Determination of the optimal rate for the microaerobic treatment of several H_2S concentrations in biogas from sludge digesters

I. Díaz, A. C. Lopes, S. I. Pérez and M. Fdz-Polanco

ABSTRACT

The treatment of H_2S in the biogas produced during anaerobic digestion has to be carried out to ensure the efficient long-lasting use of its energetic potential. The microaerobic removal of H_2S was studied to determine the treatment capacity at low and high H_2S concentrations in the biogas (0.33 and 3.38% v/v) and to determine the optimal O_2 rate that achieved a concentration of H_2S of 150 mg/Nm^3 or lower. Research was performed in pilot-plant scale digesters of sewage sludge, with 200 L of working volume, in mesophilic conditions with a hydraulic retention time of 20 d. O_2 was supplied at different rates to the headspace of the digester to create the microaerobic conditions. The treatment successfully removed H_2S from the biogas with efficacies of 97% for the low concentration and 99% for the highest, in both cases achieving a concentration below 150 mg/Nm^3. An optimal O_2 rate of 6.4 NLO_2/Nm^3 of biogas when treating the biogas was found with 0.33% (v/v) of H_2S and 118 NLO_2/Nm^3 of biogas for the 3.38% (v/v) concentration. This relation may be employed to control the H_2S content in the biogas while optimising the O_2 supply.

Key words | biogas, dose control, H_2S removal, microaerobic, optimal O_2 rate

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INTRODUCTION

The treatment of wastewater in municipal wastewater treatment plants (WWTP) generates sludge as a by-product of the overall processes employed during treatment. When disposing of this sludge, anaerobic digestion (AD) is an important step in most treatment processes. AD is able to transform a large part of the organic matter content into biogas, 60–70% (v/v) of methane.

In the AD of S-containing organic matter, H_2S is generated to a different extent (10–70 g/m^3 in the biogas) based on the outcome of the competition between sulfur-reducing bacteria and methanogens (Lens & Pol 2000). H_2S in the biogas reduces the lifetime of the pipework and other installations needed for the utilisation of biogas. For example, the trouble free operation of CHP (combined heat and power) requires limit values between 100 and 500 mg/Nm^3, depending on the specifications of the CHP manufacturer, and these values may not be exceeded. H_2S is toxic and corrosive to many types of steel (Deublein & Steinhauser 2008). Therefore, the treatment of the biogas has to be carried out to ensure the efficient long-lasting use of its energetic potential.

Biological treatment technologies have shown lower treatment costs and low or no requirements for additional chemical products compared to the traditional physico-chemical technologies (Syed *et al.* 2006). Besides, biological removal has proven successful in the large-scale employment of biotrickling filters and bioscrubbers (Janssen *et al.* 2001).

The technologies are based on the biological oxidation of H_2S, which employs O_2 as electron acceptor, carried out by sulfide-oxidising microorganisms. The final products of the biological oxidation depend on the amount of O_2 available for sulfide-oxidising bacteria. Some well-known and novel sulfur-oxidising bacteria are able to employ sulfide as an electron donor under anaerobic conditions similar to those in the AD of sludge, such as *Thiomicrospira* sp. and *Thiobacillus* sp. (Tang *et al.* 2009). The predominance of S^0 or SO_4^{2-} as the final product of the oxidation depends on the O_2 availability, thus in limited conditions (microaerobic) S^0 is the main final product (Janssen *et al.* 1995).

Microoxygenation of the 'anaerobic digester' is an alternative to perform biological removal of H_2S due to some of the bacteria responsible for the sulfur oxidation

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being present in the sludge (Abatzoglou & Boivin 2009). Several agro-industrial applications of AD perform this process in Europe by continuously supplying 4–6% of air in relation to the biogas production into the headspace of the biodigester, where sulfur-oxidising microorganisms develop, thereby reaching H_2S concentrations below 200 ppmv (Weiland 2010).

In this sense, Jenicek *et al.* (2008) reported H_2S removal from the biogas and enhanced VSS and soluble COD degradation when air was supplied during sludge recirculation and a slight decrease in some recalcitrant compounds (AOX) in full-scale sludge digesters (Jenicek *et al.* 2010).

In previous studies we have found that the removal of H_2S in the biogas produced in an anaerobic sludge digester by microoxygenation reduced the concentration of H_2S from 0.9 to 1.2% (v/v) to less than 0.3% (v/v) with no effect on digestion performance (Fdz-Polanco *et al.* 2009). The utilisation of air with a similar O_2 rate to pure O_2 was also found successful while NO_3^- could not be used to desulfurise the biogas in the case of sludge digestion (Díaz *et al.* 2010a) and the headspace was the optimal dosing point for H_2S removal from the biogas (Díaz *et al.* 2010b).

Finally, in full-scale treatment of sewage sludge, biogas production varies as a result of the variable COD and VS concentrations of the feed. Then, the O_2 rate to the bioreactor for the microaerobic removal of H_2S must vary according to the amount of H_2S produced to optimise the O_2 flow supplied and to avoid an excessive concentration of O_2 not utilised in the biogas or, otherwise, not enough for the expected H_2S removal. Khanal & Huang (2003) suggested employment of the oxidation–reduction potential (ORP) to control the O_2 dosing; however, in the particular case of sludge digestion, ORP remains invariable during microaerobic treatment (Jenicek *et al.* 2010; Díaz *et al.* 2010b), therefore a different controlling method must be found.

In this study, we focus on evaluating the performance of the H_2S removal in a wider concentration interval (0.33 and 3.3% (v/v)), and on the determination of the optimal O_2 flow for the H_2S content in the biogas, subsequently observing the feasibility of the control of the dosing by the biogas production rate.

MATERIALS AND METHODS

Pilot plant description

The treatment of sludge and the removal of H_2S were performed in pilot-plant scale reactors with a working volume of 200 L (250 L total volume), as shown in Figure 1. The reactors were insulated, and the walls were heated with electric resistance. The reactors were also mixed with biogas recirculation provided at a rate of ~4 L/min of biogas; this flow was periodically checked with a rotameter. The feed was provided from a continuously stirred tank with a peristaltic pump. Microaerobic conditions were maintained using the regulated flow of pure O_2 with a mass flow controller from an O_2 cylinder injected into the headspace. The headspace in the bioreactor (50 L) allowed the storage of ~1/4 of the daily biogas production.

Operational conditions

The pilot-plant study was developed in the anaerobic sludge digesters from previous anaerobic/microaerobic experiments. A pseudo-stationary anaerobic state was obtained prior to the beginning of the experiments by maintaining at least 20 days without any O_2 supply. Digestion of the sludge was performed in the mesophilic range ($35 \pm 1\ ^\circ C$) with an HRT of ~20 days. The feed consisted of mixed sludge (approximately 60% of primary sludge and 40% of activated sludge) from the Villalonquejar WWTP (Burgos, Spain) with a variable organic load (COD_T max–min [68–35] g/L). In experiment 1, raw sewage sludge was treated while in experiment 2, Na_2SO_4 was added to the feed with a concentration of ~2,200 mg/L of SO_4^{2-} to increase the amount of H_2S produced. O_2 supply was increased in stages until H_2S concentration in the biogas was

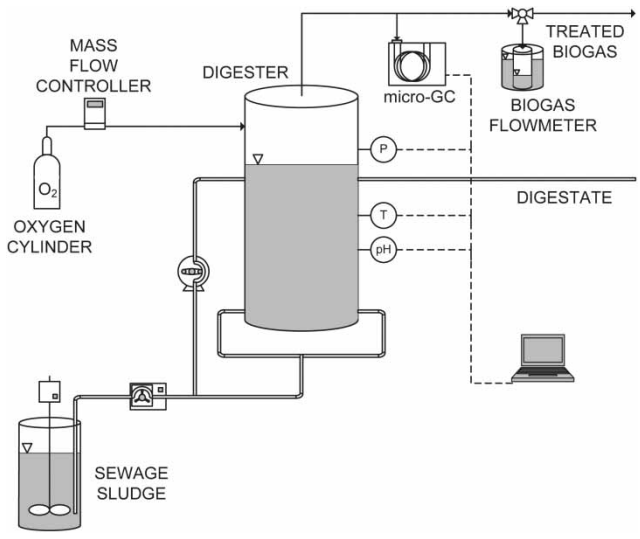

Figure 1 | Pilot-plant diagram.

Table 1 | Operational conditions during the study

	Experiment 1	Experiment 2
Duration (d)	80	45
Mixing	BR	BR
Microoxygenation		
Rates applied (NL/d)	0, 0.47, 0.51, 0.74, 0.97	0, 9.3, 10.9, 14.1
Sulfate concentration in feed (mg/L)	0	~2,200

BR: biogas recirculation.

consistently below 150 mg/Nm^3. These conditions are summarised in Table 1.

Monitoring and experimental analysis

The pilot-plant conditions were monitored online using pressure, temperature (PT100) and pH probes.

The biogas production gas measured by a fixed volume of liquid displacement (472 ± 8 Nm L) in an inverted cylinder equipped with an electrovalve. The biogas composition was measured by gas chromatography in intervals of 6 to 24 h depending on the variability of the H_2S concentration in the biogas as reported by Díaz *et al.* (2010b). The combination of biogas production and H_2S concentration in the biogas allowed us to evaluate the performance of the H_2S removal.

SO_4^{2-} and $S_2O_3^{2-}$ concentrations were measured by HPLC according to the method described by van der Zee *et al.* (2007).

Total and soluble COD concentrations as well as total dissolved S^{2-}, in feed sludge and digested sludge, were evaluated weekly according to standard methods (Clesceri *et al.* 1998). The present research is not suited to evaluating the effect of oxygen introduction on organic matter removal and biogas production; in this sense, Fdz-Polanco *et al.* (2009) and Díaz *et al.* (2010a) developed this aspect for similar O_2 rates to those employed in this research.

RESULTS AND DISCUSSION

H_2S removal capacity

The average H_2S concentration in the biogas produced during experiment 1 in the anaerobic period (without O_2 supply) was 0.33 ± 0.02% (v/v). O_2 supply to the digester started on day 10 at a rate of 0.47 NL/d and was increased in stages as shown in Figure 2(a). The final H_2S concentration in the biogas dropped gradually as O_2 rate was increased. For the highest rate (0.97 NL/d), H_2S concentration was always below 0.01% (v/v). H_2S was removed from the biogas with an efficacy higher than 97% for a rate of 0.97 NL/d of O_2.

O_2 concentration in the biogas remained below 0.1% (v/v) during the study, while H_2S was removed, and slightly increased when H_2S was totally removed indicating an excess of O_2 supplied.

CH_4 and CO_2 concentrations in the biogas remained stable during the experiment as shown in Figure 3(a), and were not affected by O_2 supply in the headspace. CH_4 accounted for an average 64.9 ± 1.4% (v/v) in the anaerobic period without O_2 supply and an average 64.5 ± 1.3% (v/v) during the microaerobic period at the highest O_2 rate (0.97 NL/d). Neither was the biogas production was affected by the limited oxygen supply to the digester.

To evaluate the result of H_2S oxidation, the sulfur species were analysed and are shown in Figure 4(a). The concentration of SO_4^{2-} in the effluent was negligible during all the experiment while $S_2O_3^{2-}$ appeared in the microaerobic period to reach a final concentration of ~10 mg/L. Total dissolved S^{2-} was ~46 mg/L in the anaerobic period and it dropped below 15 mg/L in the final microaerobic period. This shows that both gaseous and dissolved sulfide were removed as a result of the biogas recirculation.

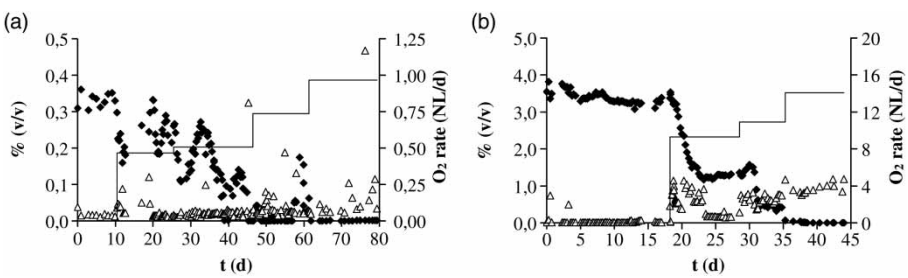

Figure 2 | H_2S (♦) and O_2 (Δ) concentrations in the biogas and O_2 rate (—) during the study. (a) Experiment 1 (raw sludge feed). (b) Experiment 2 (sludge and SO_4^{2-} feed).

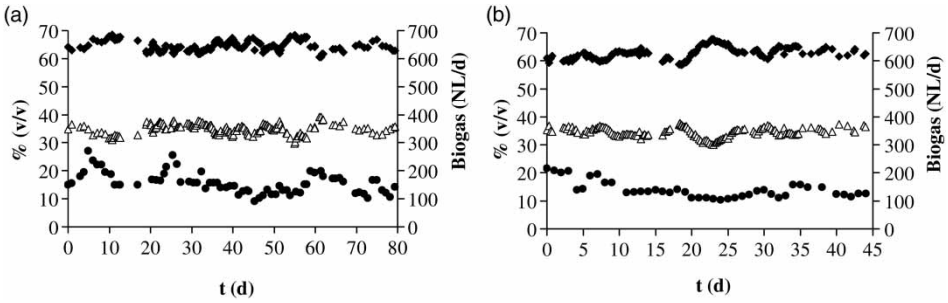

Figure 3 | CH_4 (♦) and CO_2 (Δ) concentrations in the biogas and daily biogas production (•) during the study. (a) Experiment 1. (b) Experiment 2.

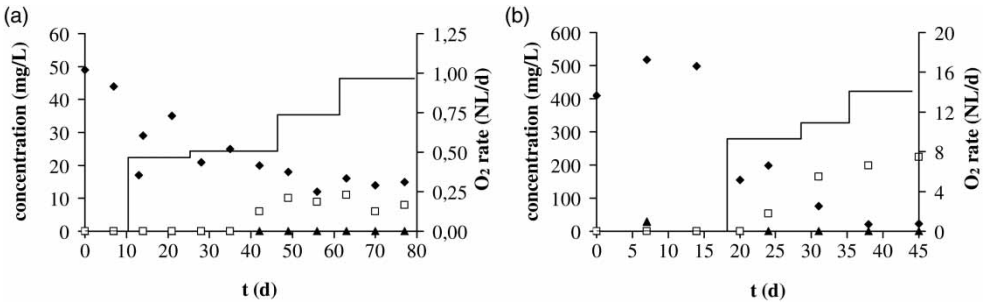

Figure 4 | Sulfur species concentration in the digester (mg/L), (♦) total dissolved S^{2-}, (□) $S_2O_3^{2-}$, (▲) SO_4^{2-}, and O_2 rate (—). (a) Experiment 1. (b) Experiment 2.

Then, it can be assumed that the main product of H_2S was S^0, limited oxygen introduction avoided SO_4^{2-} production.

During experiment 2, the average content of H_2S in the biogas in the anaerobic period was 3.38 ± 0.16% (v/v). This high concentration was the result of SO_4^{2-} addition to the feed sludge. To observe the capacity of microaerobic removal with the high concentration of H_2S produced in this study, O_2 was supplied beginning on day 18 with a rate of 9.3 NL/d of pure O_2. In the same way as in experiment 1, O_2 supply was increased in stages as shown in Figure 2(b) until the concentration was below 0.01% (v/v) in all the biogas composition analyses. Microaerobic conditions with a rate of 14.1 NL/d removed the H_2S content from the biogas with a removal efficacy higher than 99%.

In experiment 2, a final concentration of O_2 in the biogas of ~1% (v/v) was found when H_2S was totally removed. This concentration was higher compared to experiment 1 as a result of mass transfer limitations.

The concentrations of the main constituents of biogas, CH_4 and CO_2, were not reduced in this case (Figure 3(b)) despite the higher O_2 rate necessary to remove the larger amount of H_2S. CH_4 concentration in the anaerobic stage of experiment 2 was 61.5 ± 1.7% (v/v) and average concentration of CH_4 with an O_2 supply of 14.1 NL/d was 63.1 ± 1.0% (v/v). This slight increase of CH_4 in the biogas is the result of the H_2S disappearance from the biogas. This effect was also observed in the CO_2 concentration, which rose from 34.6 ± 1.2% (v/v) in the anaerobic period to 35.6 ± 1.0% (v/v) in the microaerobic period with the highest O_2 rate.

The sulfur species in experiment 2 (Figure 4(b)) showed an increase in $S_2O_3^{2-}$ concentration as O_2 rate was increased, while total dissolved S^{2-} dropped from ~475 mg/L in the anaerobic period to a final concentration of ~20 mg/L. In this case, dissolved sulfide was also removed as in experiment 1 with S^0 as the main product; nevertheless, the appearance of $S_2O_3^{2-}$ was observed until a final concentration of ~210 mg/L indicating oxidation slightly further than S^0. The formation of $S_2O_3^{2-}$ was probably because the result of a higher rate of O_2 applied to oxidise all the H_2S content and a further oxidation took place as a consequence of O_2 availability.

Therefore, limited oxygen supply to the bioreactor can be employed in a wide range of H_2S production (previous research showed 99% removal efficacy for a concentration of H_2S around 1% v/v, Fdz-Polanco *et al.* 2009) whereas the energetic content of the biogas (CH_4 concentration) was maintained in microaerobic conditions.

Optimal oxygen rate determination

The biogas production variability, a result of the variable COD in the feed sludge, caused deviations in the H_2S

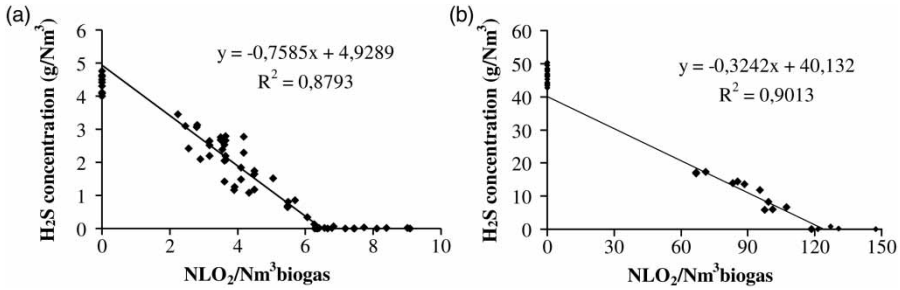

Figure 5 | Correlation between the ratio of O_2 supplied/biogas produced and the concentration of H_2S in the biogas. (a) Experiment 1. (b) Experiment 2.

concentration as O_2 is the limiting reactive for the lower O_2 rates. So, optimal O_2 rate must be adjusted to the biogas production to avoid a lack of the expected removal (when COD in the feed sludge is low) or an excess of O_2 in the biogas (for the higher COD loads in the feed sludge).

The ratio of O_2 rate/Biogas production rate was compared to the final H_2S concentration in the biogas during the study to achieve the mentioned optimal flow (Figure 5).

In experiment 1, it was found that a ratio of 6.4 NLO_2/Nm^3 of biogas or higher led to a concentration of H_2S in the biogas lower than 150 mg/Nm^3 (Figure 5(a)). This rate represents approximately 3.3 times the stoichiometric amount to oxidise both H_2S (gas) and dissolved sulphide to S^0 in the digester. So, employing such a ratio O_2 supply can be optimised to achieve a removal higher than 97% with a minimal O_2 amount unemployed for the removal.

Furthermore, a statistical analysis was performed to correlate the H_2S concentration and the ratio NLO_2/Nm^3 biogas for a ratio equal to or lower than 6.4. This data proved to follow a normal distribution ($R = 0.94$) and a linear regression ($R^2 = 0.88$) showed moderate linear behaviour during the experiment.

For experiment 2, a ratio of 118 NLO_2/Nm^3 biogas or higher resulted in a concentration of H_2S lower than 150 mg/Nm^3 (Figure 5(b)); this represents 6.5 times the stoichiometric amount to oxidise H_2S to S^0. A removal higher than 99% was achieved when this ratio or higher was achieved. Comparing this optimal rate with the one from experiment 1, a concentration of H_2S around 10 times higher required a ratio of NLO_2/Nm^3 around 20 times higher. This is the result of the higher dissolved sulfide concentration in equilibrium with the biogas in the biodigester, which was also removed by microoxygenation, and the higher production of $S_2O_3^{2-}$ in experiment 2.

The statistical analysis of the data was performed in this case only for the points where pseudo-stationary conditions were achieved for rates equal to or lower than 118 NLO_2/Nm^3 biogas, owing to the fact that transition states when O_2 rate was raised from stage to stage were longer for this experiment (see Figure 2(b)). The data were shown to follow a normal distribution ($R = 0.96$) and a strong linear behaviour ($R^2 = 0.90$).

CONCLUSIONS

The microaerobic treatment showed to effectively remove H_2S from the biogas in a wide range of the H_2S concentrations found on AD. To achieve the target, O_2 rate can be optimised to achieve low O_2 concentrations in the biogas, around 0.1% (v/v) for low H_2S anaerobic concentrations, while eliminating H_2S and controlling the final product of the H_2S oxidation. In this sense, S^0 was the main product during the treatment; however, when a higher amount of H_2S was present in anaerobic conditions, a small fraction of $S_2O_3^{2-}$ was found for the optimal rate. Finally, the ratio O_2 rate/biogas production rate was found an adequate parameter to control the O_2 dose to the digester.

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