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Operational conditions for start-up and nitrate-feeding in an anoxic biotrickling filtration process at pilot scale

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HIGHLIGHTS

- The recommended pH and inlet load for the start-up are 6.8 and 100 gS m^{-3} h^{-1}.
- The automated feeding of nitrate by ORP increases the stability system.
- The nutrient solution composition enhances the system performance.

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ABSTRACT

A real biogas effluent was desulfurized using an anoxic biotrickling filter at pilot scale. Guidelines and recommendations have been proposed to achieve the correct inoculation and biofilm development. The hydrogen sulfide inlet concentration (4100–7900 ppm_V) was not controlled. The operational variables studied were the hydrogen sulfide inlet load (37–149 gS m^{-3} h^{-1}), biogas flow rate (1–3.4 Nm^3 h^{-1}) and pH (6.8–7.4). Moreover, three nitrate-feeding modes were studied: manual, continuous and automated. Without the addition of nutrients to the nitrate solution, a removal efficiency greater than 95% was obtained for loads in the range 33–55 gS m^{-3} h^{-1} along with an elemental sulfur percentage of 85 ± 5%. The nitrate solution was mainly composed of $NaNO_3$ (500 g L^{-1}), the macronutrients KH_2PO_4 (10 g L^{-1}), NH_4Cl (5 g L^{-1}) and $MgSO_4{\cdot}7H_2O$ (4 g L^{-1}), and trace elements. The critical elimination capacity was 94.7 gS m^{-3} h^{-1} (RE > 99%) on day 119 and the maximum elimination capacity was 127.3 gS m^{-3} h^{-1} (RE = 92.6%) on day 122. The recommended operational conditions for start-up are an inlet load of 100 gS m^{-3} h^{-1}, a pH set-point of 6.8 to reduce sulfide accumulation and nitrate-feeding automated by oxide reduction potential.

1. Introduction

Hydrogen sulfide (H_2S) is the most common reduced sulfur compound in biogas. The H_2S concentration depends on the composition of the fermented organic matter and varies in the range from 500 to 20,000 ppm_V [1]. The use of biogas to generate energy requires an H_2S content below 300–500 ppm_V [2] to avoid corrosion of the machinery and to minimize the level of sulfur dioxide in the exhaust gases emitted into the atmosphere. Biogas desulfurization can be performed by conventional physico-chemical technologies, biological technologies or combined processes [3]. The physico-chemical technologies are expensive to install and maintain, they have high reactant consumption, high pressure and high temperature requirements and they also involve the use of highly toxic compounds [4]. The biological technologies developed for biogas desulfurization allow 'sweeter' operational conditions in terms of pressure, temperature and pH, lower reactant consumption and the avoidance of toxic effluents. In general terms, biotrickling filters (BTFs) are more economical and cleaner than the physico-chemical technologies such as chemical scrubbers [5]. BTFs have been used to remove H_2S from biogas under aerobic [3,6–9] and anoxic [7,10–12] conditions. The critical elimination capacity (EC_{CRIT}) in both aerobic and anoxic BTFs are in the range between 100 and 130 g S–H_2S m^{-3} h^{-1} [6,7,10,11]. The use of anoxic BTFs does have some advantages compared to aerobic systems. For example, the use of anoxic BTFs reduces the risk of explosion, avoids dilution of biogas and has lower limitations on the mass transfer for nitrate compared to oxygen absorption in aerobic BTFs [1,7,11]. In contrast, the cost and the need for large quantities of nitrate can limit the application of anoxic systems. Studies on the use of an anoxic BTF on an industrial scale have not been

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Nomenclature

BTF	Biotrickling filter
CW	Charge water
DSV	Discharge solenoid valve
EBRT	Empty bed residence time
EC	Elimination capacity
EC_{CRIT}	Critical elimination capacity
EC_{MAX}	Maximum elimination capacity
FSV	Feed solenoid valves
IL	Inlet load
OPUF	Open-pore polyurethane foam
OPR	Oxide reduction potential
r_{C,NO_3}	Nitrate consumption rate
r_{G,SO_4}	Sulfate production rate
RE	Removal efficiency
$\%S\text{-}SO_4^{2-}$	Percentage of sulfate
TLV	Trickling liquid velocity
WWTP	Wastewater treatment plant

carried out to date. In contrast, the aerobic BTF system is better understood. Full-scale BTFs have been studied for biogas flow rates between 20 and 350 $m^3\ h^{-1}$ [13] and also 80 $m^3\ h^{-1}$ [9,14].

Activated sludge from a municipal wastewater treatment plant (WWTP) can be used as the inoculum as it has a population with a high variety of microorganisms, although the start-up period can be long (42 days) [6]. An adapted consortium from the primary effluent from a WWTP can also be used [11].

Another important parameter in anoxic BTFs is the electron acceptor (nitrate or nitrite) dosage. Three nitrate-feeding regimes have been studied previously: manual, continuous and automated. In the manual feeding mode [10,12] a concentrated nitrate solution was added when the nitrate concentration measurement on the recirculating liquid was almost completed. In the continuous feeding mode a programed flow of the concentrated nitrate solution was added as a function of the H_2S inlet load (IL) [10]. Moreover, in the programed feeding regime [11] a volume of the concentrated nitrate solution was added discontinuously using the oxide reduction potential (ORP) as the control variable.

The work described here concerned a study of the influence that operational variables have on the start-up of an anoxic BTF at pilot scale to treat a real biogas effluent. The applicability of three nitrate-feeding modes was investigated in the pilot plant with real biogas, with a particular focus on the applicability to a real plant. The main aim was to propose a set of guidelines and recommendations that would enable a faster and more efficient start-up of a biotrickling filter with these features.

2. Material and methods

2.1. Experimental set-up

The anoxic BTF was installed at the WWTP 'Bahía Gaditana' (San Fernando, Spain) and it was fed with biogas from one of their anaerobic digesters. The experimental set-up is shown schematically in Fig. 1. The BTF was built from fiberglass-reinforced polyester and its dimensions were as follows: total height 2100 mm, diameter 500 mm and bed height 850 mm. Open-pore polyurethane foam (OPUF) cubes (800 units, 50 mm side length, 600 $m^2\ m^{-3}$, 35 kg m^{-3}) (Filtren TM25450, Recticel Iberica, Spain) were used as the carrier for biomass immobilization. The volume of the liquid phase under recirculation was 90 L. A gas compressor (N0150ST.9E, KNF Neuberger GmbH, Germany) was used to pump the biogas (maximum flow rate of 7.2 $m^3\ h^{-1}$). The biogas flow rate was regulated using a manual diaphragm valve (VMDV DN25, FIP, Italy) and it was measured by a rotameter (T-003-PVC DN15, Comaquinsa, Spain). The recirculating liquid was pumped using a magnetic centrifugal pump (MC.P P052PP, Plastomec, Italy). The liquid flow rate was measured by a rotameter (R-003-PVC DN40, Comaquinsa, Spain) and it was adjusted using a manual diaphragm valve (VMDV DN32, PIP, Italy). The purge flow rate was set by a diaphragm valve (VMDV DN32, PIP, Italy) and a low-pressure solenoid valve (ESM-8616 DN25, CEME, Italy) was used to automate the purge.

A pressure transmitter (PTX1400-05A-2480, Druck, UK) was installed in the compressor discharge pipeline and three temperature sensors (Pt100, 0–60 °C, 4–20 mA, Jumo, Germany) were located at the inlet/output biogas pipeline and recirculation medium pipeline. A pressure switch (XMPA 06B 0.6–6 bar, Telemecanique, France) was installed in the recirculating pump discharge. Electrical conductivity (5398, Crison Instruments, Spain), pH (5333, Crison Instruments, Spain) and ORP (5362, Crison Instruments, Spain) electrodes were placed in the recirculating pipe for online measurements (Multimeter 44, Crison Instruments, Spain). Three level switches (maximum, working and minimum) (RSF76Y100RV, Cynergy3, UK) were located at the bottom of the column. Nitrate solution and NaOH (48–50% weight/weight, Haupold, Spain) were pumped using two membrane pumps (TEKNA EVO. ALK800NHH000, SEKO, Italy). The water charge was automated using two solenoid valves (PGV-100G, Hunter Industries, USA). The pipeline for the water charge was connected to a treated water line of the WWTP.

A remote control and telemetry system from GSM/GPRS (Hermes TCR200, Microcom, Spain) was selected as a remote monitoring station to record the generated data and send alarms by short message service. The system was automated using a Logo! 0BA6 logic module (Siemens S.A., Spain).

Safety actions were programed into the logic module to protect the system from the occasional failure of certain components. The control and safety actions programed into the system are summarized in Table 1. The two safety actions were total or partial system stop. In both cases, a short message was sent to alert the operator about the stop.

2.2. Nitrate solution

Charge water (CW), i.e., treated water from the WWTP, was used to feed the BTF because of its ready availability and negligible cost. The average parameters of the CW are shown in Table 2. This water was supplemented with a nitrate solution, which was composed of $NaNO_3$ (500 g L^{-1}) in CW. This solution was enriched on day 32 in order to check whether an increase in the nutrient composition could improve the H_2S RE. The nitrate solution was modified as follows: KH_2PO_4 (10 g L^{-1}), NH_4Cl (5 g L^{-1}), $MgSO_4{\cdot}7H_2O$ (4 g L^{-1}), trace element solution SL-4 (5 mL L^{-1}) and a solution of $FeSO_4{\cdot}7H_2O$ (2 g in 1 L H_2SO_4 0.1 N) (10 mL L^{-1}).

The composition of trace element solution SL-4 was as follows: EDTA (0.5 g L^{-1}), $FeSO_4{\cdot}7H_2O$ (0.2 g L^{-1}) and trace element solution SL-6 (100.0 mL L^{-1}). Trace element solution SL-6 was composed of $ZnSO_4{\cdot}7H_2O$ (0.1 g L^{-1}), $MnCl_2{\cdot}4H_2O$ (0.03 g L^{-1}), H_3BO_3 (0.3 g L^{-1}), $CoCl_2{\cdot}6H_2O$ (0.2 g L^{-1}), $CuCl_2{\cdot}2H_2O$ (0.01 g L^{-1}), $NiCl_2{\cdot}6H_2O$ (0.02 g L^{-1}), $Na_2MoO_4{\cdot}H_2O$ (0.03 g L^{-1}).

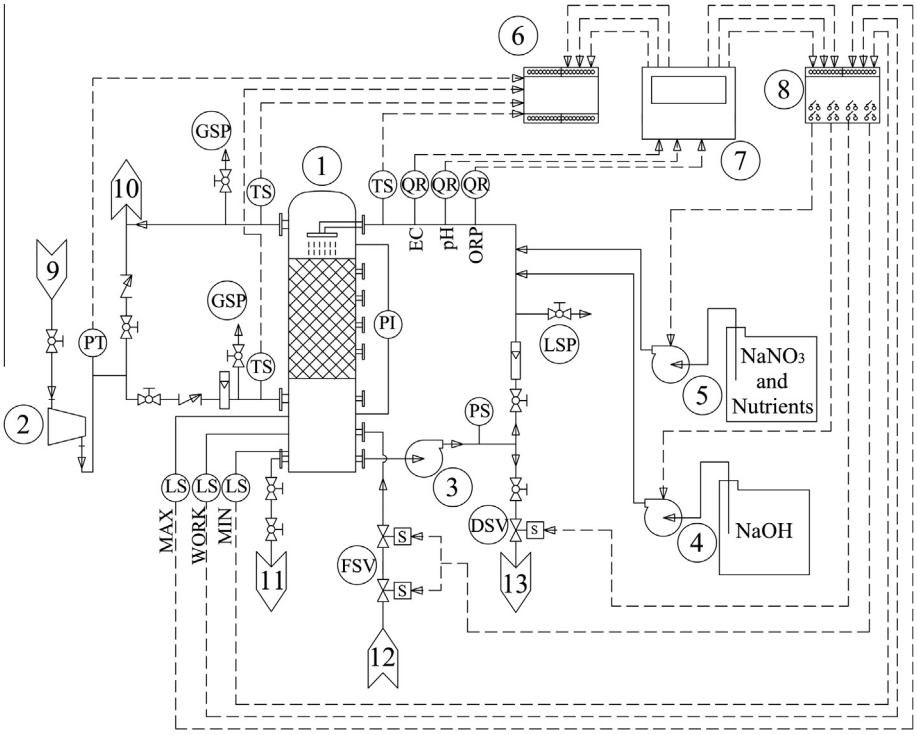

Fig. 1. Experimental set-up. (1) Biotrickling filter; (2) biogas compressor; (3) recirculating pump; (4) NaOH pump; (5) $NaNO_3$ and nutrient pump; (6) data logger TCR-200; (7) transmitter–regulator Multimeter 44; (8) logic module Logo!; (9) anaerobic digester; (10) biogas burning torch; (11) manual water discharge; (12) water charge; (13) automatic water purge; DSV, discharge solenoid valve; FSV, feed solenoid valves; GSP, gas sampling port; LSP, liquid sampling port.

2.3. Analytical methods

The concentrations of CH_4, CO_2 and H_2S in the biogas stream were measured using a gas chromatograph with a thermal conductivity detector (GC-450, BRUKER, Germany) and 'Poraplot Q plot FS 25 m × 0.53 mm' column. The oven temperature was set at 33 °C (2 min) and then ramped 33–80 °C (10 °C min^{-1}), while the injector and detector were set at 150 °C.

A specific gas sensor (GasBadge® Pro, Industrial Scientific, USA) was used to determine H_2S concentrations below 500 ppm_V. Sulfate concentration was measured using the turbidimetric method (4500-SO_4^{2-} E) [15]. Nitrite and nitrate were analyzed by a colorimetric method (4500-NO_2^- B) and an ultraviolet spectrophotometric screening method (4500-NO_3^- B), respectively [15]. Sulfide was measured using a sulfide ISE combined with an Ag/AgCl electrode as reference (sympHony™ Meter, VWR International Inc., USA).

The immobilized biomass was measured according to the method described by Gomez et al. [16] and was expressed as cells per gram of carrier.

2.4. Biotrickling filter operation

The study described here concerns the first 124 operation days of the anoxic BTF. During the start-up, the BTF was tested under different conditions to obtain a valid start-up protocol. The conditions evaluated were the regime for nitrate feeding, the need for nutrients, the influence of pH and the influence of the IL. The measurement of the main species involved made it possible to carry out the mass balances for sulfur and nitrogen and to estimate the biological consumption rates. Finally, the proposed start-up protocol was tested by varying the packing material.

The IL, removal efficiency (RE), elimination capacity (EC), trickling liquid velocity (TLV) and percentage of sulfate (%S-SO_4^{2-}) are described by the following equations:

$$\mathrm{IL}(\mathrm{gS\ m^{-3}\ h^{-1}}) = \frac{C_{in} \cdot F_G}{V_b} \tag{1}$$

$$\mathrm{RE}(\%) = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100 \tag{2}$$

$$\mathrm{EC}(\mathrm{gS\ m^{-3}\ h^{-1}}) = \mathrm{IL} \cdot \frac{\mathrm{RE}(\%)}{100} \tag{3}$$

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

$$\%\mathrm{S\text{-}SO_4^{2-}} = \frac{\mathrm{g\ S\text{-}SO_4^{2-}\ produced}}{\mathrm{g\ S\text{-}H_2S\ reacted}} = \frac{\Delta(C_{\mathrm{S\text{-}SO_4^{2-},R}} \cdot V_R) + C_{\mathrm{S\text{-}SO_4^{2-},P}} \cdot V_P}{\mathrm{EC} \cdot V_b \cdot \Delta t} \cdot 100 \tag{5}$$

where C_{in} and C_{out} are the inlet and outlet H_2S concentrations ($gS\ m^{-3}$), respectively; F_G is the biogas volumetric flow rate ($m^3\ h^{-1}$); V_b is the packed volume (m^3); A is the cross sectional area of the column (m^2); $C_{S\text{-}SO_4^{2-},R}$ and $C_{S\text{-}SO_4^{2-},P}$ are the sulfate concentrations in the recirculation liquid and in the purge liquid ($g\ S\text{-}SO_4^{2-}\ m^{-3}$), respectively; V_R is the recirculating liquid volume (m^{-3}); V_P is the liquid purged (m^{-3}) and Δt is the time increment for the sulfate percentage calculation (h).

The nitrate consumption ($r_{C,NO3}$) and the sulfate production ($r_{G,SO4}$) rates by bed volume ($mol\ m^{-3}\ d^{-1}$) are described by the following equations:

$$r_{C,NO_3^-} = \frac{\mathrm{mol\ NO_3^-\ reacted}}{\mathrm{bed\ volume} \cdot \mathrm{time\ increment}} = \frac{C_{NO_3^-,F} \cdot V_F - C_{NO_3^-,P} \cdot V_P - \Delta(C_{NO_3^-,R} \cdot V_R)}{V_b \cdot \Delta t} \tag{6}$$

Table 1
Control and safety actions programed in Logo! and TCR200.

	Signal	Localization	Limits and possible causes	Actions
Analog	Biogas pressure	Biogas line	Low level (<0.05 bar)	System fully stopped
			Biogas compressor failure	Manual resetting
			Biogas tube breaking	Send short message
			High level (>0.5 bar)	
			Obstruction in biogas line	
	pH	Recirculating liquid line	Low level (<6)	Stop pH control
			NaOH depletion	Send short message
			NaOH pump failure	
			High level (>8.5)	Activate security relay
			Controller relay failure	Send short message
			Set-point (7.4)	pH regulation
	ORP	Recirculating liquid line	Set-point (−300 mV)	Purge recirculating liquid
				Feeding CW and nitrate stock solution
	Temperature	Biogas line, Recirculating liquid line, exterior	No control	Measurement of: – Inlet biogas – Outlet biogas – Recirculating liquid – Ambient temperature
Digital	Liquid level	Bottom tower	Low level (<66 L)	System fully stopped
			FSV failure	Manual resetting
			Liquid line breaking	Send short message
			High level (>100 L)	
			FSV failure	
			DSV failure	
			Work LS failure	
			Working level (82.5 L)	CW feeding limit
	Liquid pressure	Recirculating liquid line	Low level (<0.025 bar)	System fully stopped
			Recirculating pump failure	Manual resetting
			Liquid line breaking	Send short message
			Liquid level failure	
			High level (>0.6 bar)	
			Obstruction in liquid line	

$$r_{P,SO_4} = \frac{\text{mol } SO_4^{2-} \text{ producted}}{\text{bed volume} \cdot \text{time increment}} = \frac{C_{SO_4^{2-},P} \cdot V_P + \Delta(C_{SO_4^{2-},R} \cdot V_R) - C_{SO_4^{2-},F} \cdot V_F}{V_b \cdot \Delta t} \quad (7)$$

where $C_{i,j}$ (mol m^{-3}) is the concentration of the chemical species 'i' in the liquid 'j' (F: nitrate solution; P: liquid purged; R: recirculating liquid); V_j is the volume (m^3); V_b is the bed volume (m^3) and Δt is the time increment (d).

During the experimental period the average temperature of the recirculation medium was 28.0 ± 2.8 °C. The maximum temperature was 37.2 °C (day 5) and the minimum was 20.1 °C (day 14). The average H_2S biogas concentration was 5680 ± 703 ppm_V, the maximum concentration was 7900 ppm_V (day 7) and the minimum was 4100 ppm_V (day 68).

A summary of the experimental conditions is given in Table 3. Inoculation was carried out by mixing 85 L of wastewater from the degritter–degreasing unit with 2.75 L of nitrate solution. A recirculation flow rate of 1500 L h^{-1} (TLV of 7.63 m h^{-1}) and a biogas flow rate of 1 m^3 h^{-1} (empty bed residence time (EBRT) of 600 s) were set during the first 5 days.

In the experiments the following operation variables were not adjusted: temperature of the recirculation medium, H_2S inlet concentration and CW composition. The adjusted operating variables were: biogas flow rate (from 1 to 2.5 m^3 h^{-1}) and recirculation flow rate (constant at 1.5 m^3 h^{-1}, TLV of 7.63 m h^{-1}).

A set of variables was monitored as being indicative of the start-up process (packing colonization and stable biofilm growth): H_2S outlet biogas concentration, nitrate and sulfate concentration in the recirculating liquid, ORP and pH. The most important performance indicators were the H_2S outlet biogas concentration and the rate of nitrate consumption because these are directly related to the microbial activity. The measurement of the ORP in sulfide-oxidizing bioreactors can be used to control the bioprocess [17]. Therefore, an overload in the BTF or a negative effect on microbial activity has consequences for the ORP value due to the accumulation of sulfide and the decrease in ORP.

Three regimes for nitrate feeding were tested: manual, continuous and automated. Manual nitrate feeding was tested during the first 13 days. In the manual regime, the nitrate concentration was measured *ex situ* and 2.75 L of nitrate solution were added when the nitrate concentration fell below 0.5 g N-NO_3 L^{-1}. The nitrate concentration increased to 2.5 g N-NO_3 L^{-1} after the nitrate solution was fed into the system. Continuous nitrate feeding was tested during day 13 and day 41. In the continuous method a constant flow rate of nitrate solution was fed into the system. The nitrate flow rate was modified in order to keep the nitrate concentration below 4 g N-NO_3^- L^{-1} (average: 2.3 ± 0.7 g N-NO_3^- L^{-1}). This flow rate was calculated every day depending on the measured nitrate concentration in the recirculating liquid and its consumption rate. The automated regime was a modification of the method proposed by Fernandez et al. [10]. In this feeding regime, the nitrate solution was fed in discontinuous mode using a feedback control and the ORP measurement as a control variable. When the nitrate was

Table 2
Charge water parameters.

	Average	Standard deviation
pH	7.67	0.05
SS (mg L^{-1})	19.21	6.21
COD (mg L^{-1})	73.70	12.06
BOD (mg L^{-1})	16.55	2.72
NH_4^+ (mg N L^{-1})	53.57	6.54
NO_2^- (mg N L^{-1})	0.60	0.63
NO_3^- (mg N L^{-1})	1.59	1.00
N total (mg L^{-1})	55.91	5.94
PO_4^{3-} (mg P L^{-1})	2.30	1.45
P total (mg L^{-1})	3.63	0.83
S^{2-} (mg L^{-1})	<0.1	

Table 3
Summary for operating conditions during experimentation.

Time [days]	Duration [days]	Nitrate dosage	Action	Q [$m^3 h^{-1}$]	Nutrients	pH	T [°C]	H_2S inlet [ppm_V]
0–5	5	Manual	Adaptation	1	NO	Uncontrolled (6.2 – 7.8)	24–37	4800–7100
5–11	6		High Load	2.4 and 1.6			21–36	5800–7900
11–13	2		Recovery	1			22–32	6600–7300
13–28	15	Continuous					20–34	5500–6600
28–32	4		Biogas Shutdown	0			23–31	
32–35	3				YES		24–32	
35–39	4		Low Load; pH rising	1			25–34	4600 – 5300
39–41	2					6.8	24–30	
41–54	13	Automatic					23–34	5100–5800
54–56	2			1.4			25–32	4800–5200
56–60	4					7.0	25–35	4700–4800
60–63	3					7.2	23–30	4800–4900
63–83	20					7.4	20–36	4100–5800
83–98	15		Recovery	1		6.8	21–33	4600–6000
98–124	26		Load study	1–3.4		7.4	23–33	5000–6900

depleted in the recirculation medium the decrease in the ORP value was very rapid, but once a volume of nitrate solution was fed into the system the ORP returned to normal working values. When the ORP setpoint (−300 mV) was reached two sequential actions occurred:

- Firstly, the automated control opened the discharge solenoid valve (DSV) for a programed time (estimated to purge the desired liquid volume (25 L)).
- Secondly, when the DSV was closed, the control started the nitrate feeding pump (for a programed time to reach the desired nitrate solution addition volume (2.5 L)) and opened the feed solenoid valves (FSV) until the working liquid level had been reached. At this point the nitrate concentration reached 2.1 $N\text{-}NO_3^-$ L^{-1}.

2.5. Lab-scale BTF for the verification of the start-up protocol

The verification of the start-up protocol was carried out using a lab-scale BTF fed with synthetic biogas. The diameter was 7.14 cm and the packed bed volume was 3.2 L. The packing material was 16 mm polypropylene Pall Rings (Pall Ring Company, UK). The recirculation liquid was pumped using a peristaltic pump (Masterflex®, Cole–Parmer, USA) with a counter-current flow model and with a TLV of 10 m h^{-1}.

The synthetic gas (180 s EBRT) consisted of a mixture of N_2 (65%), H_2S (ranged between 1831 and 3362 ppm_V) and CO_2 (balanced) and this was formed by mixing measured amounts of pure gases by mass flow controllers (Bronkhorst, The Netherlands). A Multimeter 44 (Crison Instruments, Spain) was used for pH and ORP measurements. The pH was controlled at 6.8–6.9 by the addition of H_3PO_4 (2 M) and NaOH (5 M). The outlet H_2S concentration was monitored on-line with an electrochemical H_2S sensor (Sure-cell, Euro-Gas Management Services Ltd., UK). The H_2S measurement range was 0–200 ppm_V. The gas stream was diluted with air to allow the H_2S measurement (dilution factor of 1:170). The outlet H_2S concentration was also monitored discontinuously using a specific gas sensor (GasBAdge® Pro, Industrial Scientific, USA).

The nitrate solution feed was carried out manually during the first 24 h. After this period, the nitrate was automated by ORP as described above.

3. Results and discussion

3.1. Manual and continuous nitrate feeding regime

In the first few days, just after the inoculation, the RE was greater than 98% (day 2). This high RE could be due to the low IL

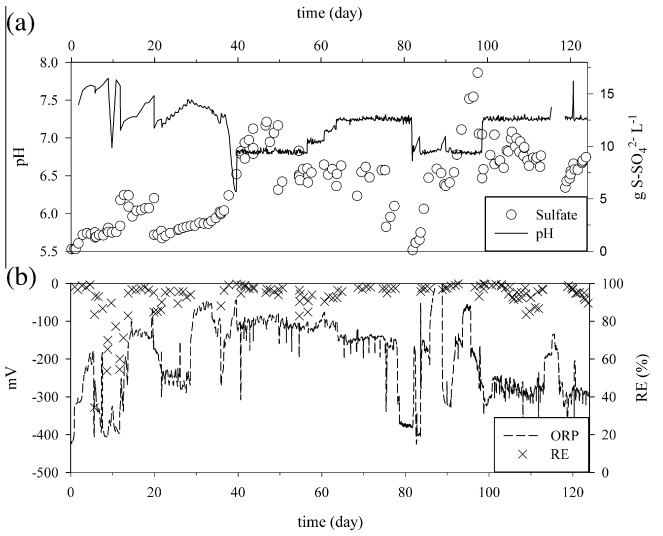

Fig. 2. Adaptation and Start-up: pH stabilization and biomass immobilization. (a) pH and sulfate. (b) ORP and RE.

(50 gS m^{-3} h^{-1}) and high EBRT (600 s) because the time is very short for a good biofilm development. The initial IL was set to 'soft' conditions compared with the EC_{CRIT} reported (around 100 gS m^{-3} h^{-1}) for anoxic laboratory BTFs [7,10,11] as such conditions are suitable for biomass immobilization in the initial steps. The ORP values increased from −422 mV to −314 mV (Fig. 2) and, consequently, the sulfide concentration in the recirculation medium decreased. The nitrate concentration decreased from 2.45 to 2.11 g $N\text{-}NO_3^-$ L^{-1} and the sulfate concentration reached 0.75 g $S\text{-}SO_4^{2-}$ L^{-1}. During the fifth day, the first manual nitrate solution dosage was carried out and, 172 min before the addition, the ORP had decreased to −406 mV due to an increase in the sulfide concentration in the recirculating liquid and the RE dropped to 34%. After the nitrate solution was fed into the system (day 5) a nitrate concentration of 2.7 g $N\text{-}NO_3^-$ L^{-1} was reached in the recirculating liquid and rapid increases in ORP (−300 mV) and RE (83%) occurred. The average RE was 98% during the first 5 days. As a result, the biogas flow rate was increased to 2.4 m^3 h^{-1} (EBRT of 250 s). The RE decreased to 55–65% due to inhibition caused by a high sulfide concentration (ORP decreased to −407 mV). The high IL (147 gS m^{-3} h^{-1}) and the lack of stable biofilm probably caused the accumulation of sulfide. During this period (days 5–11) the pH was above 7.6 (higher than the pk_{a1} (7.04)) and this favors H_2S solubility. In order to recover the high RE, the IL was reduced by decreasing the biogas flow rate to 1.6 m^3 h^{-1} (day 6–11) and this improved the RE to 89% with low sulfide accumulation (day 9).

The instability of the process for the treatment of high IL in the initial stages indicated that a stress situation should be avoided while the biofilm growth was carried out properly. Such stress could be caused by, for example, acidic pH (pH < 6) or basic pH (pH > 8) conditions, periods of nitrate exhaustion and sulfide accumulation in the recirculating liquid. A pH slightly lower (6.8) than pk_{a1} increases the stability of the biofilm formation process, because it reduces the sulfide concentration in the liquid (H_2S and dissociated species) and allows the system to function at high IL during the start-up.

During the first 40 days the pH was unstable and was difficult to adjust, as can be seen in Fig. 2(a). During this stage several actions were carried out to adjust the pH:

- The addition of an acid solution on day 11 (concentrated H_2SO_4 (96% weight/weight)). The addition of the acid solution was managed with a pH controller (set-point 6.8). Although it was possible to adjust the pH rapidly, a high consumption of acid and accumulation of sulfate in the medium were observed. This option was therefore not considered to be viable. Sulfate could have an inhibitory effect on RE and Fernández et al. [10] recommended that a sulfate concentration greater than 33 g SO_4^{2-} L^{-1} should be avoided.
- IL decrease (day 11–28). A reduction was expected in the percentage of elemental sulfur produced (Eq. (8)). During this period there was an increase in the generation of sulfate, but this was not sufficient to maintain the pH in a controlled range (6.8–6.9).
- Stopping the biogas feed (day 28–36) in order to allow the conversion of accumulated elemental sulfur in the packing bed to sulfate (Eq. (9)). There was a decrease in pH and an increase in the concentration of sulfate, which followed the same trend as in the previous stage. On day 33 a greater level of acidification was observed along with changes in the slope of the pH measurement and an increase in the generation of sulfate with respect to the previous days (28–33).

$$H_2S + 0.4NO_3^- + 0.4H^+ \xrightarrow{\text{microorganisms}} S^0 + 0.2N_2 + 1.2H_2O \quad (8)$$

$$S^0 + 1.2NO_3^- + 0.4H_2O \xrightarrow{\text{microorganisms}} SO_4^{2-} + 0.6N_2 + 0.8H^+ \quad (9)$$

- Addition of nutrients. During the early stages it was decided not to enrich the liquid recirculation with an external supply of nutrients. This did not prevent the development of a community of microorganisms capable of oxidizing H_2S and the RE was higher than 95% at certain times during the experiment. However, the low sulfate and proton production could suggest some limitation in the microbial activity due to a lack of micro- and/or macronutrients. As a consequence, the medium recirculation was enriched from day 32 (see Section 2.2). There was also a greater percentage of sulfate produced along with the consequent drop in pH and improved disposal capacity. The average RE before nutrient supply (days 22–28) was 94.2%. During the subsequent days (days 36–42), after nutrient feed, the mean RE increased to 98%. Matějú et al. [18] described several cases in which a low phosphate concentration affected the stability and performance of the denitrification process. Gauntlett [19] showed the need to supply 1.5 mg PO_4^{3-} L^{-1} to achieve stable operation in a continuous denitrification process. Therefore, it could be suggested that the phosphate concentration in the CW (Table 2) is not sufficient for proper operation of the anoxic BTF. A study into the nutrient requirements will be needed to confirm that phosphate is the limiting compound.

In summary, during the start-up of an anoxic BTF for biogas desulfurization it is very important to avoid a high sulfide concentration in the recirculation liquid. The nutrient supplement stimulates the metabolism of microorganisms and increases the percentage of sulfate produced, thus allowing better pH control. However, further studies are required on the nutrient requirements for a sulfide-oxidizing and nitrate-reducing microbial population.

3.2. Automated nitrate feeding regime

From day 41 the nitrate feeding was automated using the ORP value (see Section 2.4). The biogas flow rate was 1 m^3 h^{-1} and the pH set point was 6.8 between days 41 and 54 and, under these conditions, the average RE was 97.0%. Between days 54 and 63, the biogas flow rate was 1.4 m^3 h^{-1} and the pH set point was increased progressively from 6.8 to 7.4 without sulfide accumulation or system instability. The increase in pH led to an improvement in the RE from 90.7% to 97.8%. Thus, once good biomass growth has been achieved it is recommended that the pH set-point is increased to 7.4. The biomass concentration was $10 \pm 0.7 \times 10^{10}$ cell (g of carrier)$^{-1}$ at the bottom of the bed and $6.99 \pm 2 \times 10^{10}$ cell (g of carrier)$^{-1}$ at the top on day 56. Fernandez et al. [11] reported a lower biomass concentration ($(2.79 \pm 0.28) \times 10^{10}$ cells (g of carrier)$^{-1}$) on using an anoxic BTF and OPUF as carrier. Consequently, it was considered that good biofilm development had been achieved in the present study.

A plot of IL vs the EC is shown in Fig. 3. This study was carried out between days 98 and 111. The IL was between 40 (EBTR 600 s) and 117 gS m^{-3} h^{-1} (EBTR 273 s). The EC_{CRIT} value was 51.9 gS m^{-3} h^{-1} (RE > 99%) on day 102 and the EC_{MAX} was 109 gS m^{-3} h^{-1} (RE = 92.5%) on day 109. Both EC_{CRIT} and EC_{MAX} were lower than those reported in previous studies on a laboratory scale. The main operational conditions for the anoxic BTF and results for this work and previous studies are summarized in Table 4. Montebello et al. [7] studied an anoxic BTF on the laboratory scale with OPUF as the carrier. In this system values of 100 and 140 gS m^{-3} h^{-1} were obtained for EC_{CRIT} and EC_{MAX}, respectively. Fernandez et al. [11] also used OPUF as the carrier and they obtained similar values (99.8 and 169 gS m^{-3} h^{-1}, respectively).

The results obtained in this study were lower than those mentioned above – probably due to the scale-up process. In this

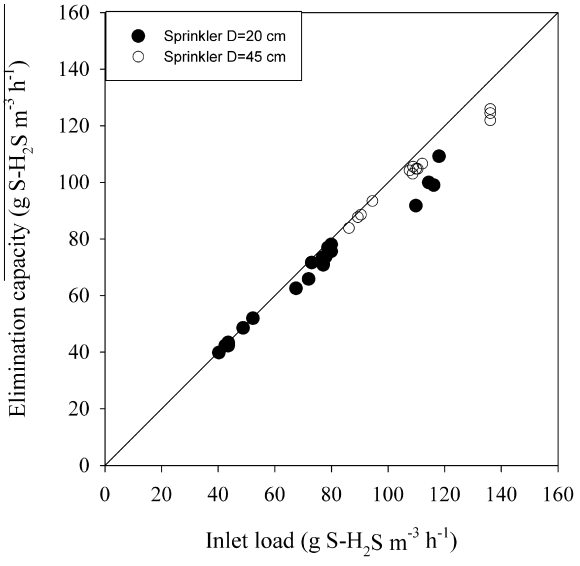

Fig. 3. Effect of the IL on the EC.

Table 4
Summary of anoxic BTF conditions and main results.

Reference	Packing material	Height/diameter	Packed bed (L)	pH	TLV ($m\ h^{-1}$)	EBRT (s)	EC_{CRIT} ($gS\ m^{-3}\ h^{-1}$)	EC_{MAX} ($gS\ m^{-3}\ h^{-1}$)
[7]	OPUF	2.6	2.37	7.4–7.5	7	30–181	100	142
[10]	Polypropylene Pall rings	2.3	2.4	7.4–7.5	2.1–18.9	144–1028	120	171
[11]	OPUF	2.6	2.37	6.8–7.5	2.3–21	144–258	130	170
[12]	Plastic fiber	4.52	12	6–7	1.7	617–4320	11.25–12.5	12.5–14.5
This work	OPUF	1.7	168	6.8–7.4	7.63	176–600	94.7	127.3

scale-up process the RE decreased, probably due to the formation of preferential paths. Therefore, a better distribution of the liquid on top of the bed is required to prevent and/or reduce the presence of dry support. As a consequence, the liquid sprinkler was replaced by a larger diameter sprinkler (20–45 cm) to increase the liquid dispersion at the top of the bed. The change in the sprinkler led to an improvement in the BTF performance and, under these new conditions, EC_{CRIT} was 94.7 $gS\ m^{-3}\ h^{-1}$ (RE > 99%) on day 119 and EC_{MAX} was 127.3 $gS\ m^{-3}\ h^{-1}$ (RE = 92.6%) on day 122.

3.3. Sulfur and nitrate mass balances and effect of the N:S ratio on H_2S removal

The average sulfate concentration was 6.1 ± 3.7 g $S\text{-}SO_4^{2-}\ L^{-1}$, the minimum concentration was 0.1 g $S\text{-}SO_4^{2-}\ L^{-1}$ (day 82) and the maximum was 17 g $S\text{-}SO_4^{2-}\ L^{-1}$ (day 97). The lowest nitrate concentration measured was 0.01 g $N\text{-}NO_3^-\ L^{-1}$ (day 40) and the highest nitrate concentration was 3.6 g $N\text{-}NO_3^-\ L^{-1}$ (day 18). The maximum nitrite concentration was 0.1 g $N\text{-}NO_2^-\ L^{-1}$ (day 88, recovery period) and in normal operation the nitrite concentration ranged between 0 and 0.01 g $N\text{-}NO_2^-\ L^{-1}$.

The evolution of sulfur species and nitrate is represented in Fig. 4(a). The elemental sulfur was estimated on the basis of the sulfur mass balance by subtracting the amount of $S\text{-}SO_4^{2-}$ produced from the $S\text{-}H_2S$ removed [20]. Two stages can be identified in this process. In the first stage, i.e., the period without nutrient supply (from day 1 to 32), the main biological product was elemental sulfur (85 ± 5%). In the second stage, once the nitrate solution had been enriched with nutrients (day 32), the sulfate percentage increased (67 ± 16%). The percentage of sulfate generated was influenced by changes in the operating conditions, mainly by the increase in the IL and/or the increase in the available sulfide. Thereby, a drop in the sulfate percentage was observed between days 5 and 8, from 17% to 8%, because the IL increased from 45 to 110 $gS\ m^{-3}\ h^{-1}$. Furthermore, the increase in the sulfide solubility caused by the rising pH between days 54 and 68 led to a decrease in the sulfate percentage (69–40%). Thereafter, at the same IL and pH, the sulfate percentage increased to 95% and it can be suggested that the microbial community had adapted to the new operating conditions and a high sulfate percentage production was recovered.

During the first 13 days the nitrate consumption rate was 22.0 mol $N\text{-}NO_3^-\ m^{-3}\ d^{-1}$, the sulfate production rate was 7.3 mol $S\text{-}SO_4^{2-}\ m^{-3}\ d^{-1}$ and the N:S molar ratio was 0.5. From day 40, once the nutrient supply had started, the nitrate consumption rate increased appreciably. The minimum value was coincident with day 40 and this was 42.5 mol $N\text{-}NO_3^-\ m^{-3}\ d^{-1}$. The maximum value was 91.6 mol $N\text{-}NO_3^-\ m^{-3}\ d^{-1}$ on day 109, which was also the day with the highest IL (120.3 $gS\ m^{-3}\ h^{-1}$).

Biological denitrification has been widely studied and the results obtained in this work are consistent with data published by other authors. Matějů et al. [18] studied a system with fixed beds and they reported maximum nitrate consumption rates of 107 and 77 mol $N\text{-}NO_3^-\ m^{-3}\ d^{-1}$ for heterotrophic and autotrophic denitrification, respectively. For the anoxic biological desulfurization of biogas the available literature data have lower values.

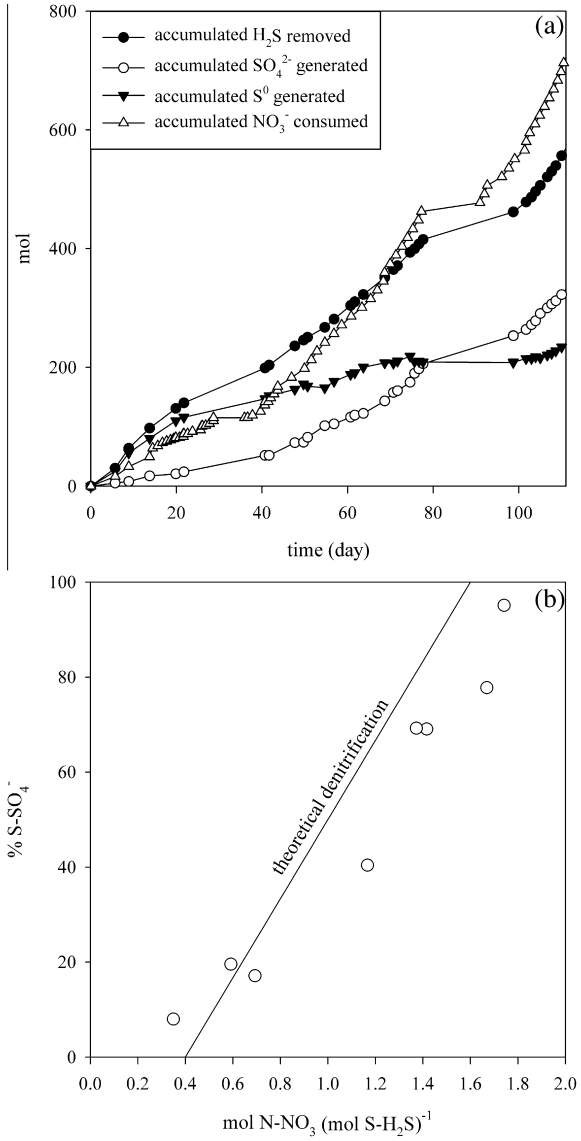

Fig. 4. (a) Consumption and production of the sulfur species and nitrate. (b) Relationship between the percentage of sulfate and the N:S molar ratio. The points represent experimental data and the line represents a theoretical complete denitrification.

Fernandez et al. [11] obtained a nitrate consumption rate between 10.3 ± 2.9 and 68.3 ± 13.3 mol $N\text{-}NO_3^-\ m^{-3}\ d^{-1}$, with the lower value obtained for IL up to 74 $gS\ m^{-3}\ h^{-1}$ and a maximum nitrate concentration of 0.43 g $N\text{-}NO_3^-\ L^{-1}$. The higher value was obtained with IL up to 186 $gS\ m^{-3}\ h^{-1}$ and a maximum nitrate concentration of 1.7 g $N\text{-}NO_3^-\ L^{-1}$.

The relationship between the sulfate produced and the N:S molar ratio is represented in Fig. 4(b). The experimental N:S molar ratio was between 0.34 and 1.74 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$ for

percentages of sulfate produced of 8% and 95%, respectively. These experimental results are consistent with complete denitrification. Soreanu et al. [12] observed a nitrogen requirement between 0.57 and 1.07 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$ for 35% sulfate produced and this N:S molar ratio was higher due to the accumulation of nitrite as an intermediate in the reaction. Soreanu et al. [21] found in steady-state operation an N:S molar ratio of 0.78 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$, 15% of sulfate and 31% nitrite formed. Fernandez et al. [10] reported an average N:S molar ratio of 0.77 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$ and a sulfate percentage of 31.6% under nitrate limiting conditions, and these values are consistent with the results obtained in this work. Fernandez et al. [11] plotted the N:S molar ratio (from 0.47 to 1.61 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$) versus the percentage of sulfate (30–83%) for IL between 57 and 167 gS m^{-3} h^{-1}. The N:S molar ratio was slightly higher than that obtained in present work, probably due to nitrite accumulation.

The process favors the complete oxidation of H_2S to sulfate and this avoids the accumulation of elemental sulfur in the bed (reducing clogging problems). However, this process increases the nitrate and base (e.g., NaOH) consumption (Eqs. (8) and (9)). In contrast, when the production of elemental sulfur is favored the nitrate spend is reduced and this causes proton consumption, which in turn requires acid to adjust the pH. Currently, the accumulation of elemental sulfur is avoided by carrying out scheduled stops in which the biogas feed is stopped for a period of time, with the consequent loss of the overall performance of the process. Alternatively, this problem can be solved by mechanical cleaning or replacement of the packing material, both of which increase the cost of the process. In each case, an individual economic study must be carried out to analyze the most desirable subproduct, e.g., when a cheap nitrate source is available a process guided to produce sulfate will reduce operational problems without increasing the cost.

In summary, it can be concluded that in the anoxic pilot BTF the denitrification is complete and the sulfate percentage depends on the N:S molar ratio. In addition, it can be concluded that in periods of stress (lack of nutrients, high IL and/or pH) the percentage of sulfate was lower than in normal operation.

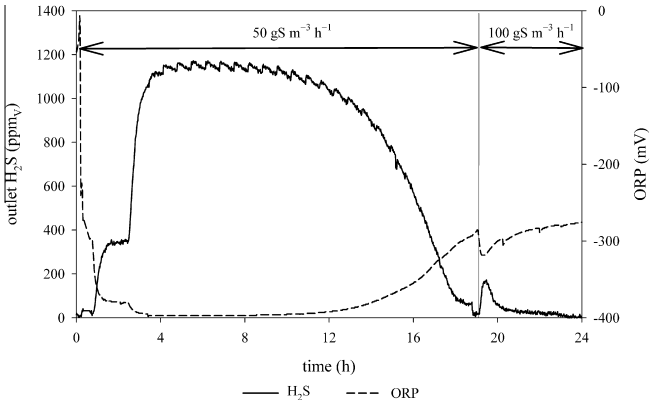

Fig. 5. Outlet H_2S concentration and ORP in the first 24 h of the inoculation verification.

3.4. Start-up protocol verification

The proposed start-up protocol contains three main recommendations:

(1) Soft IL (100 gS m^{-3} h^{-1} in the first 24 h).
(2) pH = 6.8 to reduce sulfide accumulation.
(3) Initial nitrate concentration of 2.5 g $N\text{-}NO_3^-$ L^{-1} and nitrate feeding automated by ORP after 24 h.

The start-up protocol was verified on a lab-scale system (see Section 2.5). The outlet H_2S concentration and the ORP during the first 24 h of the inoculation period are shown in Fig. 5. During the first 19 h the input load was 50 gS m^{-3} h^{-1}, the outlet H_2S concentration increased to 1172 ppm_V (RE = 36%) and the ORP dropped to −398 mV (first 4 h). In the period between hours 8 and 12, the outlet H_2S concentration decreased and the ORP increased due to the microbial activity. At hour 19, which is marked by arrows in Fig. 5, the IL increased to 100 gS m^{-3} h^{-1}. The increase in the IL did not have any effect on the biotrickling filter performance after 1 h. The RE was higher than 99% over the next 24 h. The biotrickling filter had been running for 5 months with an average input load of 100 gS m^{-3} h^{-1} and an RE higher than 99%.

In the first 24 h the average nitrate consumption rate was 7.8 mol $N\text{-}NO_3^-$ m^{-3} d^{-1}, the sulfate production rate was 4.24 mol $S\text{-}SO_4^{2-}$ m^{-3} d^{-1} and the N:S molar ratio was 0.4 (22% $S\text{-}SO_4^{2-}$). In the following 10 days the sulfate percentage produced rose to 60% and the N:S molar ratio to 1.13 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$. In subsequent days up to the 16th day, the sulfate percentage was 71 ± 2% and the N:S molar ratio was 1.24 mol $N\text{-}NO_3^-$ (mol $S\text{-}H_2S)^{-1}$. The N:S molar ratio is consistent with complete denitrification, i.e., similar to that obtained at the pilot scale. We considered that the start-up period had ended at day 16 because the N:S molar ratio and the sulfate production rate had been constant over the previous few days.

3.5. Resolving operational problems in the pilot scale biotrickling filter

Four operational problems occurred in the pilot scale BTF (Table 5). The mechanical pressure switch failure was caused by vibrations due to the recirculation pump and the power shutdown was caused by the electricity supplier. In both cases, the system was completely stopped for periods between 4 and 6 h but these shutdowns did not have any adverse effect on the RE. On two occasions the charge water supply fell and in these cases the control actions were modified: the purge water was canceled when the water level did not reach the work level switch for 5 min. The final general problem was clogging of the packed bed by the accumulation of elemental sulfur. This failure caused a rapid accumulation of sulfide and a subsequent fall in ORP below the set-point (#A in

Table 5
System component malfunctions, their effect on the system and resolution of the problems.

General problem	F[a]	Result/effect on system	Resolution
Mechanical switch pressure fail	4	The BTF was shutdown	Replacement of mechanical pressure switch by a digital one and manual resetting
Power shutdown	1	The BTF was shutdown	Manual resetting
Charge water supply fell down.	2	Recirculation water discharge till to reach minimum level switch and then the BTF was shutdown	Change in the control actions. Manual resetting
Clogging	1	ORP decreased; nitrate solution was exhausted; water were continuously feeding and NaOH was consumed	Change in the control actions. Replace sprinkler

[a] Frequency.

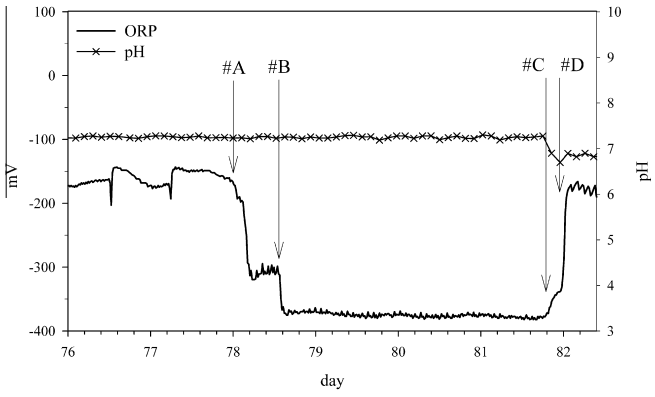

Fig. 6. ORP and pH during sprinkler failure by clogging. #A: rapid accumulation of sulfide; #B: depletion of the nitrate solution; #C: depletion of the NaOH solution; #D: manual resetting.

Fig. 6). Therefore, the nitrate solution (#B in Fig. 6) and the NaOH solution (#C in Fig. 6) were depleted. Manual resetting of the system was performed (#D in Fig. 6) and the control actions were modified: The system was fully stopped when the ORP value was below the ORP setpoint for 30 min. A recovery stage (16 days) was subsequently carried out: the pH set-point was set to 6.8 and the biogas flow rate was decreased from 1.4 to 1 $m^3\ h^{-1}$. In any case, during the recovery stage the RE reached values up to 97%.

4. Conclusions

A set of guidelines should be considered to ensure the proper start-up of an anoxic biofilter for the removal of H_2S present in biogas:

- In the early stages of inoculation it is important to avoid, where possible, the accumulation of sulfide. We recommend a soft input load, around 100 gS $m^{-3}\ h^{-1}$, and a pH set-point of 6.8 to reduce sulfide solubility.
- Even without the addition of external nutrients, a good RE is achieved for a load of around 50 gS $m^{-3}\ h^{-1}$ but nutrient dosage favors the complete oxidation of hydrogen sulfide to sulfate, thus delaying the possible problems of clogging caused by accumulation of elemental sulfur and allowing better control of pH by the addition of NaOH.
- The automated feeding of nitrate was controlled by measuring ORP. This approach was suitable to avoid extended periods of depletion and accumulation of sulfide in the recirculation medium, but it does not prevent a drop in performance when the nitrate concentration is low.

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