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The headspace of microaerobic reactors: Sulphide-oxidising population and the impact of cleaning on the efficiency of biogas desulphurisation

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HIGHLIGHTS

- Microaerobic conditions are applied in order to control the H_2S content of biogas.
- The S^0-rich deposits found in the HS of two microaerobic reactors are removed.
- H_2S-free biogas is rapidly achieved after cleaning the HS.
- A cleaning interval of less than 14 months ensures minimum micro-oxygenation cost.
- Moisture level determines the composition, richness and size of the SOB population.

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ABSTRACT

O_2-limiting/microaerobic conditions were applied in order to control the H_2S content of biogas. The S^0-rich deposits found all over the headspace of two pilot reactors (R1 and R2) as a result of operating under such conditions for 7 and 15 months (respectively) were sampled and removed. After restarting micro-oxygenation, H_2S-free biogas was rapidly obtained, and the O_2 demand of R2 decreased. This highlighted the need for a cleaning interval of less than 14 months in order to minimise the micro-oxygenation cost. The H_2S removed from R2 after approximately 1 month was recovered from its headspace as S^0, thus indicating that the biogas desulphurisation did not take place at the liquid interface. Denaturing gradient gel electrophoresis indicated that the composition, species richness and size of the sulphide-oxidising bacteria population depended on the location, and, more specifically, moisture availability, and indicated increasing species richness over time. Additionally, a possible succession was estimated.

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1. Introduction

H_2S is a common biogas compound arising from the anaerobic digestion of proteins and S-containing compounds. It can exceed concentrations of 0.05% v/v and up to 2.0% v/v, which inevitably causes corrosion problems in combustion engines, and the release of SO_x in flue gases (Fortuny et al., 2008). Therefore, most manufacturers of combined heat and power installations recommend a biogas sulphide content of less than 0.01% or 0.03% v/v, depending on the equipment concerned (Peu et al., 2012).

H_2S can be controlled either at the source, by controlling the feedstock, at the end, by desulphurising the biogas in a later stage, or at process level, directly inside the anaerobic digester (Peu et al., 2012). The first solution is not realistic, and it is in fact the latter H_2S removal from biogas which is the most established method in practice, as it can be carried out during digestion or in an additional unit (Cirne et al., 2008). The most common end-of-pipe techniques for H_2S removal are based on physical–chemical processes. However, their high costs of both operation and by-product disposal have encouraged research and the application of biological processes (Park et al., 2011). Specifically, biological desulphurisation has been reported to be approximately 62% cheaper than chemical absorption (Burgess et al., 2001). Furthermore, it can achieve more complete removal due to the extremely high affinity of sulphide-oxidising bacteria (SOB) for the substrate (Kobayashi et al., 2012).

Abbreviations: DGGE, denaturing gradient gel electrophoresis; HS, headspace; PCR, polymerase chain reaction; SOB, sulphide-oxidising bacteria; TS, total solids.

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The most widespread biotechnologies for H_2S removal are biofilters, biotrickling filters and bioscrubbers, in which aerobic species of chemolitotrophic SOB oxidise the sulphide mainly to S^0 or SO_4^{2-}, depending on the O_2 availability (Tang et al., 2009). Besides requiring fourfold less O_2, the conversion of H_2S into S^0 is preferred over conversion to SO_4^{2-} due to the fact that S^0 is harmless and can be recovered from liquid streams and reused in bioleaching and agriculture (Kleinjan, 2005). Inside these biological systems, sulphide can be also chemically oxidised to $S_2O_3^{2-}$ (Lohwacharin and Annachhatre, 2010). Importantly, this oxidation mechanism can be catalysed by any metal ion present in the bioreactor (Kleinjan, 2005). As a result, SOB have to contend with chemical sulphide oxidation for O_2. According to Robertson and Kuenen (2006), they compete effectively at very low O_2 and sulphide concentrations. However, the contribution of the chemical mechanisms increases at high sulphide loads due to limitations in biological activity.

As an economically attractive alternative to employing additional units (that is, a process-level solution), H_2S can be removed from biogas simply by imposing microaerobic conditions in the anaerobic reactor. In Europe, this technique has been applied by injecting air directly into the headspace (HS) of the digester in order to maintain 4–6% of air in the biogas, and as a result, S^0 deposits have been found at the liquid interface and on other surfaces of the gas space (Abatzoglou and Boivin, 2009). This is partly consistent with the results of Díaz et al. (2010), who demonstrated that the desulphurisation process basically occurs in the HS independently of both the O_2 (or air) dosing point and the mixing method, but in this case neither S^0 nor SOB were found at the liquid interface . Similarly, Rodríguez et al. (2012) only identified representatives of this microbial group in the S^0-rich biomass attached to the HS, although micro-oxygenation was introduced from the bottom of the reactor.

It is essential to know how the increasing accumulation of S^0 in the headspace over time affects the O_2 transfer conditions and, therefore, the performance of the biogas desulphurisation, since this could lead to a reduction in the intervals of time at which the digester must be cleaned. Although the S^0 accumulation could also significantly reduce the volume of the gas space in microaerobic reactors in the long-term, Ramos et al. (2012) demonstrated that a biogas residence time of approximately 1 h sufficed to achieve H_2S removal efficiencies similar to those obtained at around 7 h. Díaz and Fdz-Polanco (2012) reported that the desulphurisation performance in a microaerobic digester treating sewage sludge was very similar just before HS cleaning and 30 h later, after almost 21 months intercalating anaerobic and microaerobic experiments. Moreover, they highlighted the rapidity with which the H_2S was removed from the biogas just after cleaning the HS, which suggested extremely high activity levels of SOB at the liquid interface and/or a great contribution by the chemical oxidation mechanisms. With regard to this, it must be noted that Ramos et al. (2012) provided evidence that this process is predominantly biological.

Likewise, it is of utmost importance to know how SOB grow in the HS to optimise the efficiency of H_2S removal from biogas in microaerobic reactors. However, only Kobayashi et al. (2012) have provided valuable information in this area. They showed that both cell density and bacterial activity in the HS were much higher in the areas nearest the liquid phase, which was attributable to an increased availability of water and nutrients.

Based on the points outlined above, the main objectives of this study were:

- To evaluate the impact of HS cleaning on the efficiency of biogas desulphurisation.
- To investigate where exactly the biogas desulphurisation takes place in the HS.
- To characterise and locate the SOB population that is removing H_2S during sewage sludge digestion.
- To approach the temporal differences in the SOB population.

2. Methods

2.1. Pilot plant scale reactors

Research was carried out in two continuous stirred tank reactors (R1 and R2) with 200 L (250 L of total volume) treating sewage sludge with a variable organic and sulphur load at 19d of hydraulic retention time. A diagram of the digesters is shown in Fig. 1. Temperature (35 °C) was monitored by probes and was regulated by electric resistors surrounding their walls, which were in turn covered with insulation. Mixing was carried outat approximately 50 L/h by peristaltic pumps. Microaerobic conditions were implemented by making a single-point injection of pure O_2 into the HS using mass flow controllers. Biogas composition was determined by gas chromatography (Díaz et al., 2010), and its production was measured volumetrically.

2.2. Digestion monitoring

Digestion performance was assessed by measuring total and soluble chemical oxygen demand (COD), total solids (TS), volatile solids (VS), volatile fatty acids, total kjeldahl nitrogen and ammonia according to APHA (1998). Total dissolved sulphide and SO_4^{2-} concentrations were measured by the potentiometric and the chromatographic method, respectively (APHA, 1998). $S_2O_3^{2-}$ was measured by high liquid performance chromatography according to the procedure described by van der Zee et al. (2007). A LECO CS-225 was utilised to determine elemental composition in terms of S and C.

2.3. Experimental procedure

The operational sequence is schematised in Fig. 2. The HS of R2 was cleaned at $t = 0$ (Fig. 2); however this reactor was operated for several months before beginning this research under the aforementioned conditions. Seven months afterwards (at $t = 8$), R1 was started up with sludge from R2. Thereafter, both digesters operated in parallel and under the above conditions. Until $t = 15$, they basically operated under microaerobic conditions; micro-oxygenation was rarely interrupted.

At $t = 15$, the ceiling of both reactors was removed. Six samples (A–F) were taken from different points of the HS for TS, elemental, and microbial analysis (Fig. 3a). As indicated in Fig. 2, A1–F1 were retrieved from R1, and A2–F2 belonged to R2. The A and B samples were taken from the walls (the lowest and the upper area, respectively), the C samples were taken from the ceiling, the D and E samples were taken from the dip tube (the upper and the lowest area, respectively), and the F samples were taken from the liquid interface (Fig. 3a). After sampling, all the surfaces were cleaned, and the liquid interface (approximately 250 mm of sludge from the surface) was removed.

Once sealed, the digesters were operated under anaerobic conditions for 1 month (Fig. 2).

Micro-oxygenation was restarted at $t = 16$. At $t = 17$, R2 was uncovered again, and the S^0-rich deposits accumulated in the HS were retrieved separately according to Fig. 3a. As shown in Fig. 2, those samples were called A3–F3. After drying them, they were weighed and characterised in terms of S and C percentages in order to estimate the amount of S^0 deposited.

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