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Hydrogen sulphide removal in the anaerobic digestion of sludge by micro-aerobic processes: pilot plant experience

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ABSTRACT

H_2S removal from biogas produced in anaerobic digestion of sludge through the introduction of oxygen under micro-aerobic conditions is studied. Research was carried out in two pilot plant reactors (working volume, 200 L each) treating sludge from WWTP with HRT of 20 days. Mixing was provided via sludge or biogas recirculation. Introduction of very low oxygen flow (0.013–0.024 $L/L_{reactor}$ d) successfully removed H_2S content in biogas with an efficiency above 99%. Reactor performance during micro-aerobic operation in terms of biogas production, methane yield and COD removal were not affected by the amount of oxygen supplied, remaining stable and similar to the anaerobic behaviour. Sludge recirculation (~50 L/h) and biogas recirculation (~3.5 L/min) as mixing methods were found not significant in H_2S removal from biogas while biogas recirculation reduced by 10 times dissolved sulphide concentration compared to sludge recirculation.

Key words | anaerobic digestion, biogas, micro-aerobic, sludge, sulphide

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INTRODUCTION

Biogas energetic potential is one of the most attractive advantages of anaerobic treatment to minimize sludge from waste water treatment plants (WWTP) (Lettinga 1996); however, H_2S formation during the reduction of sulphur containing compounds often exceeds technical limits of energetic use technologies (Noyola *et al.* 2006) as well as corrosion, toxicity and odour associated problems. Oxygenation of the "anaerobic bioreactor" has been recently reported as an alternative to high energy requirements of biogas stripping or high chemical and disposal for sulphide precipitation (Hulsfoff Pol *et al.* 1998) in the treatment of sulphate-rich wastewater to reduce H_2S in biogas and sulphide toxicity to methane producing bacteria (Fox & Venkatasubbiah 1996; Zitomer & Shrout 1998; Khanal & Huang 2003). Sulphide oxidation takes place both chemically and biologically (Janssen 2005) and it is believed to begin with polysulphides formation which may be further oxidized to elemental sulphur lately (Steudel 1996) under oxygen limited conditions. Moderate aeration in low-sulphate wastewaters has also been probed successful, showing an effective competence for available oxygen of sulphide oxidation versus other oxidative processes (van der Zee *et al.* 2007). There is a lack of knowledge in pilot plant and full-scale micro-aerobic operation (Cirne *et al.* 2008) even when biodesulphuration is already being employed in industrial scale (Cline *et al.* 2003). This study is focused on the feasibility and mechanism of H_2S removal from biogas produced in the anaerobic digestion of sludge in pilot plant scale by the introduction of a limited amount of oxygen directly to the bioreactor under different mixing conditions and the impact of micro-aerobic conditions on anaerobic digestion performance.

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MATERIALS AND METHODS

Reactors

Research was carried out in two anaerobic continuous stirred-tank reactors (CSTR), named S1 and S2, in mesophilic range (35 ± 1°C) with a total volume of 247 L each (working volume, 200 L) and a HRT of ~20 days. Mixing was provided via sludge (Bredel SPX15, ~50 L/h) or biogas (electroAD C5, ~3.5 L/min) recirculation as shown in Figure 1. Micro-aerobic conditions were provided introducing a continuous oxygen flow controlled with needle valves during the first stages of research and with mass flow controllers (Cole-Parmer EW-32660-26) lately. Reactors were equipped with electrodes for on-line pH and redox potential (ORP) measurement (Cole-Parmer EW-05993-10 and EW-27301-19, respectively). Biogas production was calculated by pulses with inverted cylinder and electrovalve through a fixed volume displacement (550 ± 10 mL). Reactors were fed with sludge from WWTP in Villalonquéjar (Burgos, Spain). Organic load in sludge varied seasonally (COD_T max-min [90–37] g/L) so reactors worked with variable OLR. Approximately 1,090 ppm of Na_2SO_4 were added to feed sludge.

Seed sludge and start-up

Seed sludge (27 g VS/L) was taken from working anaerobic bioreactors for sludge treatment from WWTP mentioned above. Anaerobic digestion was started-up decreasing progressively (during the initial 20 days) HRT from 40 to 20 days.

Analyses

Reactor performance was evaluated by conventional anaerobic parameters; biogas composition was determined by gas chromatography as described by M. Fdz.-Polanco (2001) with injection of 500 μL of sample directly in the column. Sulphate and thiosulphate concentrations were measured by high performance liquid chromatography. The samples were centrifuged 15 min at 6,000 rpm and filtrated to 45μm followed by the method reported by van der Zee *et al.* (2007). COD, TS, VS, sulphate and dissolved sulphide were determined according to standard methods (APHA 1998).

RESULTS AND DISCUSSION

Reactors S1 and S2 were started-up decreasing HRT in steps from initial ~40 d to ~20 d during 18 days. After 30 days operation, ~735 ppm of SO_4^{2-} as Na_2SO_4 were added to feed sludge in order to increase H_2S concentration in biogas. Reactors S1 and S2 were operating under anaerobic conditions during 71 and 146 days, respectively, before oxygen dosing. After this initial anaerobic period, micro-aerobic conditions were applied as shown in Table 1. Reactors S1 and S2 treated sludge under micro-aerobic conditions during 150 and 102 days respectively.

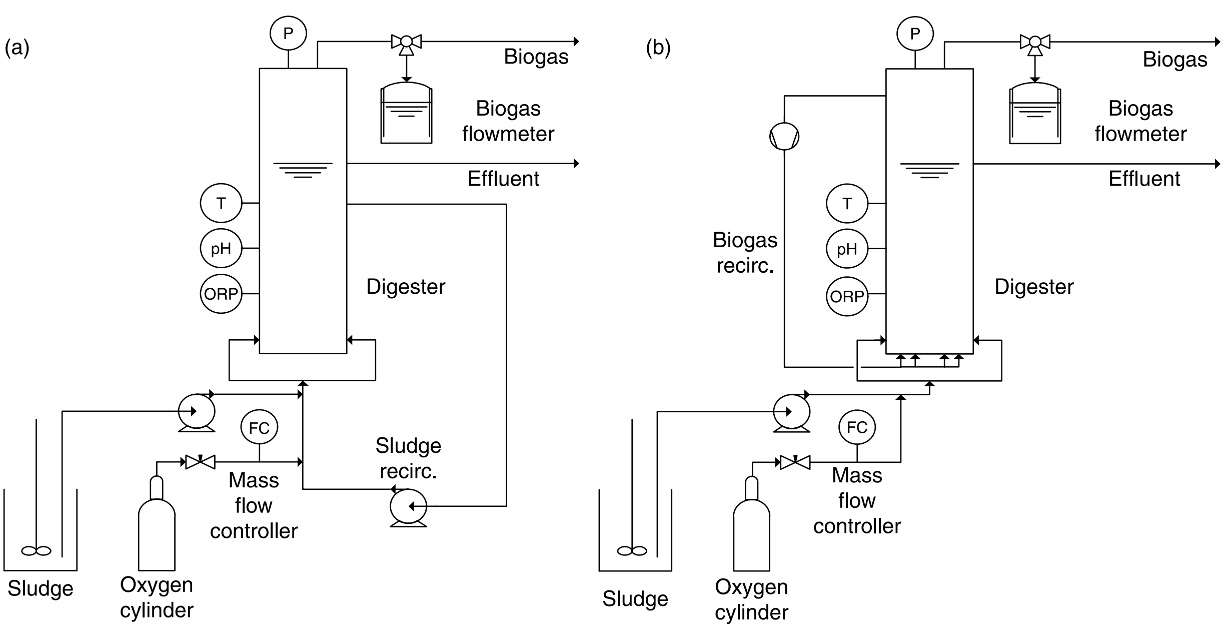

Figure 1 | Pilot plant diagram. (a): mixing provided by sludge recirculation. (b): mixing provided by biogas recirculation.

Table 1 | Conditions applied to reactors S1 and S2

	Time (d)	Mixing	Oxygen flow (mL/min)
Reactor S1			
A	0	Sludge recirc.	0
B	71	Sludge recirc.	~3.3
C	97	Sludge recirc.	~1.8
D	149	Sludge recirc.	~3.3
E	168	Sludge recirc.	2.8 ± 0.1
Reactor S2			
A	0	Sludge recirc.	0
B	146	Sludge recirc.	~2.0
C	195	Biogas recirc.	3.18 ± 0.02

S-removal and optimal oxygen flow

Reactor S1 produced, in anaerobic conditions (period A) with sludge recirculation, a biogas with an average H_2S concentration of 9,318 ± 2,148 ppm. After 72 days, micro-aerobic conditions (oxygen flow ~3.3 mL/min) were applied to the reactor, leading to a H_2S removal from biogas higher than 99% as shown in Figure 2. During this period (B) average H_2S in biogas gas 51 ± 46 ppm. As H_2S concentration reached was considerably low, further research on oxygen optimal flow was carried out. On day 149, oxygen supply was reduced to ~1.8 mL/min. An operation failure on day 111, forced to stop oxygen supply during 10 days. Excluding this repairing period, average H_2S concentration in biogas was 303 ± 126 ppm in period C. Oxygen flow was restored to ~3.3 mL/min on day 149 (D), because of an increase in H_2S concentration, resulting in average H_2S concentration of 50 ± 34 ppm. Finally, oxygen flow was adjusted to an intermediate flow, between those experimented, of 2.8 ± 0.1 mL/min (E). These micro-aerobic conditions were held during 52 days, removing H_2S from biogas to an average 114 ± 88 ppm.

Reactor S2 produced a biogas with an average H_2S concentration of 10,361 ± 1,918 ppm in anaerobic conditions. Micro-aerobic conditions led to an average

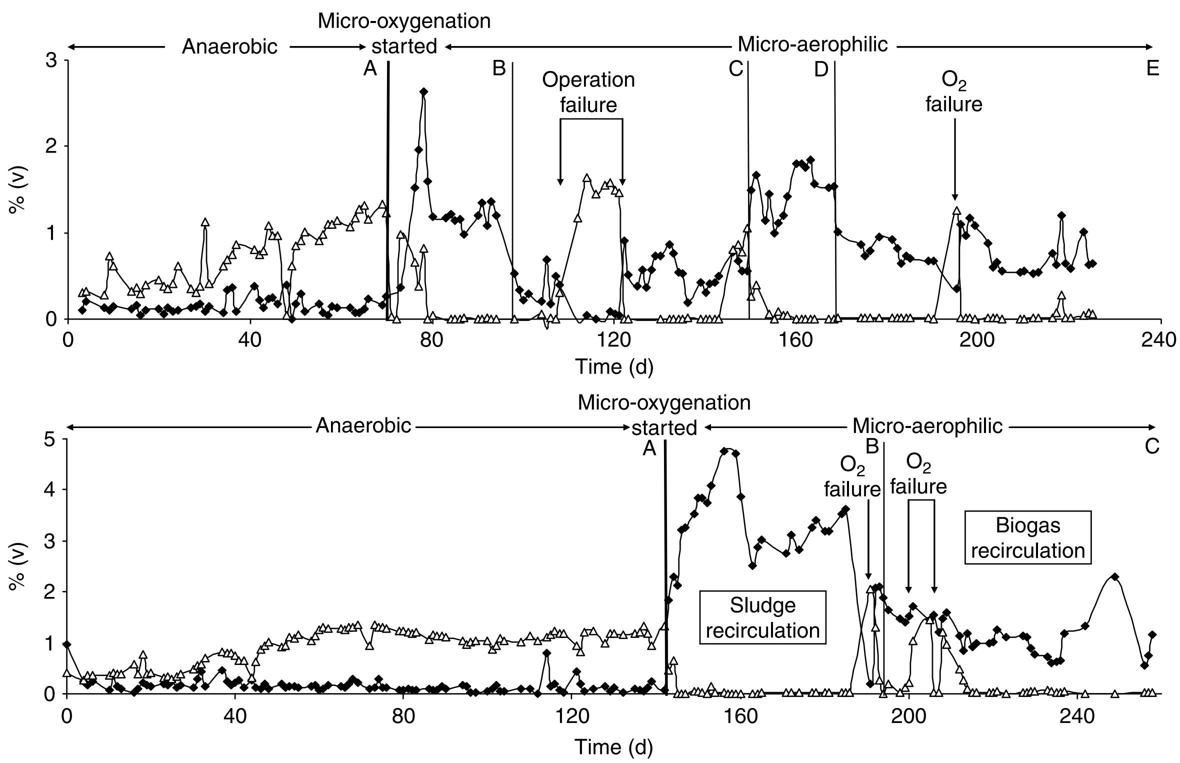

Figure 2 | Hydrogen sulphide and oxygen in biogas. Hydrogen sulphide (open triangles), oxygen (closed rhombuses). Upper figure: reactor S1, lower figure: reactor S2. Periods related to Table 1.

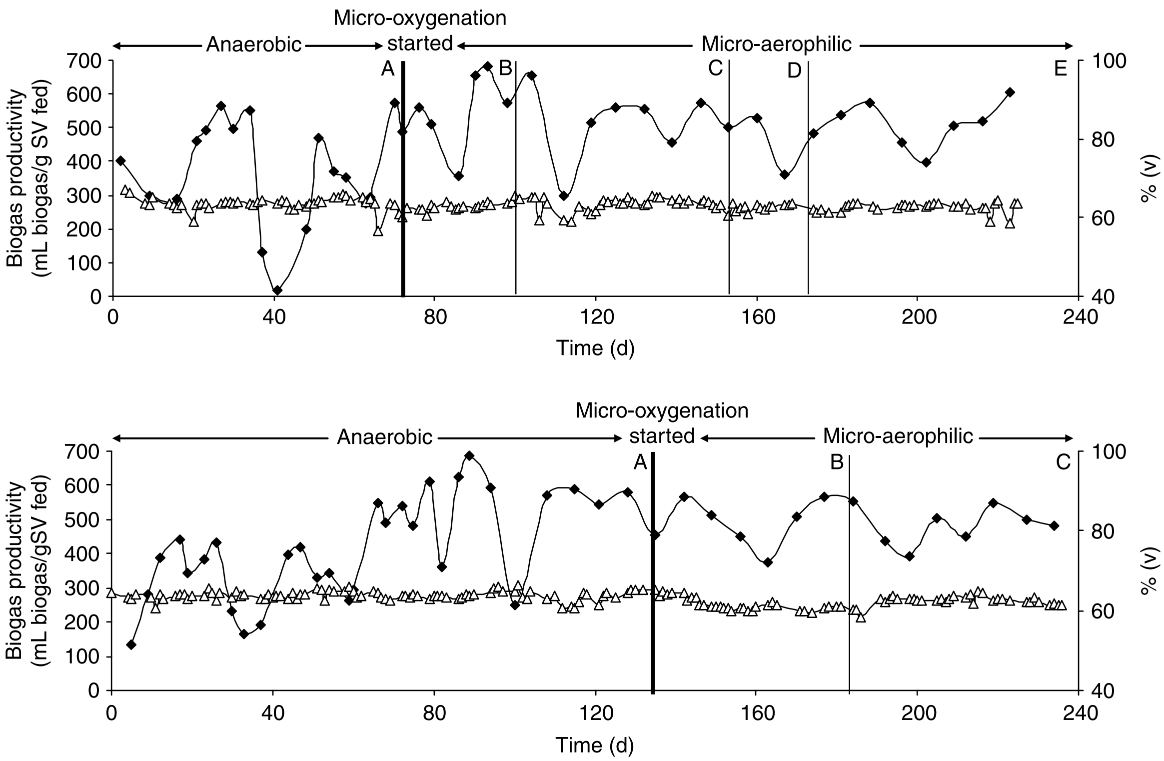

Figure 3 | Biogas productivity and methane content in biogas. Upper panel: reactor S1, lower panel: reactor S2. Biogas productivity (closed rhombuses), methane concentration (open triangles).

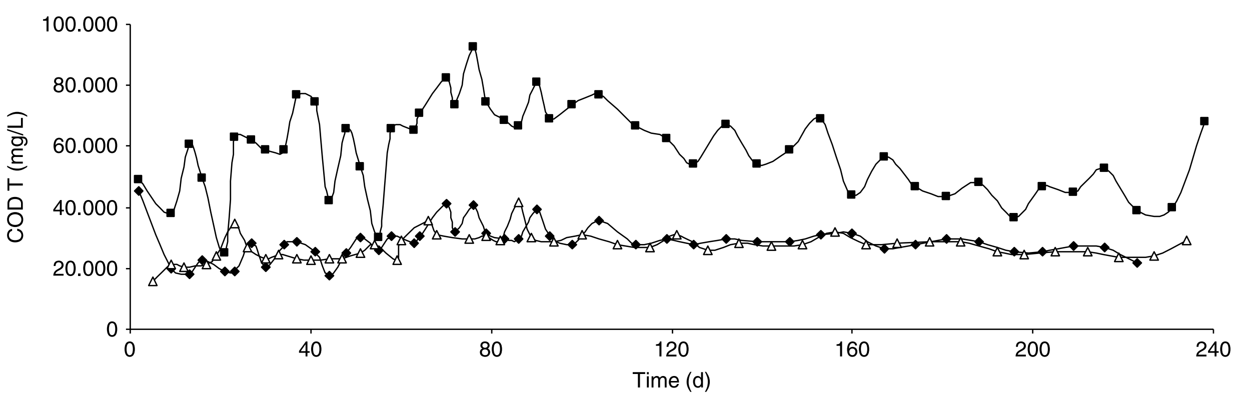

Figure 4 | COD_T removal achieved. Feed sludge (closed squares), reactor S1 effluent (closed rhombuses), reactor S2 effluent (open triangles).

concentration of H_2S in biogas (period B) of 218 ± 159 ppm with sludge recirculation and 320 ± 177 ppm with biogas recirculation (C) as shown in Figure 5.

Biogas production and COD removal

Biogas production and methane yield were not affected by micro-aerobic conditions (Figure 3). Biogas productivity remained around 500–600 mL biogas/g VS fed in both reactors after the start-up period and CH_4 concentration in biogas was not significantly reduced by oxygen supply. Both observations suggest a strong tendency towards sulphide oxidation in micro-aerobic conditions versus other oxidative processes.

Furthermore, COD was removed during the process in both reactors leading to an effluent with ~23 g COD_T/L,

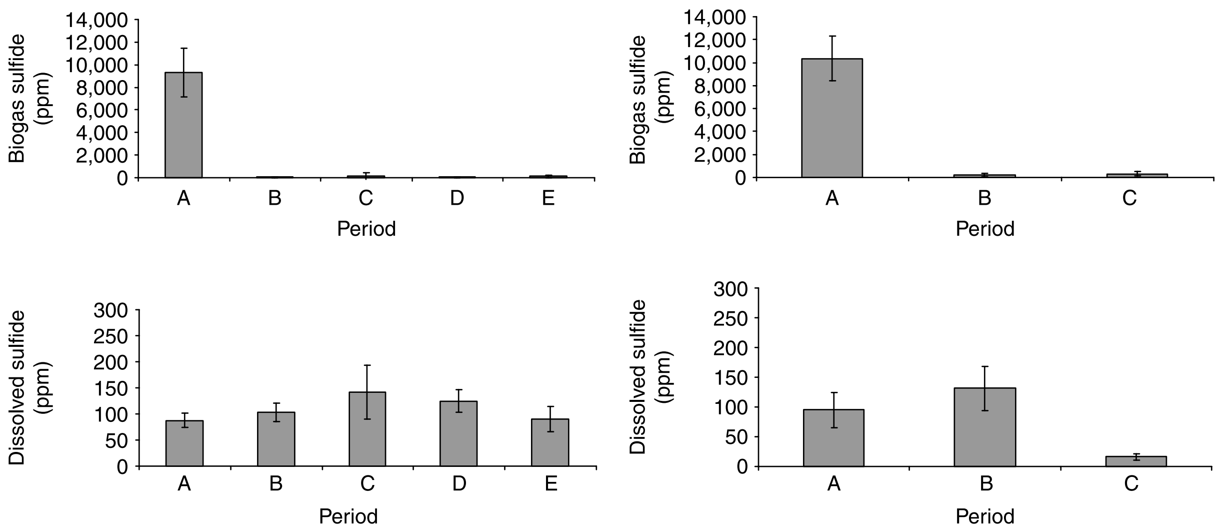

Figure 5 | Average biogas hydrogen sulphide and dissolved sulphide concentrations in reactors S1 and S2. Left panels: reactor S1, right panels: reactor S2. Upper panels: average biogas sulphide, lower panels: average dissolved sulphide.

both in anaerobic and micro-aerobic periods (Figure 4). Reactor worked with variable OLR as HRT was kept constant and COD of feed sludge varied seasonally. A better performance in terms of COD removal was obtained when high influent COD was treated, ~55% of COD_T removal vs. ~30% for low feed sludge organic load.

Mechanism of H_2S removal

In reactor S1, with sludge recirculation during whole research, dissolved sulphide concentration remained stable around 100–150 ppm with effective removal of H_2S in biogas. From the other side, biogas recirculation under micro-aerobic conditions in reactor S2 provided a similar H_2S removal compared to sludge recirculation while dissolved sulphide concentration was reduced considerably during biogas recirculation in reactor S2. Dissolved sulphide was removed from 100–150 ppm in anaerobic and micro-aerobic with sludge recirculation to ~16 ppm (reactor S2, period C).

From the observations on H_2S (g) and total dissolved sulphide shown in Figure 2, in which H_2S removal from biogas was carried out keeping a constant dissolved sulphide concentration during sludge recirculation and biogas recirculation drastically reduced dissolved sulphide concentration; it is suggested a mechanism of oxidation of dissolved sulphide with oxygen (gas) promoted by a better contact, thus accessibility of oxygen, between gas and liquid phases during biogas recirculation. As a result of this study, limiting step in H_2S removal was presumably the transfer of oxygen. Further studies will be carried out to explore this mechanism (Figure 5).

CONCLUSIONS

It can be achieved a high H_2S removal (>99%) in biogas produced in the anaerobic treatment of sludge in pilot plant scale under micro-aerobic conditions with little to none effect on COD removal, biogas production and methane yield.

Sludge recirculation and biogas recirculation as mixing method in CSTR showed no difference on H_2S removal in biogas under the micro-aerobic conditions studied.

Observations on dissolved sulphide concentration and hydrogen sulphide content in biogas, in anaerobic, micro-aerobic with sludge recirculation, and micro-aerobic with biogas recirculation conditions; suggest a mechanism of dissolved sulphide oxidation in the interface liquid/gas with oxygen in gas phase.

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