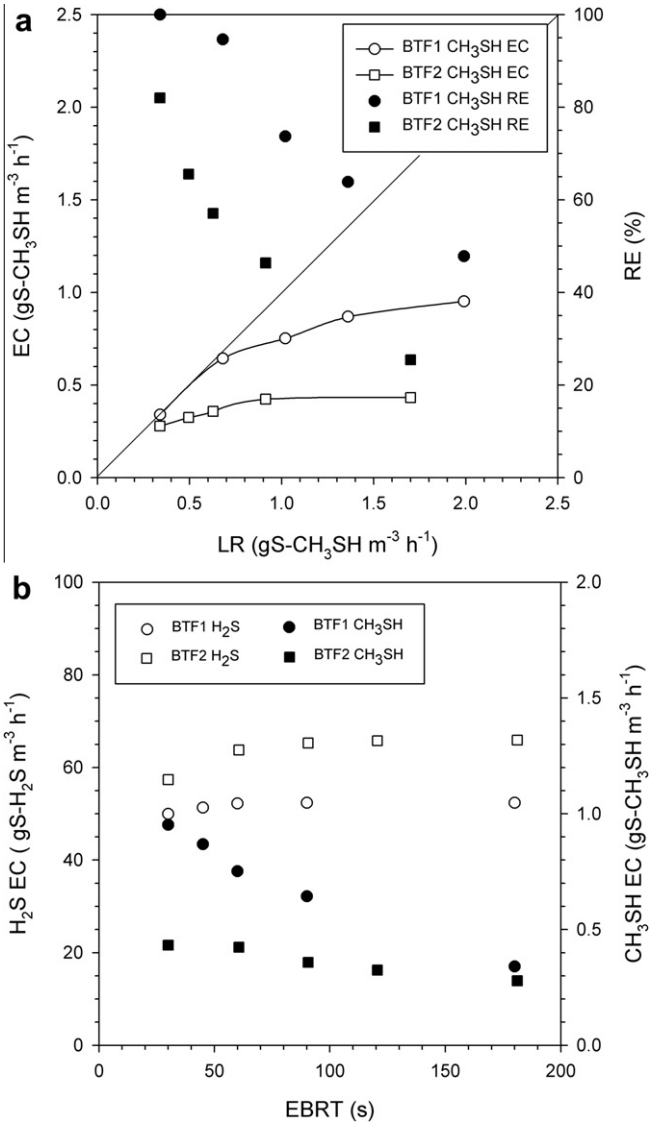

Fig. 5. (a) Elimination capacity and removal efficiency in front of the load of CH_3SH for BTF1 and BTF2 during E2. (b) Elimination capacity of H_2S and CH_3SH in function of the EBRT in BTF1 and BTF2 during E2.

BTF2 showed a decrease of the H_2S RE from 100% to 47% in E3. The critical H_2S EC for BTF2 during E3 was around 100 g$S\text{-}H_2S$ m^{-3} h^{-1}, while the maximum EC was 142 g$S\text{-}H_2S$ m^{-3} h^{-1}. Such ECs are markedly higher than the results obtained by Soreanu et al. [9], who reported a critical EC between 10.6 and 11.8 g$S\text{-}H_2S$ m^{-3} h^{-1} in an anoxic biotrickling filter packed with plastic fibers (EBRT 18 min), and operated with sole H_2S [35]. In addition, a maximum EC of 50 g$S\text{-}H_2S$ m^{-3} h^{-1} was reached at an EBRT of 6 min by Soreanu et al. [38] in an anoxic biotrickling filter. It should be highlighted that such remarkable results found in the anoxic biotrickling filter herein are not necessarily due to the presence of CH_3SH but to other design and operational factors since previous works in the same biotrickling filter without CH_3SH [6] already provided larger ECs than those of Soreanu et al. [38]. For polypropylene Pall rings (specific surface area of 320 m^2 m^{-3}) similar results were obtained with the same inoculum and operational conditions (critical EC of 120 g$S\text{-}H_2S$ m^{-3} h^{-1}, maximum EC of 170 g$S\text{-}H_2S$ m^{-3} h^{-1}) [39]. Thus, the increased EC was attributed to the specific microbial population and its activity developed in the anoxic biofilm. Further research to assess microbial popula-

tions as well as their activity in both biotrickling filters is warranted.

Although not measured, the TDS concentration in the liquid phase probably increased since the ORP dropped from −132 mV (at 180 s, LR of 57 gS-H_2S m^{-3} h^{-1}) to −267 mV (at 30 s, LR of 301 gS-H_2S m^{-3} h^{-1}). Such correlation between TDS and ORP has been previously described by other authors [40,20,21]. In consequence, the anoxic reactor was probably biologically limited at this point. Mass transfer limiting conditions were not observed. Interestingly, the ratio SO_4^{2-}/S^0 produced decreased from 6.2 to 1.2 at LR from 57 to 301 gS-H_2S m^{-3} h^{-1}, respectively, corresponding to an elemental sulfur production increase from 14% to 45%, according to sulfur mass balances. Correspondingly, the NO_3^- supplied versus H_2S removed ratio decreased from an initial value of 1.46 mol N/mol S to 0.6 mol N/mol S at the highest H_2S LR, confirming that the reactor operated under nitrate limiting conditions for complete H_2S oxidation to sulfate. Wang et al. [41] tested several N/S ratios (0.2, 0.4, 0.6 and 0.8 mol N/mol S) during autotrophic denitrification by *T. denitrificans* in flask reactors. They found a large biosulfur production at N/S ratios of 0.6–0.4 mol mol^{-1} when the sulfide concentration was controlled below 300 mg L^{-1}. Also, the $S - SO_4^{-2}/S^0$ ratio obtained by Soreanu et al. [10] was between 0.18 and 0.5 during anoxic biofiltration of H_2S. In addition, incomplete sulfide oxidation was found under nitrate limiting conditions by Krishnakumar and Manilal [42]. Interestingly, complete sulfide oxidation to sulfate was found by Manconi et al. [11] at a N/S ratio of 0.89. The BTF2 behavior was in agreement with such N/S ratios previously reported.

At this point, it is difficult to confirm the cause of such negative effect in the CH_3SH EC due to the H_2S LR increase. Since H_2S is an intermediate product of the biological CH_3SH oxidation [12,43], the biological oxidation of H_2S is preferred by microorganisms over CH_3SH. However, the higher oxygen requirements for the aerobic CH_3SH oxidation Eq. (4) in comparison with the oxygen requirement for H_2S aerobic oxidation Eq. (2) may have also influenced the results under aerobic conditions and, probably, also under anoxic conditions. In the anoxic biotrickling filter, the same trend for the EC of CH_3SH was found even if such EC reduction was not so important as in the case of BTF1 probably due to a larger amount of electron acceptor supplied in the liquid phase compared to that in the aerobic reactor. In any case, both biotrickling filters were at some point limited by the electron acceptor available in the reactor to end up with sulfate as final product of H_2S oxidation. Thus, improving the electron acceptor supply in both systems is warranted to reduce biosulfur accumulation in the packed bed. Variable, H_2S load-depending strategies for the electron acceptor supply are an alternative instead of constant feeding of oxygen or nitrate to the reactor. In addition, since microorganisms involved in CH_3SH and H_2S are not totally identical, further research is needed to identify the microbial populations in the reactor as well as their degradation activities to understand the underlying mechanisms observed in the reactors.

Critical EBRTs for the removal of H_2S during E3 were found around 120 s for both reactors (Fig. 7), which are significantly higher than those obtained during E2 due to the considerably higher H_2S LR applied to the reactors. Overall, results obtained during EBRT reduction experiments indicate that both reactors are capable of treating a H_2S LR as high as 100–140 gS-H_2S m^{-3} h^{-1} at an EBRT of around 120 s. ECs of around 100 gS-H_2S m^{-3} h^{-1} are obtained at an EBRT of 90 s, corresponding to a slight reduction in the RE of both reactor to approximately 95%, suggesting that for EBRTs lower than 90 s, the mass transfer limitation is the main

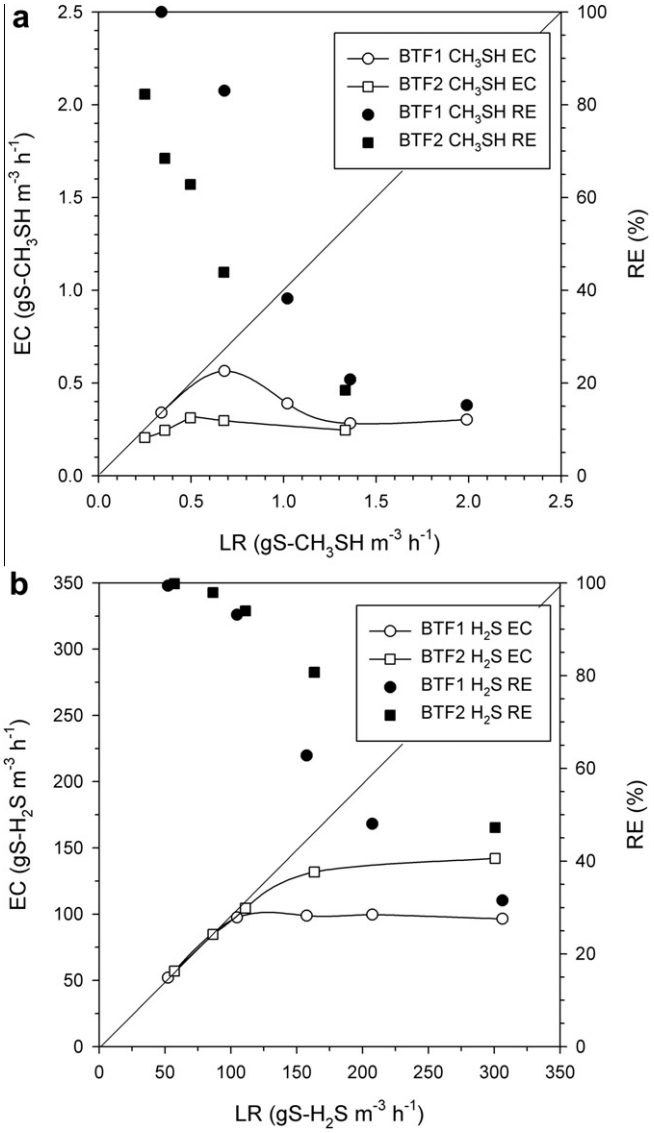

Fig. 6. Elimination capacity and removal efficiency for BTF 1 and BTF2 during E3 in front of the load of (a) CH_3SH and (b) H_2S.

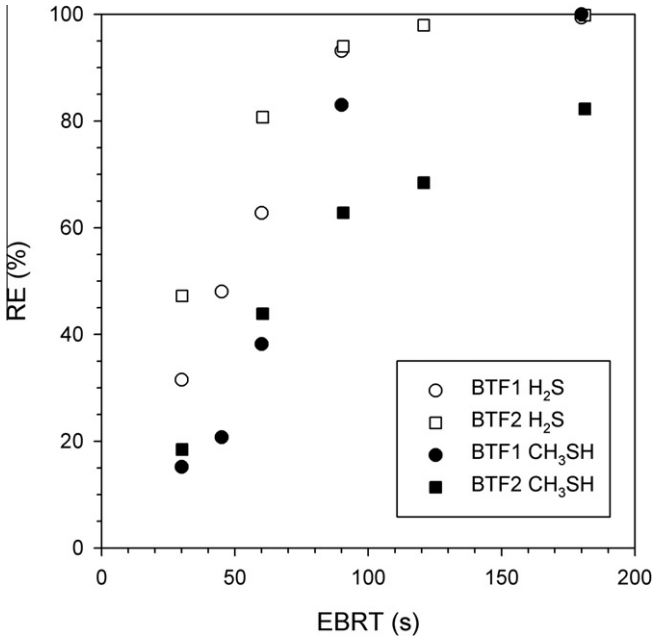

Fig. 7. Removal efficiency of H_2S and CH_3SH as a function of the EBRT in BTF1 and BTF2 during E3.

restriction for the simultaneous removal of CH_3SH and H_2S at the tested conditions, for both aerobic and anoxic reactors. However, such high loads have a detrimental effect over CH_3SH removal.

4. Conclusions

Overall, results showed that co-treatment of H_2S and CH_3SH in biotrickling filters is feasible under aerobic and anoxic conditions, with no detrimental effects in H_2S removal under the typical concentrations of CH_3SH found in biogas. Oppositely, a beneficial effect was found on the performance of the reactors due to the chemical reaction of CH_3SH with elemental sulfur, enhancing the overall reactors performance by minimizing the effects of sulfur accumulation inside the filter bed. Maximum ECs found were 100 g$S\text{-}H_2S$ m^{-3} h^{-1} and 140 g$S\text{-}H_2S$ m^{-3} h^{-1} for the aerobic and anoxic biotrickling filters, respectively. Both reactors were able to treat CH_3SH without prior inoculation because of the already existing sulfide-oxidizing microorganisms grown in the reactors during H_2S treatment. However, an H_2S LR above 100 g$S\text{-}H_2S$ m^{-3} h^{-1} had a negative impact in the CH_3SH treatment capacity mainly caused by substrate competition. The EBRT was parameterized for both aerobic and anoxic biotrickling filters either for H_2S and CH_3SH as main pollutants in biogas desulfurization. According to the results, the EBRT at which the H_2S desulfurization units were sized provided adequate results in terms of CH_3SH treatment.

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