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Where does the removal of H_2S from biogas occur in microaerobic reactors?

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HIGHLIGHTS

- The location for H_2S 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, H_2S-free biogas is achieved.
- The H_2S concentration approaches anaerobic values with a smaller headspace (0.3 L).
- The biogas O_2 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 micro-aerobic 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 H_2S concentration in the biogas varied between 0.21 and 0.38%v/v. Next, O_2 was supplied from the bottom of the reactor. At 0.25–0.30 NLO_2/L_{fed}, the biogas was entirely desulphurised, and its O_2 content remained below 1.03%v/v, when the digester had 25.0 L of gas space. However, with almost no headspace, the H_2S content in the biogas fluctuated from 0.08 to 0.21%v/v, while the average O_2 concentration was 1.66%v/v. The removed H_2S accumulated in the outlet pipe of the biogas in the form of S^0 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/m^3, it has a good calorific value (5000 kcal/m^3) (Abbasi et al., 2012).

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 CH_4 and CO_2 in a ratio of 3:1, and other minor constituents; among them, H_2S is of particular interest due to its corrosive, toxic and environmentally hazardous properties. Along with CH_4, 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 H_2S 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, H_2S also causes the deterioration of the lubrication oil (Weiland, 2010). Consequently, H_2S production must be prevented, or H_2S must be removed from the biogas.

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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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, H_2S 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 H_2S 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 (S^0) 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 H_2S is first oxidised by ferric iron to generate S^0 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 H_2S removal from biogas consist of a chemical scrubber, in which the H_2S 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 H_2S can also be chemically oxidised in biological reactors, especially if the H_2S load is high, and in this case $S_2O_3^{2-}$ is the main by-product (Lohwacharin and Annachhatre, 2010).

The direct injection of O_2 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 SO_4^{2-}, whereas under O_2-limiting conditions, they oxidise sulphide to S^0 (van der Zee et al., 2007). Evidently, both reactants, O_2 or air, are supplied in limited amounts in order to minimise both the surplus of O_2 and the presence of N_2 in the biogas leaving the digester, and the operating costs. It must be noted that O_2 transfer has been suggested to be the limiting step during H_2S removal from biogas in these reactors, which are usually referred to as microaerobic reactors (Fdz-Polanco et al., 2009). Therefore, the use of O_2 is recommended instead of air (Díaz et al., 2010a); thus, additional dilution by N_2 is avoided (Jenicek et al., 2010; Díaz et al., 2010a). As a result, S^0 is the main by-product of H_2S oxidation during microaerobic digestion.

Neither the digestion performance nor the productivity or the CH_4 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 O_2 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, S^0 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 S^0 generated as a result of O_2 injection into the HS of a dairy cow manure digester and the H_2S oxidation, was deposited all over the HS. Likewise, Jenicek et al. (2011) indicated that H_2S conversion into S^0 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), S^0 produced during microaerobic digestion of synthetic vinasse was deposited in the HS despite O_2 being introduced from the bottom of the system; this compound was indeed the main by-product of the H_2S oxidation. Besides, they found SOB only in the gas space. These contradictory results certainly point to O_2 transfer limitations; Rodríguez et al. (2012) detected a considerable part of the O_2 injected into the reactor in the biogas, which still contained significant amounts of H_2S. Nevertheless, Díaz et al. (2010b) reported that increasing the O_2 transfer to the liquid phase of a sewage sludge digester did not lead to a higher efficiency of biogas desulphurisation, while the O_2 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 O_2 dosing point and the mixing method. Accordingly, the optimum configuration of a microaerobic reactor aiming for biogas desulphurisation consists of O_2 or air injection into the HS and liquid recirculation.

Considering the inconsistent results concerning the predominant location for H_2S 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 O_2 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 CH_4, CO_2, N_2, O_2 and H_2S 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,

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