



Where does the removal of H₂S from biogas occur in microaerobic reactors?



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HIGHLIGHTS

- The location for H₂S removal from biogas in microaerobic reactors is studied.
- A reactor with a total volume of 266 L and variable volume of headspace is operated.
- With 25.0 L of gas space, H₂S-free biogas is achieved.
- The H₂S concentration approaches anaerobic values with a smaller headspace (0.3 L).
- The biogas O₂ content increases drastically when the gas space is reduced.

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ABSTRACT

In order to maximise the efficiency of biogas desulphurisation and reduce the oxygen cost during microaerobic digestion, it is essential to know how the process occurs. For this purpose, a reactor with a total volume of 266 L, treating 10 L/d of sewage sludge, was operated with 25.0 L and without headspace. Under anaerobic conditions, the H₂S concentration in the biogas varied between 0.21 and 0.38%v/v. Next, O₂ was supplied from the bottom of the reactor. At 0.25–0.30 NLO₂/L_{fed}, the biogas was entirely desulphurised, and its O₂ content remained below 1.03%v/v, when the digester had 25.0 L of gas space. However, with almost no headspace, the H₂S content in the biogas fluctuated from 0.08 to 0.21%v/v, while the average O₂ concentration was 1.66%v/v. The removed H₂S accumulated in the outlet pipe of the biogas in the form of S⁰ due to the insufficient headspace.

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1. Introduction

Anaerobic digestion is a well-established technology that transforms a large part of the organic matter content of many wastes into a renewable energy source: biogas. It is utilised for heat, steam, electricity, cooling, chemical and protein production, as fuel for vehicles and fuel cells, and for injection into natural gas grids (Holm-Nielsen et al., 2009). Though substantially inferior to other common fuels such as compressed natural gas, which produces 8600 kcal/m³, it has a good calorific value (5000 kcal/m³) (Abbasi et al., 2012).

Abbreviations: BRT, biogas residence time; HRT, hydraulic retention time; HS, headspace; OLR, organic loading rate; SOB, sulphide-oxidising bacteria; VS, volatile solids.

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Biogas is a mixture of gases whose composition depends on the type of material to be digested, as well as on the operational conditions in the reactor (Noyola et al., 2006). It is generally composed of CH₄ and CO₂ in a ratio of 3:1, and other minor constituents; among them, H₂S is of particular interest due to its corrosive, toxic and environmentally hazardous properties. Along with CH₄, whose concentration determines the calorific value therein, it has the greatest impact when the traditional applications of biogas are considered (Rasi et al., 2011). The biogas sulphide content can vary from 0.01 to 1.00%v/v (Tippayawong and Thanompongchart, 2010). However, as an example, for trouble free operation of combined heat and power stations, the H₂S concentration in the biogas must be lower than 0.01 or 0.03%v/v, depending on the equipment concerned (Peu et al., 2012). Besides causing corrosion, H₂S also causes the deterioration of the lubrication oil (Weiland, 2010). Consequently, H₂S production must be prevented, or H₂S must be removed from the biogas.

Due to the high technicality and cost of sulphide emission control by adding selective inhibitors of sulphidogenic bacteria or sulphide scavengers to precipitate sulphide in the digester, H₂S removal from biogas is the most consolidated strategy in practice (Cirne et al., 2008; Peu et al., 2012). For this purpose, a wide range of physical, chemical and biological methods exist. The first two categories include techniques based on absorption and adsorption processes (reactive or non-reactive), while technologies using microorganisms capable of oxidising sulphide (such as bioscrubbers, biofilters and biotrickling filters) belong to the third category (Abatzoglou and Boivin, 2009). Though rapid and effective, the physical and chemical methods for H₂S removal are costly and produce secondary wastes, which in turn gives rise to another pollution problem (Lin et al., 2013). The biological processes have the potential to overcome these disadvantages. Besides, they can achieve greater depth of desulphurisation (Kobayashi et al., 2012) and generate by-products (S⁰) that can be used in other industrial processes (Kleinjan et al., 2005). In fact, chemical and biological processes are usually combined. In the system proposed by Ho et al. (2013), the H₂S is first oxidised by ferric iron to generate S⁰ in a chemical reactor, and the resulting ferrous iron is then oxidised in a biological reactor by iron-oxidising bacteria. Likewise, the only two patented technologies specifically developed for H₂S removal from biogas consist of a chemical scrubber, in which the H₂S is washed from the biogas, and a bioreactor, where the dissolved sulphide is utilised by sulphide-oxidising bacteria (SOB) (Fortuny et al., 2008). It should be mentioned that H₂S can also be chemically oxidised in biological reactors, especially if the H₂S load is high, and in this case S₂O₃²⁻ is the main by-product (Lohwacharin and Annachhatre, 2010).

The direct injection of O₂ or air into anaerobic reactors was proposed in order to carry out both the production and desulphurisation of biogas in a single unit; SOB are naturally present therein (Weiland, 2010). In fact, this process has been reported to proceed mainly through biological reactions (Ramos et al., 2012). Under fully oxygenated conditions, SOB generate SO₄²⁻, whereas under O₂-limiting conditions, they oxidise sulphide to S⁰ (van der Zee et al., 2007). Evidently, both reactants, O₂ or air, are supplied in limited amounts in order to minimise both the surplus of O₂ and the presence of N₂ in the biogas leaving the digester, and the operating costs. It must be noted that O₂ transfer has been suggested to be the limiting step during H₂S removal from biogas in these reactors, which are usually referred to as microaerobic reactors (Fdz-Polanco et al., 2009). Therefore, the use of O₂ is recommended instead of air (Díaz et al., 2010a); thus, additional dilution by N₂ is avoided (Jenicek et al., 2010; Díaz et al., 2010a). As a result, S⁰ is the main by-product of H₂S oxidation during microaerobic digestion.

Neither the digestion performance nor the productivity or the CH₄ content of biogas are significantly reduced under microaerobic conditions (Fdz-Polanco et al., 2009); they can even be increased (Jenicek et al., 2008). In fact, the introduction of limited amounts of O₂ is a general practice in agricultural reactors; an air flow rate of 2–6%v/v of the biogas production is introduced in the headspace (HS) or, occasionally, in the feed stream. As a result, S⁰ has been reported to accumulate on surfaces in the gas space, or to leave the digester with the effluent, respectively (Cirne et al., 2008). Similarly, Kobayashi et al. (2012) found that the S⁰ generated as a result of O₂ injection into the HS of a dairy cow manure digester and the H₂S oxidation, was deposited all over the HS. Likewise, Jenicek et al. (2011) indicated that H₂S conversion into S⁰ took place as air was supplied to the recirculation stream of a reactor treating waste activated sludge; the increase in digestate S content was consistent with the efficiency of the biogas desulphurisation. However, in accordance with Rodríguez et al. (2012), S⁰ produced during microaerobic digestion of synthetic vinasse was deposited

in the HS despite O₂ being introduced from the bottom of the system; this compound was indeed the main by-product of the H₂S oxidation. Besides, they found SOB only in the gas space. These contradictory results certainly point to O₂ transfer limitations; Rodríguez et al. (2012) detected a considerable part of the O₂ injected into the reactor in the biogas, which still contained significant amounts of H₂S. Nevertheless, Díaz et al. (2010b) reported that increasing the O₂ transfer to the liquid phase of a sewage sludge digester did not lead to a higher efficiency of biogas desulphurisation, while the O₂ consumption in other oxidative processes rose. This was indeed consistent with the previous findings (Fdz-Polanco et al., 2009). Moreover, they also found SOB only in the HS. As a result, Díaz et al. (2010b) indicated that biogas desulphurisation took place in the HS independently of both the O₂ dosing point and the mixing method. Accordingly, the optimum configuration of a microaerobic reactor aiming for biogas desulphurisation consists of O₂ or air injection into the HS and liquid recirculation.

Considering the inconsistent results concerning the predominant location for H₂S removal from biogas produced during microaerobic digestion, Ramos et al. (2012) designed an experiment which aimed to clarify this question. Although their results indicate that the process takes place predominantly in the gas space, they are not conclusive due to the short duration of the experimentation. The research presented here extends the results obtained in that preliminary study, and proposes the principles of the process of biogas desulphurisation accordingly.

2. Methods

2.1. Digester

Digestion was carried out in a continuous stirred tank reactor with total volume of 266 L. As shown in Fig. 1, it consisted of a conical ceiling with a transparent cylindrical piece on top. For further details of the reactor, see Ramos et al. (2012).

Before this study, the digester operated during several months under microaerobic conditions and hydraulic retention time (HRT) of 20 d. The present research was conducted at 22 and 24 d of HRT, depending on the liquid level inside the digester, or equivalently, the presence (25.0 L) or the absence (lower than 0.3 L) of HS, respectively, while the feeding rate was maintained constant (Fig. 1a and c, and b, respectively). The reactor volume was increased with digestate thereof. Mixed sludge from a municipal wastewater treatment plant was continuously fed to the bioreactor; its composition varied widely during the research (Table 1). The digestion temperature (35 °C) was maintained by an electric resistor surrounding the walls of the digester, which were in turn insulated. The ceiling was insulated. Microaerobic conditions were implemented by supplying pure O₂ from the bottom of the system, just where the streams sludge recirculation and feeding converged. The recirculated flow was obtained at 50 L/h. As shown in Fig. 1b, the level of the outflow valve of the recirculation stream was raised when the HS volume was reduced in order to ensure mixing in the upper part of the liquid phase.

2.2. Monitoring and experimental analysis

Digestion pressure was monitored by a sensor (Fig. 1a). Temperature was measured by a PT100 probe (Fig. 1a, b and c). Biogas production was quantified volumetrically (Fig. 1a). The CH₄, CO₂, N₂, O₂ and H₂S content of biogas was determined by gas chromatography (VARIAN CP-3800 GC) according to Díaz et al. (2010a), and a 100 µL-syringe was used.

Total and soluble chemical oxygen demand, total solids, volatile solids (VS), volatile fatty acids, total kjeldahl nitrogen, ammonia,

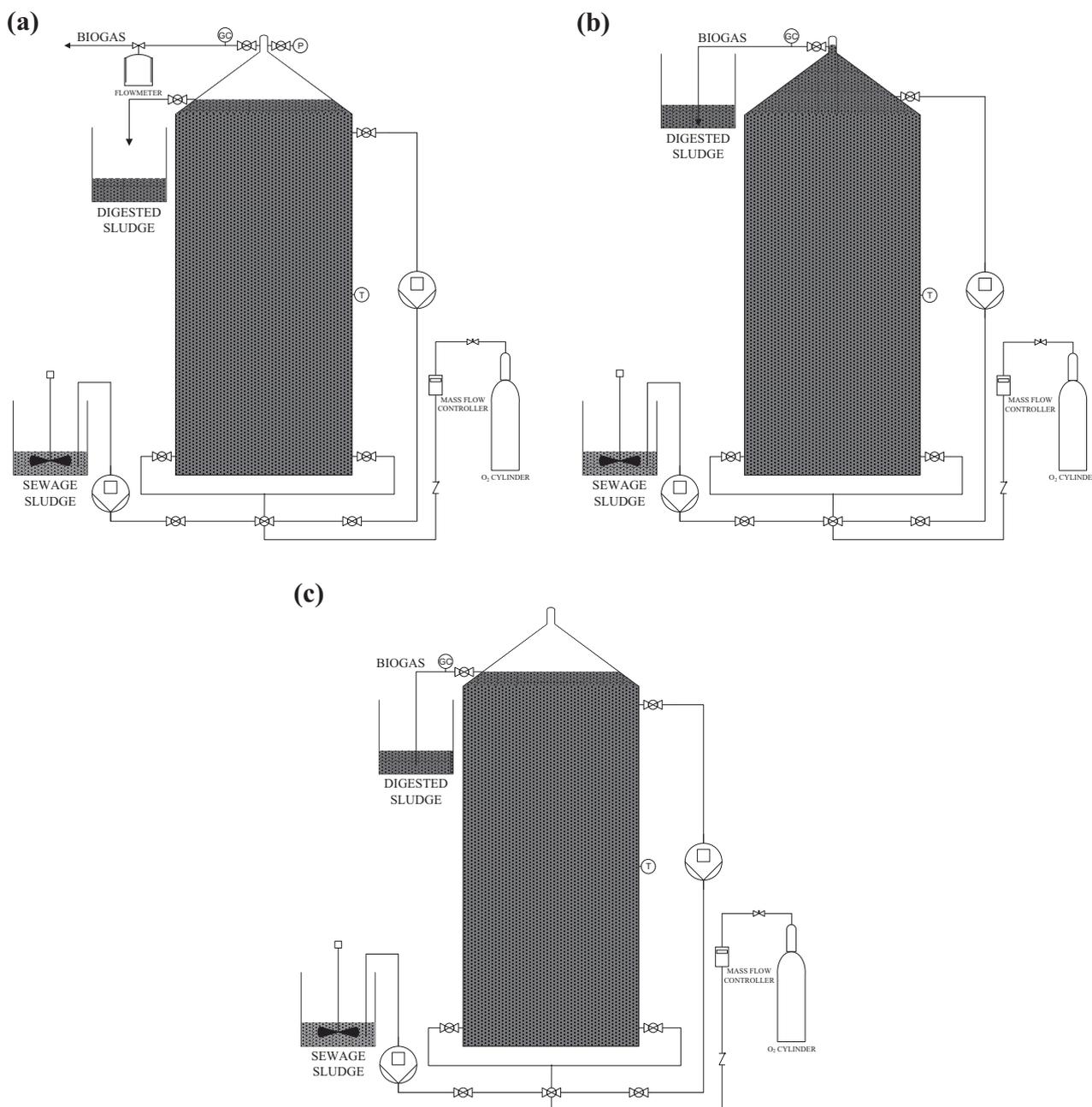


Fig. 1. Digester diagram in periods A1, M1 and A2 (a), M2 and M4 (b), and M3 (c).

Table 1
Sequence of variations applied and response of the digester.

Period ^a	HS volume (L)	HRT (d)	OLR (kg _{vs} /m ³ /d)	O ₂ supply (NL/L _{fed})	Biogas production (NL/d)	H ₂ S (%v/v)	O ₂ (%v/v)
A1	25.0	22	0.8	0	77.3	0.31	0.03
M1	25.0	22	0.9	0.21	95.3	0.03	0.86
M2	0.3	24	1.0	0.25	–	0.14	1.83
M3	25.0	22	1.4	0.28	–	0.00	0.59
M4	0.3	24	1.0	0.30	–	0.13	1.41
A2	25.0	22	0.8	0	89.4	0.24	0.03

^a A = anaerobic, M = microaerobic.

S₂O₃²⁻ and SO₄²⁻ were measured. Except for S₂O₃²⁻, which was determined according to the procedure described by van der Zee et al. (2007), the rest of the parameters were analysed according to APHA (1998).

2.3. Experimental procedure

This research was divided into six periods, according to the HS volume of the digester (Table 1). In A1 and A2, the reactor operated

under anaerobic conditions, and from M1 to M4, it operated under microaerobic conditions. The digester configuration in A1, M1 and A2 is shown in Fig. 1a; in these periods, the generated biogas was quantified. Fig. 1b shows the reactor configuration maintained during M2 and M4, and Fig. 1c illustrates the reactor configuration in M3.

3. Results and discussion

3.1. Experimental results

3.1.1. Period A1

During the first 12 days of the research (period A1), the bioreactor operated under anaerobic conditions with 25.0 L of HS (HRT = 22 d) (Fig. 1a). The H_2S concentration in the biogas varied widely (Fig. 2), which was attributed to changes in the relative composition of the sewage sludge in terms of S-containing organic compounds, such as proteins, and/or variations in the feeding sulphide content. The concentration of SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ in the raw sludge was negligible (data not shown), while the organic loading rate (OLR) remained almost constant ($0.8 \text{ kg}_{\text{VS}}/\text{m}^3/\text{d}$), which in turn resulted in biogas process stability (Table 1). Just before implementing microaerobic conditions, the biogas sulphide content was $0.36\% \text{v/v}$; this value was considered the baseline for the subsequent calculations.

3.1.2. Period M1

At day 12 (period M1), O_2 was supplied to the reactor at a rate of $0.18 \text{ NL}/L_{\text{fed}}$, equalling a ratio of $\text{O}_{2\text{injected}}/\text{H}_2\text{S}_{\text{produced}}$ of 5.4 v/v (Fig. 1a). This was based on the previous study (Ramos et al., 2012) while gaseous sulphide flow rate was considered. On the following day, H_2S removal efficiency was 66%, and O_2 concentration in the biogas was around $0.82\% \text{v/v}$. This highlighted the inefficient O_2 transfer conditions in the digester, since approximately 48% of the supplied O_2 remained unused in the biogas.

On the 13th day, the O_2 flow rate was raised to $0.23 \text{ NL}/L_{\text{fed}}$. Thus, the $\text{O}_{2\text{injected}}/\text{H}_2\text{S}_{\text{produced}}$ ratio rose to approximately 6.5 (v/v), which resulted in a higher gradient concentration across the gas–liquid interface, thereby increasing the O_2 transfer rate. The amount of O_2 leaving the digester as a percentage of the total O_2 supply specifically decreased to an average of 36%. As a result, although the somewhat higher OLR ($0.9 \text{ kg}_{\text{VS}}/\text{m}^3/\text{d}$) could increase the biogas production, the biogas was desulphurised, and its O_2 content hardly changed (Fig. 2).

Taking into account the significant fluctuations in the H_2S production during A1, the O_2 supply was increased further on the 14th

day (just before raising the liquid level) in order to ensure a removal efficiency of 100% from then on (Fig. 2). Moreover, although the reactor content would be increased only by 9% (from 241 to almost 266 L) when the liquid level was raised, the amount of O_2 per volume of sludge would decrease slightly. On the other hand, the increase of content extended the contact time between the biogas and the liquid phase, which could slightly improve the O_2 transfer to the liquid media. At a micro-oxygenation rate of $0.25 \text{ NL O}_2/L_{\text{fed}}$, the O_2 content in the biogas rose slightly due to the biogas production being somewhat lower; however, the additional O_2 supplied was consumed in the bioreactor (this being approximately 70% of the O_2 injected).

As indicated, the amount of O_2 consumed in the digester during M1 rose as the micro-oxygenation level was raised; it was specifically estimated to be about 62% of the O_2 injected, on average. Thus, the $\text{O}_{2\text{injected}}/\text{H}_2\text{S}_{\text{produced}}$ ratio was increased from 2.2–5.9. At such high O_2 availabilities, H_2S could be converted into SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ and S^0 . However, the SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ concentrations in the digestate were both negligible (data not shown). Moreover, although the absence of S^0 in the liquid phase was not analytically ruled out, it is worth noting that S^0 was not observed when the reactor's content was sampled. This pointed to the removal of H_2S from the biogas in the HS; in this location, these by-products probably accumulated on the areas nearest the liquid phase due to the greater availability of moisture and nutrients. Kobayashi et al. (2012) reported that these were the key factors controlling the activity levels of SOB. Although many researchers have reported the presence of S^0 all over the gas space (Díaz et al., 2010b; Kobayashi et al., 2012; Ramos et al., 2012; Rodríguez et al., 2012), it could be expected that the H_2S removal from the biogas in early stages of the process might occur in the areas nearest the liquid phase, where the growing conditions for SOB are more favourable. In fact, although its characteristic yellowish-white colour enabled the S^0 to be visually recognisable, it was not deposited in the cylindrical piece on top of the digester (Fig. 1a).

3.1.3. Period M2

On the 15th day, the liquid level in the reactor was raised in order to virtually eliminate the gas space (period M2), while the O_2 flow rate was maintained at $0.25 \text{ NL}/L_{\text{fed}}$ (Table 1). Thus, the HRT was increased to 24 d; here it should be emphasised that the feeding rate did not change. Under such conditions, both the effluent and the biogas left the reactor by the same pipe, and the digestate overflowed from the digester 60 mm below the uppermost point of the reactor (Fig. 1b). Consequently, sludge was deposited all over the cylindrical piece of the HS due to splashes,

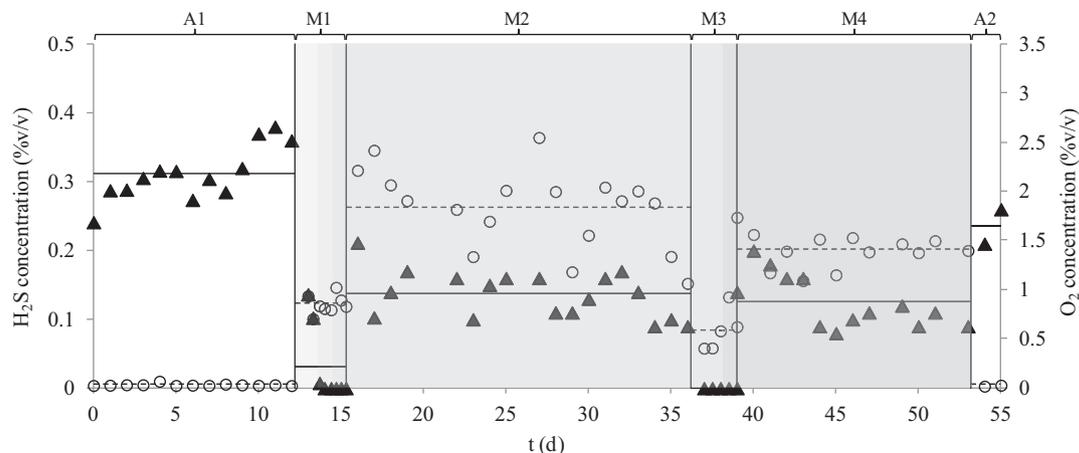


Fig. 2. H_2S (▲) and O_2 (○) concentration in biogas. The intensity of the shaded area indicates the micro-oxygenation level: $\square = 0.18$, $\square = 0.23$, $\square = 0.25$, $\square = 0.30$ (in NL of O_2 injected per L of sewage sludge fed). The horizontal lines indicate the average H_2S (continuous lines) and O_2 concentration (discontinuous lines) in every period.

which made it impossible to see what happened in that area thereafter. For this reason, HS was estimated to be 0.3 L at most. In order to keep the reactor under pressure, a liquid column was always maintained in the effluent collection tank.

On day 16, the biogas composition was almost equal to that in M1, which was attributed to the sulphide-oxidising activity in the outlet pipe of biogas and digestate due to the relatively large amount of S^0 accumulated therein over the last day (Fig. 1b). This compound was attached at both shores of the digestate stream, in addition to some S^0 in the digestate inside the effluent tank. However, it was not observed when the reactor's content was sampled, which suggested that it formed in the pipe and was dragged by the effluent stream; in fact, it is possible that some H_2S could be converted into S^0 inside the effluent tank. Therefore, in order to obtain a sample which was as representative as possible of the biogas leaving the HS of the digester, the outlet pipe was cleaned at pressure in order to remove the biomass attached until then, and once the air was displaced from the pipe (around 20 min after cleaning), the biogas was sampled again. As a result, the H_2S and O_2 content of the biogas both increased significantly in relation to M1 (Fig. 2); they were 0.21 and 2.22%v/v, respectively. The large increase in the O_2 concentration suggested that the H_2S was oxidised mainly to SO_4^{2-} during the preceding period.

The sampling procedure described above was applied daily until the 53rd day. H_2S concentrations of up to 0.10%v/v were recorded in M2 (Fig. 2). However, it was proven that the more time that elapsed since the outlet pipe was cleaned, the lower the concentration of H_2S . The highly favourable growing conditions for SOB in the outlet pipe were considered to be the factor determining the rapidity of the sulphide oxidation; it must be considered that fresh digested sludge flowed continuously (Fig. 1b). Although the habitat for SOB in the 0.3 L-HS was also highly favourable, presumably negligible amounts of H_2S were removed there; S^0 was not observed in the outlet valve of the biogas and digestate when the pipe was removed for cleaning. In fact, if this compound had formed in the 0.3 L-HS, clogging problems would probably have arisen. The biogas residence time (BRT) in the HS was lower than in the pipe, whose volume was approximately 0.7 L.

Considering the OLR (Table 1), the BRT in the outlet pipe during M2 was estimated to be at most 12 min, which could certainly limit the transfer of O_2 , thereby preventing H_2S conversion into SO_4^{2-} and promoting S^0 formation. The large amounts of this compound deposited from day to day, indicated thus that S^0 was the only by-product of sulphide-oxidising activity. By contrast, the BRT maintained in M1 (approximately 6 h) could certainly suffice to provide the different surfaces of the HS with the O_2 required for further oxidation of H_2S .

The correlation between the profile of H_2S and O_2 concentration in biogas in M2 was high; in general, the higher the O_2 concentration, the lower the biogas sulphide content, which suggested higher consumption of O_2 due to biogas desulphurisation (Fig. 2). Furthermore, both profiles varied, and this was attributed to fluctuations in biogas production and H_2S concentration; these variables determined the O_2 transfer and demand, respectively. Specifically, the higher the biogas flow rate was, the shorter the BRT, and the higher the turbulence in the digester. Moreover, the lower the H_2S flow rate, the lower the demand of O_2 , and the higher the efficiency of biogas desulphurisation. As in A1, although the content of S-containing anions (SO_4^{2-} and $S_2O_3^{2-}$) of the feeding was negligible, the H_2S concentration could oscillate during M2. Moreover, since the OLR increased up to 1.2 $kg_{VS}/m^3/d$ from approximately the 25th day, presumably the biogas production increased significantly; the OLR remained stable around 0.8 $kg_{VS}/m^3/d$ until that day (Table 1).

As noted, S^0 was not observed in the samples retrieved directly from the reactor. Additionally, neither SO_4^{2-} nor $S_2O_3^{2-}$ were

detected in significant amounts. Therefore, it was concluded that the O_2 utilised in H_2S oxidation during M1 left the HS unused during M2 due to the reduced volume of the gas space. Next, the pipe functioned as an external HS, a concept that has indeed already been exploited (Ramos et al., 2013). H_2S probably dissolved all over the outlet pipe; besides sludge, presumably water was deposited through the condensation of moisture contained in the biogas. However, as noted, it was oxidised on the areas surrounding the effluent stream, namely, on both the sludge remaining attached in the pipe, and the wet areas due to condensation which were occasionally reached by sludge droplets. This was related to the higher availability of both water and nutrients for SOB, and also the presence of catalysts (metal ions), which could in turn promote the abiotic H_2S oxidation (Kleinjan et al., 2005).

3.1.4. Period M3

The liquid level was lowered on the 36th day in order to increase the HS volume to 25.0 L again (period M3). Importantly, the configuration of the reactor was not modified in order to sample biogas under identical conditions and by using the same procedure (Fig. 1c). Although the O_2 flow rate was maintained at 0.25 NL/ L_{fed} , the biogas was entirely desulphurised, and the biogas O_2 content decreased to around 0.56%v/v (Fig. 2), which was consistent with the previous results; it suggested that SO_4^{2-} was the main by-product of the H_2S oxidation during M3. In contrast to M2, S^0 was not deposited in the outlet pipe. Nevertheless, this compound was not observed in the samples taken from the reactor, which either had significant concentrations of SO_4^{2-} or $S_2O_3^{2-}$.

Although presumably the biogas production in M3 was significantly higher than in the preceding periods due to the larger OLR, which could certainly result in a higher H_2S flow rate to remove, the O_2 supply was still sufficient to achieve H_2S -free biogas (Table 1). An increased H_2S production could indeed justify the lower O_2 concentration maintained in M3, in comparison with M1 (days 14 and 15), when the digester operated at same micro-oxygenation level (Fig. 2). Nonetheless, the presumably larger biogas production could improve the O_2 transfer to the liquid phase, which could also explain the lower biogas O_2 content.

As in M1, the O_2 flow rate was raised further from the 38th day (just before raising the liquid level) in order to ensure H_2S -free biogas thenceforth; the micro-oxygenation level was set at 0.30 NL/ L_{fed} . The sulphide content of biogas remained at 0, and a slight increase in the O_2 concentration was detected; however, the rise of OLR from 1.3 to 1.5 $kg_{VS}/m^3/d$ during M3, and the results obtained in M1 suggested that a part of the additional O_2 injected into the bioreactor from the 38th day could be consumed therein. The larger amount of O_2 available in the liquid phase was expected to encourage biogas desulphurisation there. As noted, although a considerable percentage of the O_2 supplied was consumed in the liquid phase until then, it did not seem to be utilised in this process; it must be considered that many facultative microorganisms grow in the sludge along with SOB.

3.1.5. Period M4

On the 39th day, the HS was virtually eliminated by raising the liquid level in the digester again (period M4). The biogas composition was determined just before and immediately after that; its content of both H_2S and O_2 from 0 and 0.63%v/v rose to 0.14 and 1.74%v/v, respectively (Fig. 2). Moreover, S^0 was seen once again to accumulate in the outlet pipe of the biogas and the digestate (Fig. 1b). In fact, the average H_2S and O_2 concentration in biogas during M4 were 0.13 and 1.41%v/v, respectively. In the meantime, as in M2, increasing amounts of S^0 were deposited from day to day, and this compound was not observed either in the HS, when the pipe was removed for cleaning, or in the sludge retrieved from the reactor. Furthermore, the SO_4^{2-} and $S_2O_3^{2-}$ concentrations in

the digester were both negligible. Assuming that the amount of H_2S produced in A2 was similar to that produced in M4, at least from the 44th day, when the OLR remained almost constant, it was estimated that around 121 mg of S^0 accumulated daily in the pipe (Table 1). At this point, it is worth mentioning that the significant decrease in the H_2S concentration in biogas occurring on the 44th day was related to a change in the OLR, which specifically dropped from 1.4 to 0.8 $kg_{VS}/m^3/d$ (Table 1). Therefore, O_2 transfer to the liquid phase was proved unnecessary in order to desulphurise biogas due to the fact that the process took place in the gas space.

3.1.6. Period A2

In A2, the digester operated with 25.0 L of HS, and under anaerobic conditions and approximately 0.8 $kg_{VS}/m^3/d$ of OLR (Table 1). The sulphide content of biogas was 0.24%v/v (Fig. 2).

3.2. Biogas desulphurisation

The O_2 that was supplied from the bottom of the reactor dissolved only partially in the liquid phase, due to O_2 transfer limitations. Although the O_2 availability was sufficient for H_2S oxidation, the habitat was more favourable for other microorganisms instead of SOB, such as facultative (Botheju and Bakke, 2011). Hence, the unidentified oxidising microorganisms consumed all the dissolved O_2 more rapidly than SOB due to their higher activity levels. Additionally, assuming that biogas was also desulphurised by chemical mechanisms, the reaction rates of abiotic H_2S oxidation should be also lower than the yields of those facultative microorganisms.

Next, the H_2S -laden biogas reached the HS along with the O_2 not dissolved in the liquid phase. The gas space (the lower part of the walls) was covered with sludge due to splashes and occasional momentary rises in the liquid level. The upper area (that is, the conical ceiling) could also contain some moisture from the condensation of water contained in the biogas, due to it being not surrounded with electric resistor. As a result, H_2S and O_2 both dissolved on different surfaces of the HS, thereby enabling SOB to develop. Since that environment was more stringent than that existing in the liquid phase due to much more limited availability of nutrients and organic substrates, the activity rates of other O_2 -utilising microorganisms, such as acidogenic bacteria, was limited. Some SOB seem to have relatively low nutrients requirements indeed (Ramos et al., 2013). As a result, H_2S was oxidised, preferentially on the area nearest the sludge due to the higher accessibility of water and nutrients in this area, and maybe also the increased availability of the catalyst for chemical oxidation. Finally, the biogas left the reactor, along with O_2 unused in either H_2S oxidation or in other oxidative processes.

This study highlights the importance of ensuring sufficient O_2 transfer to the different surfaces of the gas space in order to efficiently desulphurise biogas during microaerobic digestion. Furthermore, it indicates that the most economical configuration of microaerobic reactors consists of O_2 injection into the HS and liquid recirculation. Thus, the O_2 consumption in other oxidative processes taking place in the liquid phase is minimised (Díaz et al., 2010b).

4. Conclusions

A pilot reactor was operated with and without HS in order to investigate where the process of biogas desulphurisation predominantly took place when O_2 was injected into the liquid phase. H_2S was removed from the biogas when the digester had 25.0 L of HS. However, at equal O_2 supplies, and with almost no HS, the H_2S con-

centration approached anaerobic values, and the biogas O_2 content doubled. Moreover, the H_2S removed under such conditions had not been oxidised in the reactor due to insufficient HS, but it had been deposited in the form of S^0 in the outlet pipe of biogas.

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References

- Abatzoglou, N., Boivin, S., 2009. A review of gas purification processes. *Biofuels, Bioprod. Biorefin.* 3, 42–71.
- Abbasi, T., Tauseef, S.M., Abbasi, S.A., 2012. Anaerobic digestion for global warming control and energy generation – an overview. *Renew. Sustain. Energy Rev.* 16, 3228–3242.
- APHA, 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association/American Water Works Association/Water Environmental Federation, Washington, DC, USA.
- Botheju, D., Bakke, R., 2011. Oxygen effects in anaerobic digestion – a review. *Open Waste Manage. J.* 4, 1–19.
- Cirne, D.G., van der Zee, F.P., Fdz-Polanco, M., Fdz-Polanco, F., 2008. Control of sulphide during anaerobic treatment of S-containing wastewaters by adding limited amounts of O_2 or nitrate. *Rev. Environ. Sci. Biotechnol.* 7, 93–105.
- Díaz, I., Pérez, S.I., Ferrero, E., Fdz-Polanco, M., 2010a. Performance evaluation of oxygen, air and nitrate for the microaerobic removal of hydrogen sulphide in biogas from sludge digestion. *Bioresour. Technol.* 101, 7724–7730.
- Díaz, I., Lopes, A.C., Pérez, S.I., Fdz-Polanco, M., 2010b. Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters. *Bioresour. Technol.* 102, 3768–3775.
- Fdz-Polanco, M., Díaz, I., Pérez, S.I., Lopes, A.C., Fdz-Polanco, F., 2009. Hydrogen sulfide removal in the anaerobic digestion of sludge by micro-aerobic processes: pilot plant experience. *Water Sci. Technol.* 60, 3045–3050.
- Fortuny, M., Baeza, J.A., Gamisans, X., Casas, C., Lafuente, J., Deshusses, M.A., Gabriel, D., 2008. Biological sweetening of energy gases mimics in biotrickling filters. *Chemosphere* 71, 10–17.
- Ho, K.-L., Lin, W.-C., Chung, Y.-C., Chen, Y.-P., Tseng, C.-P., 2013. Elimination of high concentration hydrogen sulfide and biogas purification by chemical-biological process. *Chemosphere* 92, 1396–1401.
- Holm-Nielsen, J.B., Al Seadi, T., Oleskowicz-Popiel, P., 2009. The future of anaerobic digestion and biogas utilization. *Bioresour. Technol.* 100, 5478–5484.
- Jenicek, P., Keclik, F., Maca, J., Bindzar, J., 2008. Use of microaerobic conditions for the improvement of anaerobic digestion of solid wastes. *Water Sci. Technol.* 58, 1491–1496.
- Jenicek, P., Koubova, J., Bindzar, J., Zabranska, J., 2010. Advantages of anaerobic digestion of sludge in microaerobic conditions. *Water Sci. Technol.* 62, 427–434.
- Jenicek, P., Celis, C.A., Koubova, J., Pokorna, D., 2011. Comparison of microbial activity in anaerobic and microaerobic digesters. *Water Sci. Technol.* 63, 2244–2249.
- Kleinjan, W., 2005. *Biologically Produced Sulfur Particles and Polysulfide Ions: Effects on a Biotechnological Process for the Removal of Hydrogen Sulfide from Gas Streams* (PhD Thesis). Wageningen University, ISBN 90-8504-232-1, Wageningen, The Netherlands.
- Kobayashi, T., Li, Y.Y., Kubota, K., Harada, H., Maeda, T., Yu, H.-Q., 2012. Characterization of sulfide-oxidizing microbial mats developed inside a full-scale anaerobic digester employing biological desulfurization. *Appl. Microbiol. Biotechnol.* 93, 847–857.
- Lin, W.-C., Chen, Y.-P., Tseng, C.-P., 2013. Pilot-scale chemical-biological system for efficient H_2S removal from biogas. *Bioresour. Technol.* 135, 283–291.
- Lohwacharin, J., Annachhatre, A.P., 2010. Biological sulfide oxidation in an airlift bioreactor. *Bioresour. Technol.* 101, 2114–2120.
- Noyola, A., Morgan-Sagastume, J.M., López-Hernández, J.E., 2006. Treatment of biogas produced in anaerobic reactors for domestic wastewater: odor control and energy/resource recovery. *Rev. Environ. Sci. Biotechnol.* 5, 93–114.
- Peu, P., Picard, S., Diara, A., Girault, R., Béline, F., Bridoux, G., Dabert, P., 2012. Prediction of hydrogen sulphide production during anaerobic digestion of organic substrates. *Bioresour. Technol.* 121, 419–424.
- Ramos, I., Díaz, I., Fdz-Polanco, M., 2012. The role of the headspace in hydrogen sulfide removal during microaerobic digestion of sludge. *Water Sci. Technol.* 66, 2258–2264.
- Ramos, I., Pérez, R., Fdz-Polanco, M., 2013. Microaerobic desulphurisation unit: a new biological system for the removal of H_2S from biogas. *Bioresour. Technol.* 142, 633–640.
- Rasi, S., Lätälä, J., Rintala, J., 2011. Trace compounds affecting biogas energy utilisation – a review. *Energy Convers. Manage.* 52, 3369–3375.
- Rodríguez, E., Lopes, A., Fdz-Polanco, M., Stams, A.J., García Encina, P.A., 2012. Molecular analysis of the biomass of a fluidized bed reactor treating synthetic

- vinasse at anaerobic and micro-aerobic conditions. *Appl. Microbiol. Biotechnol.* 93, 2181–2191.
- Tippayawong, N., Thanompongchart, P., 2010. Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor. *Energy* 35, 4531–4535.
- van der Zee, F.P., Villaverde, S., García-Encina, P.A., Fdz-Polanco, F., 2007. Sulphide removal by moderate oxygenation of anaerobic sludge environments. *Bioresour. Technol.* 98, 518–524.
- Weiland, P., 2010. Biogas production: current state and perspectives. *Appl. Microbiol. Biotechnol.* 85, 849–860.