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

Fernando Almenglo *, Martín Ramírez, José Manuel Gómez, Domingo Cantero

Department of Chemical Engineering and Food Technologies, Faculty of Sciences, University of Cadiz, Campus de Excelencia Agroalimentario ceiA3, 11510 Puerto Real (Cádiz), Spain

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

* Corresponding author. Tel.: +34 956016561; fax: +34 956016411.
E-mail address: fernando.almenglo@uca.es (F. Almenglo).

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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}).