Robustness of the microaerobic removal of hydrogen sulfide from biogas

I. Díaz and M. Fdz-Polanco

ABSTRACT

Several disturbances presented in full-scale digesters can potentially affect the efficiency of the microaerobic removal process. This study evaluates the variation of the sulfur load and the performance of the system in situations of oxygen lack or excess and after normal rates are recovered. The process was shown to recover from oxygen lack or excess within 28 h when the original conditions were restored in a pilot-plant digester of 200 L treating sewage sludge with HRT of 20 days. The decrease of the sulfur load to the digester did not affect the biogas composition in the short-term and when oxygen rate was reduced to adjust to the lower hydrogen sulfide production, the removal proceeded normally with a lower unemployed oxygen amount. The digester opening to remove accumulated sulfur in the headspace did not alter process performance once the microaerobic removal was restarted.

Key words | biogas, hydrogen sulfide, microaerobic, robustness, stability, sulfur

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INTRODUCTION

Anaerobic digestion (AD) is a technology widely employed to reduce the amount of sludge generated during the traditional activated sludge treatment of wastewaters since it is able to transform a large part of the organic matter in biogas with a content of methane between 60 and 70% (v/v) that can be energetically used.

However, the AD of S-containing organic matter generates hydrogen sulfide as a result of the competition between methanogens and sulfur-reducing bacteria (Lens & Pol 2000). This concentration typically varies from 0 to 6,075 mg/Nm^3 for the AD of sewage sludge (Petersson & Wellinger 2009). Hydrogen sulfide in the biogas reduces the lifetime of pipework and other installations needed for the utilization of biogas, it is toxic and corrosive to many types of steel (Deublein & Steinhauser 2007).

Therefore, hydrogen sulfide must be removed before methane can be transformed to energy. In this sense, microaerobic removal of hydrogen sulfide has proven to be an effective method to achieve a very low concentration of the pollutant (41 mg/Nm^3) in the biogas while maintaining methane production and organic matter removal (Jenicek *et al.* 2008). Microaerobic removal consists of limited oxygen supply to the 'anaerobic digester' so that hydrogen sulfide is chemically and biologically oxidized (by sulfide-oxidizing bacteria, SOB) to produce mainly elemental sulfur, partly accumulated in the headspace (HS) of the digester (Díaz *et al.* 2011a), according to Equation (1):

$$H_2S + \frac{1}{2}O_2 \rightarrow S^\circ + H_2O \quad \Delta G^\circ = -209.4\ \text{kJ/reaction} \qquad (1)$$

Previous studies have indicated the potential use of microaeration for hydrogen sulfide removal without significantly affecting the organic matter removal efficiency and methane yield (Fdz-Polanco *et al.* 2009; Díaz *et al.* 2011a). However, the introduction of microaeration in full-scale digesters may possibly shorten the digester cleaning interval, which can negatively affect the process economy. Such periodic digester cleaning might also alter the process efficiency upon restart, due to the possibility of washing away sulfur and SOB (Díaz *et al.* 2011a) during cleaning.

Apart from HS cleaning, the microaerobic removal in full-scale digesters can also suffer variations as a result of the variable sulfur and organic load of the sludge, process failure or maintenance actions in the digester. OLR variations to the anaerobic digester are intrinsic to the process as sludge production varies depending on the overall wastewater treatment process (Appels *et al.* 2008). A fixed oxygen rate to the digester would result in a lack or excess depending

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on variable biogas production; therefore, the removal requires the control of the oxygen supply so that removal happens properly and the methane/oxygen relation remains far from the flammable zone for the biogas (typically for concentrations of methane between 5 and 15% in air) described by Dupont & Accorsi (2006) and Speece (2008).

In the present study, the stability and robustness of the microaerobic removal is observed when intrinsic variations to real digesters operation happen. The variation of the sulfur load of the sludge, lack or excessive oxygen rate to the digester and cleaning of the HS are evaluated.

METHODS

Pilot-plant digesters

The study of the process robustness was performed in a pilot-plant scale reactor with a working volume of 200 L (250 L total volume). The reactor was insulated, and the wall was heated with electric resistance. The reactor was mixed with sludge recirculation with a peristaltic pump (~50 L/h). The feed was provided from a continuously stirred tank with a peristaltic pump. Micro-oxygenation was maintained using the regulated flow of pure oxygen with a mass flow controller from an oxygen cylinder; oxygen was employed instead of air to avoid biogas dilution by means of nitrogen. Oxygen was supplied to the HS, which allowed the storage of ~1/4 of the daily biogas production (50 L). The pilot-plant diagram is shown in Figure 1.

The digester was employed for previous anaerobic/microaerobic experiments during ~350 d. Digestion was performed in the mesophilic range ($35 \pm 1\ ^{\circ}C$) with a hydraulic retention time (HRT) of ~20 days. The feed consisted of mixed sludge from the Villalonquejar wastewater treatment plant (WWTP) (Burgos, Spain) with a variable organic load (VS max–min [41–21] g/L). Sludge was sampled every week and conserved at 4 °C. To increase the amount of hydrogen sulfide produced during digestion, sodium sulfate was added to the feed to achieve a final concentration of sulfate of ~750 mg/L. Micro-oxygenation was initially performed at a flow rate of 2.5 ± 0.1 NmL/min; this represents ~0.33 NL of oxygen per L of feed sludge.

The digester was opened after ~2 years of operation. The HS was photographed and deposited sulfur was removed from the top and the walls of the reactor above the liquid surface. Micro-oxygenation was performed at ~0.25 NL of oxygen per L of feed sludge before the reactor opening and the same rate was applied once sulfur was removed and the reactor closed again.

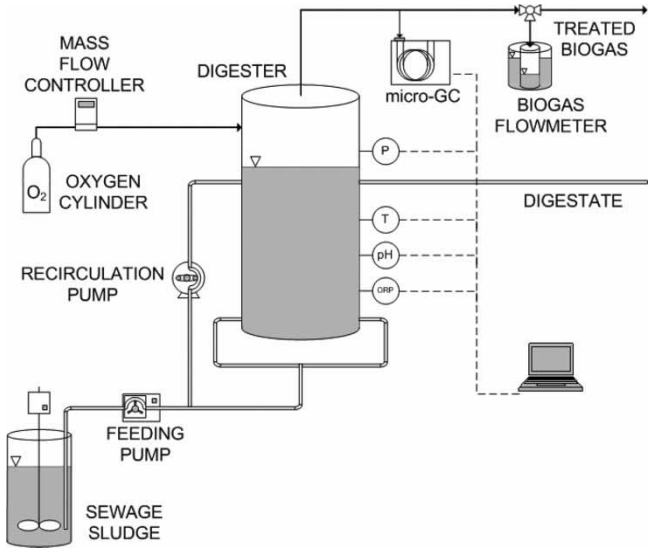

Figure 1 | Scheme of the experimental pilot-plant digester.

Analytical methods

Biogas composition was measured online for the robustness analysis and external oxidation by gas chromatography (GC) in a VARIAN Micro-GC equipped with thermal conductivity detector and sulfate concentration in the digesters and in the feed sludge was determined by high performance liquid chromatography (HPLC) in a Waters Millipore temperature control module, both following the method described in Díaz *et al.* (2010).

Sulfate concentration in the digesters and in the feed sludge was determined as reported by Díaz *et al.* (2011a), thiosulfate was determined following the methods described in van der Zee *et al.* (2007) and sulfide was determined by the Ion-selective Electrode Method (Clesceri *et al.* 1998).

Total solids (TS) and volatile solids (VS) were evaluated according to Standard Methods (Clesceri *et al.* 1998).

RESULTS AND DISCUSSION

Process stability

The oxygen flow and the concentration of sulfate in the feed were altered from stationary conditions. The response of the system in terms of biogas concentration is shown in Table 1. The stop in the oxygen supply on day 15 led to an

Table 1 | Sequence of variations applied in the robustness study and observed response

Condition	1	2	3	4	5	6	7
Disturbance	N.A.	Suppression of oxygen flow	Recovery of stationary conditions	Increased oxygen flow by 140%	Recovery of stationary conditions	Reduced amount of sulfur in feed	Reduction of oxygen rate by 60%
t (d)	0	15	24	31	39	47	61
Oxygen rate/ feed rate (L/L)	0.33	0	0.33	0.79	0.33	0.33	0.13
Sulfate addition to sludge (mg/L)	750	750	750	750	750	0	0
Response	N.A.	Increased pollutant concentration to anaerobic values within 7 h	Removal recovered after 28 h	Oxygen excess in biogas reaching 4% (v/v)	Oxygen dropped to stationary values in 8 h. Slightly increased sulfide concentration during transition state	No effect on biogas composition during 14 days	Effective removal with lower oxygen concentration in the biogas. ~0.2% (v/v)

increase of hydrogen sulfide concentration from a concentration lower than 70 mg/Nm^3 to the anaerobic values within 7 h (from 14,100 to 22,500 mg/Nm^3), as shown in Figure 2. Once oxygen flow was restored on day 24, the pollutant concentration dropped gradually until it reached the previous stationary values. The drop was not as fast as the increase when oxygen was removed; it took more than 1 day to achieve the stationary values. However, the stop in the oxygen supply did not result in a deterioration of the removal capacity as the same stationary values were found.

On day 31, an oxygen overload was tested by increasing the oxygen flow by 140%. Removal was maintained at the previous values and the remaining oxygen concentration was found as high as 4% (v/v). Such a failure in the supply still remained far from the inflammable zone reported by Dupont & Accorsi (2006). Nevertheless, inflammable zones are empirical findings and oxygen flow must be controlled to avoid any risk whether by oxygen probes in the HS of the digester or by exhaustive dosing controlled rates. Additionally, excessive oxygen in the biogas may result in methane concentration dilution negatively impacting the performance of the combustion engine (Porpatham *et al.* 2007).

An oxygen excess could also be found if the organic loading rate (OLR) to the digester decreased in real operation. A lower VS content in the sludge will result in a lower biogas production, lower release of sulfur compounds and an excess of oxygen in the biogas if not conveniently reduced to adequate to lower hydrogen sulfide production rates. When oxygen was restored to the stationary values (day 39), oxygen concentration dropped in 8 h to stationary values; however, during the transition state, hydrogen sulfide concentration rose, reaching values above 3,000 mg/Nm^3 to later decrease to the stationary values. This effect is related to the adaptation of the system to the reduced oxygen flow.

The effect of the sulfur load in sludge was studied by altering the amount of sulfate. Sulfate was removed from the feed on day 47 and the biogas composition was not substantially altered; previous studies on the treatment of the raw sludge in anaerobic conditions showed a concentration of hydrogen sulfide between 4,000 and 5,000 mg/Nm^3 (Díaz *et al.* 2011b). This must be due to the long HRT (20 days) of the reactor, which results in a slowly responding hydraulic system to the variations in feed characteristics (biogas residence time in HS is ~8 h).

While the changes in oxygen flows provoke variations of hydrogen sulfide concentration in the biogas within hours,

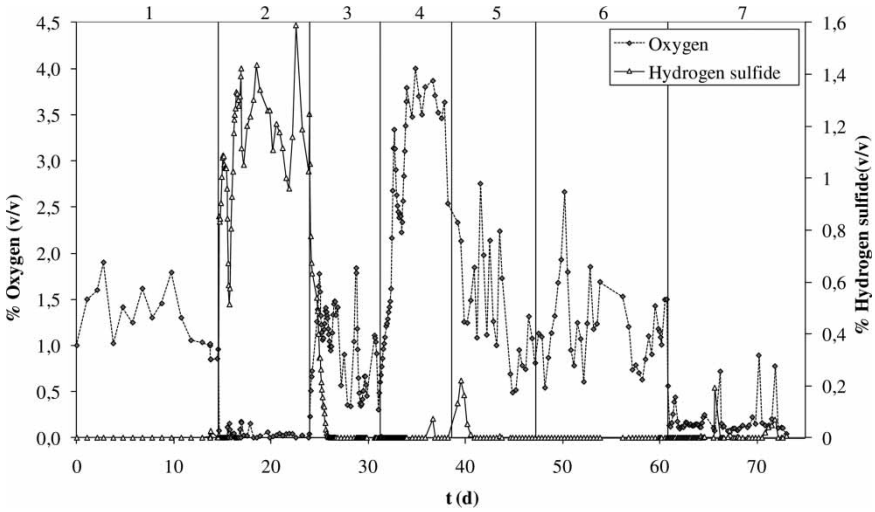

Figure 2 | Oxygen and hydrogen sulfide concentrations in the biogas during the study.

the increase or reduction of the sulfur concentration in the feed gradually affects the concentration of the biogas taking longer than one HRT. Nevertheless, oxygen was reduced by 60% on day 61 to explore the removal for a lower production of sulfide, and microaerobic removal developed satisfactorily (hydrogen sulfide concentration lower than 70 mg/Nm^3). Therefore, it was found that lower productions of the pollutant could be removed while the average remaining oxygen in this case was lower than 0.2% (v/v).

The introduction of oxygen did not alter VS removal during the study (Figure 3(a)). Organic load was variable to the digester as a result of the variable VS content of raw sludge; however the VS concentration in the effluent was stable during the experiment.

Another important aspect is the effect that limited oxygen supply provoked in the dissolved sulfur species. Sulfate was totally absent in the digester liquid indicating a total transformation to sulfide by sulfate-reducing bacteria (Figure 3(b)). Total dissolved sulfide remained at values around 90 mg/L at a pH between 7.2 and 7.4, similar to the anaerobic period, during the first stages of the experiment before sulfate was removed from the feed on day 47, indicating that removal proceeded in the HS of the digester and dissolved sulfide was not affected as a result of poor mixing between biogas and liquid phase. From day 47, sulfide concentration gradually dropped as a consequence of the absence of sulfate. A low concentration of thiosulfate (below 10 mg/L) was detected in some samples which might be the result of slight further oxidation by SOB.

HS cleaning

The microaerobic removal led to the production, and partly accumulation, of elemental sulfur (according to Equation (1))

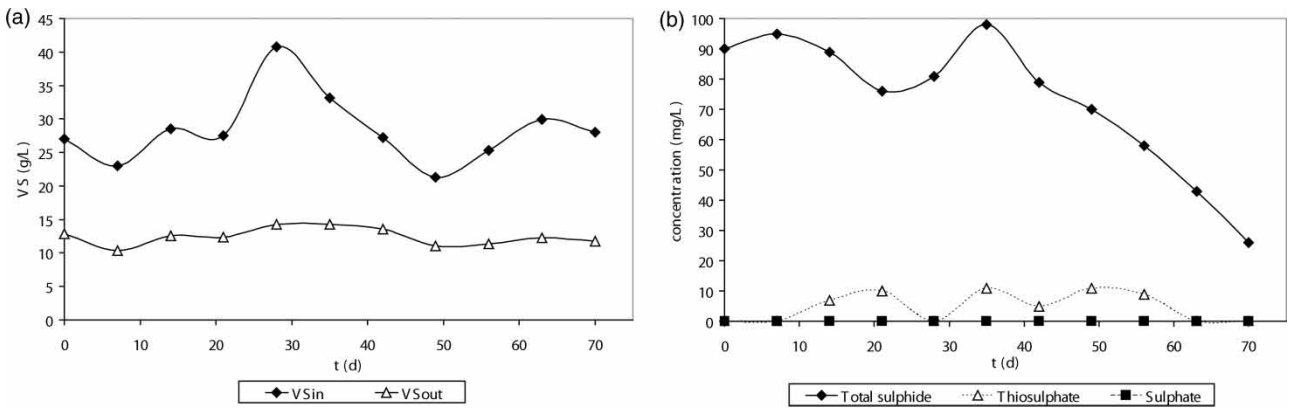

Figure 3 | VS concentration and sulfur species in the digester. (a) VS concentration in raw and treated sludge; (b) concentration of dissolved sulfur species.

Figure 4 | Sulfur deposition in the headspace. Left: top of the reactor. Right: walls above the liquid surface.

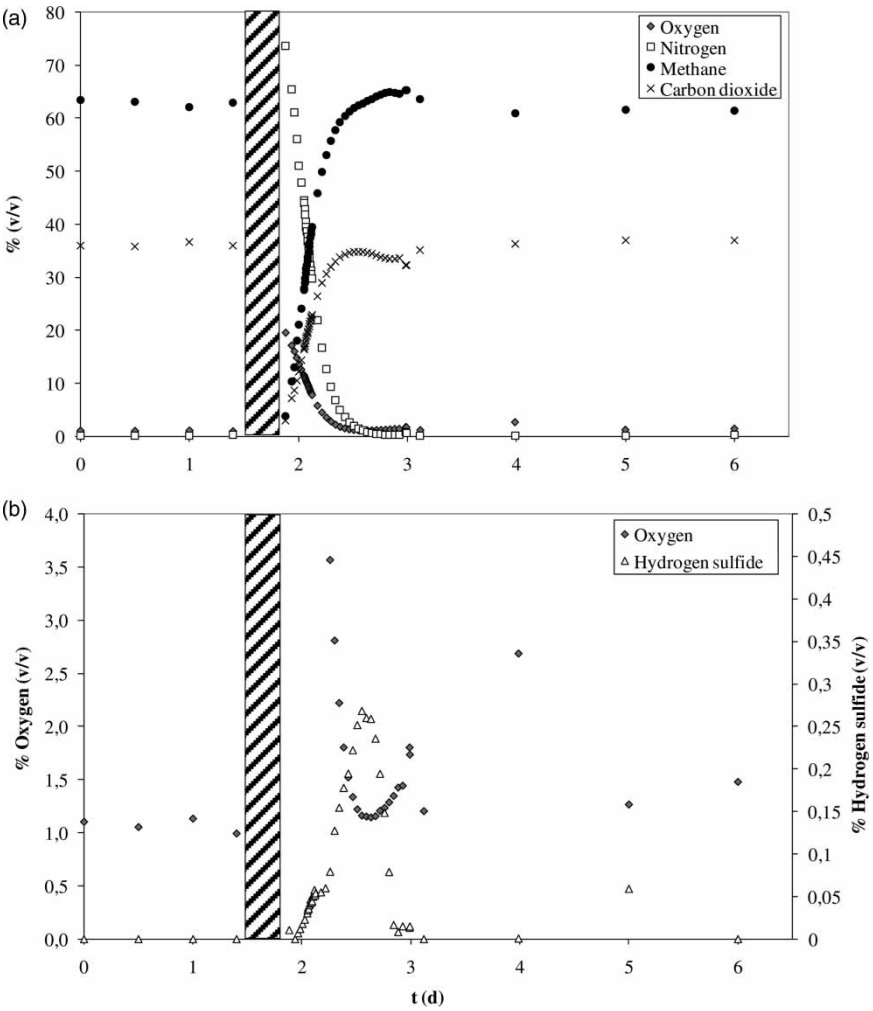

Figure 5 | Biogas composition before and after sulfur removal from the headspace.

in the HS of the digester; reported by Díaz *et al*. (2011a) and shown on Figure 4. The accumulation can cause clogging problems in the digester and, probably, the reduction of the effectiveness of the microaerobic removal because of a lower capacity of biogas storage. Then, the application of the microaerobic removal might require periodic cleaning of the HS of the digester. When HS is cleaned, both sulfur and developed SOB are removed from the HS. The impact of the cleaning was studied in the digester after 620 days of operation. The digester was opened and accumulated sulfur was removed; after that, the digester was sealed again, the microaerobic operation was restarted and the evolution of the biogas composition was followed.

Figure 5 shows different aspects of the biogas composition prior to and after the cleaning. Once sulfur was removed, the same oxygen rate was applied (0.13 L of oxygen per L of feed). The main constituents of biogas (Figure 5(a)) reached the stationary concentration in approximately 1 day. A similar behaviour was found for hydrogen sulfide. As shown in Figure 5(b), the hydrogen sulfide concentration increased during the first 16 h after the digester was closed to a peak of 0.27% (v/v), lately, the concentration dropped and the concentration was similar to the previous period within 30 h.

Conversely, oxygen concentration dropped to a minimum after 16 h, with a slight increase as sulfide concentration dropped latterly. The time employed to recover the stationary concentrations (~30 h) was similar to that employed after oxygen supply restoration shown in Figure 2. This evolution reflects that sulfur removal did not disturb the microaerobic removal after the restarted operation despite the removal of SOB in the HS. This could indicate that the chemical contribution to the oxidation was higher than the biological or that the presence of SOB in the liquid interphase is enough to properly remove hydrogen sulfide after cleaning the HS.

In the first situation, the presence of any substance in the liquid of the digester could be catalysing the oxidation in the gas–liquid interphase, as the removal of SOB did not affect the process. Direct oxidation of sulfide has a low kinetics however it is known to be catalysed by heavy metals (Andreev *et al*. 1996; Iliev *et al*. 2000) present in the sludge from a WWTP. About the second hypothesis, these results would indicate that the community of SOB created in the HS (Díaz *et al*. 2011a) is not relevant for the removal process and that SOB present in the gas–liquid interphase of the reactor can outcompete most of the microorganisms for available oxygen and perform the oxidation of sulfide. In this sense, Jenicek *et al*. (2011) found that the activity of SOB in digester liquid was increased with microaeration. As a result, further research is necessary to explore the mechanism of oxidation in the rich atmosphere for chemical and biological oxidation of sludge digestion under microaerobic conditions.

CONCLUSIONS

The application of several disturbances to a digester with microaerobic removal of hydrogen sulfide was studied. The process recovered from oxygen supply withdrawal within hours when the original conditions were restored. The decrease of the sulfur load did not affect the concentration of hydrogen sulfide in the biogas in the short term and the reduction of the oxygen flow to adjust to the lower hydrogen sulfide production resulted in effective removal of the pollutant. The operation of HS cleaning did not negatively affect the removal process once it was restarted and proceeded normally after 30 h of stabilization.

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