



Performance evaluation of oxygen, air and nitrate for the microaerobic removal of hydrogen sulphide in biogas from sludge digestion

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ABSTRACT

The removal performance of hydrogen sulphide in severely polluted biogas produced during the anaerobic digestion of sludge was studied by employing pure oxygen, air and nitrate as oxidant reactives supplied to the biodigester. Research was performed in a 200-L digester with an hydraulic retention time (HRT) of ~20 days under mesophilic conditions. The oxygen supply (0.25 N m³/m³ feed) to the bioreactor successfully reduced the hydrogen sulphide content from 15,811 mg/N m³ to less than 400 mg/N m³. The introduction of air (1.27 N m³/m³ feed) removed more than 99% of the hydrogen sulphide content, with a final concentration of ~55 mg/N m³. COD removal, VS reduction and methane yield were not affected under microaerobic conditions; however, methane concentration in the biogas decreased when air was employed as a result of nitrogen dilution. The nitrate addition was not effective for hydrogen sulphide removal in the biogas.

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1. Introduction

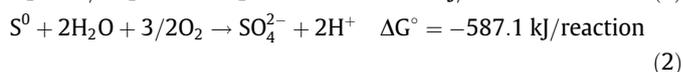
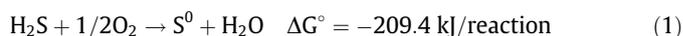
The treatment of wastewater in municipal waste water treatment plants (WWTP) generates sludge as a by-product of the overall processes employed during treatment. For example, nearly 10 million tons of dry sludge is produced per year in the EU (Appels et al., 2008). When disposing of this sludge, anaerobic 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.

The biogas produced during AD of sludge is a promising renewable energy source. Biogas can be directly converted into electrical power (e.g., in a fuel cell) (Martinez et al., 2008), burnt to release heat at high temperature or burnt for the simultaneous production of heat and power (CHP). In any of these cases, the biogas contains impurities that must be removed, depending on the further utilisation of the biogas.

In the AD of S-containing organic matter, hydrogen sulphide is generated to a different extent based on the outcome of the competition between sulphur-reducing bacteria and methanogens (Lens and Pol, 2000). Hydrogen sulphide in the biogas reduces the lifetime of pipework and other installations needed for the utilisation of biogas. For example, the trouble free operation of CHP requires limit values between 100 and 500 mg/N m³, depending on the specifications of the CHP manufacturer, and these values may not be exceeded. Hydrogen sulphide is toxic and corrosive to many

types of steel (Deublein and Steinhauser, 2008). The appropriate conditioning of sludge can limit the hydrogen sulphide content in the biogas (Dewil et al., 2008); however, the treatment of the biogas has to be carried out to ensure the efficient long-lasting use of its energetic potential.

The biological treatment of biogas to remove hydrogen sulphide has proven successful in the large-scale employment of trickling filters and bioscrubbers (Cline et al., 2003). The mechanism of removal, sulphide oxidation, takes place both chemically and biologically (Kleinjan, 2005) and is believed to begin with the formation of polysulphides, which may be further oxidised to elemental sulphur (Steudel, 1996) under oxygen-limited conditions. The final products of the biological oxidation depend on the amount of oxygen available for sulphide-oxidising bacteria, according to the following reactions (Madigan et al., 2009):



Some well-known and novel sulphur-oxidising bacteria are able to employ sulphide 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 use of these bacteria to perform the biodesulphurisation in the anaerobic digester helps avoid a high investment in additional equipment (Cirne et al., 2008).

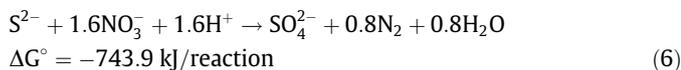
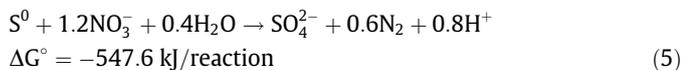
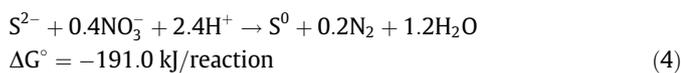
Oxygenation of the “anaerobic bioreactor” has been reported as an alternative to the high energy requirements of biogas stripping

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or the high chemical and disposal needs of sulphide precipitation (Pol et al., 1998) used in the treatment of sulphate-rich wastewater to reduce hydrogen sulphide in biogas and to reduce sulphide toxicity to methane-producing bacteria (Fox and Venkatasubbiah, 1996; Khanal and Huang, 2003). Moderate aeration in the anaerobic treatment of low-sulphate wastewaters has also proven successful, showing an effective competence of sulphide oxidation versus other oxidative processes for available oxygen (van der Zee et al., 2007). Additionally, methanogens have shown a higher tolerance to low oxygen concentrations than it was classically accepted, both in granular (Kato et al., 1994; Zitomer and Shrouf, 1998; Durán et al., 2008) and suspended sludge (Estrada-Vázquez et al., 2003). In the same way, the removal of hydrogen sulphide in the biogas produced in an anaerobic sludge digester by micro-oxygenation successfully reduced the concentration of hydrogen sulphide to less than 500 mg/N m³, with no effect on digestion performance (Fdz-Polanco et al., 2009), while enhancing VSS and soluble COD degradation when air was supplied during sludge recirculation (Jenicek et al., 2008).

Air is a costless oxygen source for microaerobic processes and is an effective and affordable alternative for hydrogen sulphide removal; however, the effect of nitrogen introduction and the subsequent dilution of the biogas must be investigated in terms of the energetic efficiency of the technology used for the biogas, as this efficiency may be considerably reduced.

The employment of nitrate instead of oxygen for sulphide removal is an alternative when chemolithoautotrophic denitrification can be carried out by using reduced sulphur compounds as electron donors (Fernández et al., 2008). This combination has been successfully applied for moderate volumetric treatment capacities (Kleerebezem and Mendezà, 2002) and in pilot-plant scale studies, reaching sulphide removal efficiencies of over 90% (de Lomas et al., 2005). As observed when microaerobic conditions are created by the injection of oxygen, the results of hydrogen sulphide oxidation with nitrate depend on the ratio of sulphide/nitrate (Cardoso et al., 2006; Cai et al., 2008), according to the following equations:



The main advantage of nitrate is that the solubility and mass transfer problems associated with oxygen are avoided; while oxygen or air are supplied as a gas with gas-to-liquid mass transfer limitations, nitrate is highly soluble. One potential issue is an observed drop in the performance of sulphide oxidation with nitrate when the organic load increases. This result could be due to a higher employment of nitrate for the heterotrophic denitrification process (Li et al., 2009). Therefore, it is interesting to study the utilisation of nitrate for hydrogen sulphide removal in the AD of sludge, where the autotrophic process is clearly unfavoured and heterotrophic denitrification is the pathway probably employed for nitrate utilisation.

The performance of hydrogen sulphide removal from biogas at the pilot-plant scale was investigated by employing microaerobic processes with oxygen (pure oxygen and air) and nitrate.

2. Methods

2.1. Pilot plant description

The treatment of sludge and the removal of hydrogen sulphide were performed in pilot-plant scale reactors with a working vol-

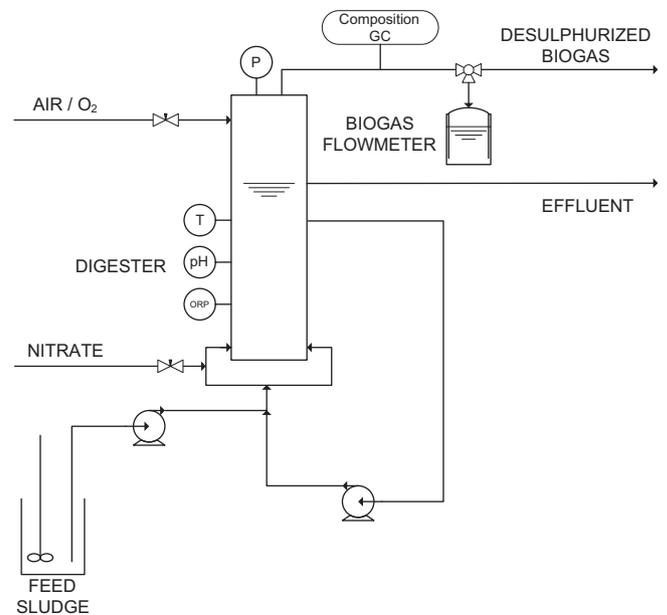


Fig. 1. Pilot plant diagram.

ume of 200 L (250 L total volume), as shown in Fig. 1. The reactors were insulated, and the walls were heated with electric resistance. The reactors were also mixed with sludge recirculation provided by a Bredel peristaltic pump. The feed was provided by a continuously stirred tank with a Watson-Marlow peristaltic pump. Microaerobic conditions were maintained using the regulated flow of pure oxygen with a Cole-Parmer EW-32660-26 mass flow controller from an oxygen cylinder; when air was employed as an oxygen source, it was supplied with a Watson-Marlow peristaltic pump, and both were injected into the headspace. The headspace in the bioreactor (50 L) allowed the storage of ~1/4 of the daily biogas production. Finally, tygon tubing was used as the conduction material for the biogas.

2.2. 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 oxygen supply. Digestion of the sludge was performed in the mesophilic range (35 ± 1 °C) with an HRT of ~20 days. The feed consisted of mixed sludge from the Villalonquejar WWTP (Burgos, Spain) with a variable organic load (COD_T max–min [80–37] g/L). To increase the amount of hydrogen sulphide produced during digestion, sodium sulphate was added to the feed as follows: 809 ± 148 mg/L of sulphate in the case of removal with air, 773 ± 116 mg/L of sulphate when pure oxygen was employed and 781 ± 97 mg/L for the experiment with nitrate. Mixing was provided via sludge recirculation at 50 L/h. Microaerobic conditions with oxygen/air are summarised in Table 1. In the nitrate experiment, 200 mL of a solution containing 8.5 g/L of nitrate (NaNO₃, Mg(NO₃)₂, KNO₃) with a mass ratio of Na:Mg:K of 1:1:2 were batch-supplied to the reactor during the HRT period (20 days).

2.3. Monitoring and experimental analysis

The pilot-plant conditions were monitored online using pressure, temperature (PT100), pH and ORP probes (Cole-Parmer EW-05993-10 and EW-27301-19, respectively).

Table 1
Operational variables during research with oxygen and air.

	Pure oxygen			Air		
	Anaerobic	Microaerobic		Anaerobic	Microaerobic	
Operation time (d)	26	25	36	14	43	24
<i>Mixing</i>						
Sludge recirculation (L/h)	50	50	50	50	50	50
<i>Microaerobic conditions</i>						
Oxygen flow rate (N m ³ O ₂ /m ³ feed)	0	0.25	0.20	–	–	–
Air flow rate (N m ³ air/m ³ feed)	–	–	–	0	1.27	0.94
Sulphate feed concentration (mg/L)	773 ± 116			809 ± 148		

The biogas production gas measured by a fixed volume of liquid displacement (472 ± 8 N mL) in inverted cylinder equipped with an electrovalve. The biogas composition was measured by sampling (100 μ L) and subsequent injection in a gas chromatograph (GC). Gas chromatography was carried out in a VARIAN CP 3800 GC with VARIAN capillary columns (TCD); a CP-Molsieve 5A (15 m \times 0.53 mm, df 15 μ m) was used for oxygen, nitrogen and methane analysis, and a CP-PoraBond Q (25 m \times 0.53 mm, df 10 μ m) was used for carbon dioxide and hydrogen sulphide analysis, with helium as the carrier gas in both cases.

The nitrate and nitrite concentrations in the digesters were determined weekly by high performance liquid chromatography (HPLC). Samples were centrifuged at 5000 rpm for 10 min, and the supernatant was filtered at 0.45 μ m. Subsequently, a 1.5-mL sample was centrifuged again at 10,000 rpm for 10 min, and the supernatant was filtered at 0.22 μ m. Finally, the filtered sample was injected in the HPLC. The HPLC equipment has a conductivity detector (Waters Millipore TCM) and an anionic column (Waters Millipore IC-pack A-HR 4.6 \times 150 mm). The method worked at 20 °C and used 5.51 g/L potassium hydrogen phthalate as the liquid carrier.

Sulphate and thiosulphate were measured by HPLC according to the method described by van der Zee et al. (2007).

The sulphur content in the sludge was estimated from an elemental analysis of sulphur. Samples were dried at 95 °C, cooled and analysed in a LECO SC32 oven. Analysis was carried out by combustion of the samples at 1350 °C; as a result, the sulphur was completely oxidised to SO₂ and evaluated in the detection cell (TCD). The sulphur estimation was the result of subtracting the content of the other analysed sulphur species (sulphate, thiosulphate) of the sample from the total sulphur content.

Digestion performance was evaluated by conventional parameters for sludge digestion. Total and soluble COD, TS, VS, TKN, ammonium and total sulphide concentrations were evaluated weekly according to standard methods (Clesceri et al., 1998).

3. Results and discussion

3.1. Supply of oxygen/air

3.1.1. Supply of pure oxygen

Mixed sludge was anaerobically digested in the pilot-plant reactor, producing a biogas with an average concentration of hydrogen sulphide of $15,811 \pm 1277$ mg/N m³. During AD, the average biogas productivity in mLbiogas/gVSfed was 503 ± 71 , with a methane yield of 267 ± 38 mgCH₄/gVSfed. In terms of digestion efficiency, COD removal was 52%, and VS reduction was 53%. These parameters, summarised in Table 2, constitute the basis for comparing the digestion performance between anaerobic and microaerobic conditions in the present research.

Sulphate was almost totally consumed by sulphate-reducing microorganisms. The inorganic sulphur species concentrations

during this period were ~ 1 mg/L of sulphate, ~ 32 mg/L of thiosulphate and ~ 135 mg/L of total dissolved sulphide.

Micro-oxygenation started on day 27. Oxygen was supplied to the headspace of the bioreactor at a flow rate of 2.0 ± 0.1 mL/min (0.25 N m³/m³ feed sludge). The hydrogen sulphide concentration fell to an average of 116 ± 76 mg/N m³ as a result of oxygen introduction and subsequent hydrogen sulphide oxidation. Fig. 2a shows the evolution of hydrogen sulphide and oxygen during this period (from day 26 to 51). Oxygen was not totally utilised during hydrogen sulphide oxidation. The fraction of oxygen leaving the bioreactor with the biogas represented an average of 1.5 (v/v)% of the biogas composition.

Table 2 shows the impact of microaerobic conditions over AD performance. Biogas productivity was not affected by a pure oxygen supply and remained between 500 and 510 mLbiogas/gVSfed. The methane yield was around 265 mgCH₄/gVSfed, both in the anaerobic and microaerobic conditions with a pure oxygen supply. This result shows that oxygen was not employed for the aerobic degradation of organic matter, and methanogens were not inhibited in the presence of oxygen in the headspace.

COD removal (47%) and VS reduction (49%) were slightly lower than in anaerobic conditions; however, this effect is related to the variable organic load rate (OLR) to the bioreactor rather than a direct effect of the microaerobic conditions. We consistently observed that the higher the OLR (VS), the higher the efficiency of the AD of sludge.

The concentration of sulphur-oxidised species represented ~ 8 mg/L of sulphate and ~ 56 mg/L of thiosulphate, similar to or slightly higher than the anaerobic conditions because of the greater oxidation of sulphide than elemental sulphur. The sulphide concentration was ~ 149 mg/L, similar to the anaerobic period, showing that only hydrogen sulphide in the gas phase was removed by micro-oxygenation under the studied conditions.

A moderate excess of oxygen was observed in the biogas during this stage; therefore, the oxygen flow to the bioreactor was reduced to 1.6 ± 0.1 mL/min on day 51, representing 0.2 N m³/m³ of feed sludge. The average hydrogen sulphide remaining in the biogas during this period was 129 ± 57 mg/N m³, which was slightly higher than the previous period. The oxygen remaining in the biogas was reduced to $0.9 \pm 0.2\%$ when compared to the previous microaerobic period, as shown in Table 3.

The average biogas productivity was 510 ± 65 mL/gVSfed, and the methane yield was 266 ± 34 mgCH₄/gVSfed, showing no effect on the methanogenic capacity of the bioreactor. COD removal was 40% with 39% VS reduction, which was lower than that under anaerobic conditions due to a lower OLR, as mentioned before.

The concentration of sulphate in the digested sludge was ~ 2 mg/L, whereas that of thiosulphate was ~ 44 mg/L. Both values were similar to the anaerobic period and the previous micro-oxygenation stage. The sulphide concentration was ~ 125 mg/L, similar to previous periods and unaffected by the microaerobic conditions in the headspace.

Table 2
Digestion performance under anaerobic and microaerobic conditions with oxygen and air supply.

	N m ³ O ₂ /m ³ feed			N m ³ air/m ³ feed		
	0.00	0.25	0.20	0.00	1.27	0.94
COD in (g/L)	59.4 ± 16.7	54.0 ± 11.3	45.6 ± 5.0	64.8 ± 6.5	70.9 ± 13.6	65.8 ± 13.6
COD out (g/L)	28.4 ± 2.3	28.6 ± 2.6	27.4 ± 1.6	27.9 ± 3.7	27.7 ± 4.8	29.0 ± 4.6
% COD removal	52	47	40	57	61	56
VS in (g/L)	33.4 ± 5.6	29.9 ± 2.6	25.4 ± 2.0	38.0 ± 5.4	39.1 ± 2.9	35.8 ± 1.9
VS out (g/L)	15.7 ± 0.7	15.4 ± 0.6	15.4 ± 0.8	16.0 ± 0.6	15.4 ± 0.5	15.4 ± 0.5
% VS removal	53	49	39	58	52	54
Biogas productivity (mL/VSfed)	503 ± 71	507 ± 23	510 ± 65	491 ± 60	537 ± 83	555 ± 52
Methane yield (mgCH ₄ /gVSfed)	267 ± 38	265 ± 12	266 ± 34	220 ± 27	226 ± 35	242 ± 23

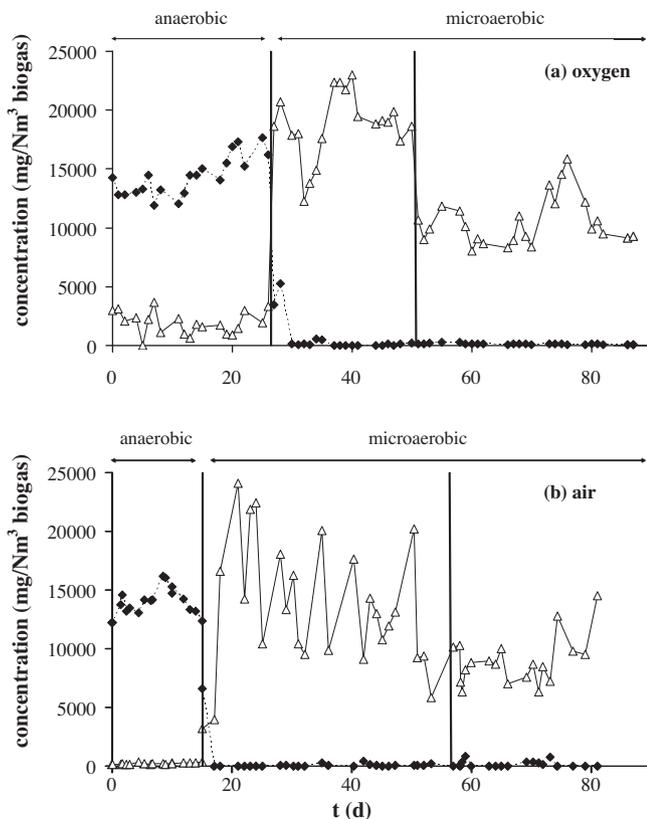


Fig. 2. Hydrogen sulphide (♦) and oxygen (Δ) concentrations under anaerobic and microaerobic conditions. (a) Supply of pure oxygen and (b) supply of air.

Table 3
Average biogas composition (v/v)% during anaerobic and microaerobic conditions.

	O ₂	N ₂	CH ₄	CO ₂	H ₂ S
<i>N m³ O₂/N m³ feed</i>					
0.00	0.2 ± 0.1	0.7 ± 0.6	63.7 ± 1.9	34.4 ± 1.9	1.0 ± 0.3
0.25	1.5 ± 0.2	0.4 ± 0.2	62.8 ± 0.8	35.3 ± 0.9	0.0 ± 0.0
0.20	0.9 ± 0.2	0.8 ± 0.2	62.8 ± 0.8	35.6 ± 0.8	0.0 ± 0.0
<i>N m³ air/N m³ feed</i>					
0.00	0.0 ± 0.0	0.2 ± 0.2	62.7 ± 0.9	36.1 ± 0.9	1.1 ± 0.1
1.27	1.0 ± 0.5	5.7 ± 1.4	58.8 ± 1.5	34.5 ± 1.7	0.0 ± 0.0
0.94	0.7 ± 0.2	4.7 ± 1.7	60.9 ± 1.5	33.7 ± 1.8	0.0 ± 0.0

The pH was stable between 7.0 and 7.2 during the study and showed no differences between anaerobic and microaerobic conditions. ORP in the bioreactor was between −515 and −492 mV. The relationship between micro-oxygenation and ORP was not considered significant and was in contrast to the moderate oxygenation of the bioreactors studied by Khanal and Huang (2003).

In short, the microaerobic conditions resulting from the oxygen supplied to the bioreactor removed more than 99% of the hydrogen sulphide produced during the mesophilic digestion of sludge, with no effect on methanogenic capacity and digestion performance.

3.1.2. Supply of air

The AD of sludge at the beginning of the experiment, before air introduction, produced a biogas with a concentration of hydrogen sulphide of $14,075 \pm 284$ mg/N m³. In these conditions, biogas productivity was 491 ± 60 mLbiogas/gVSfed, with a methane yield of 220 ± 27 mgCH₄/gVSfed. COD removal was 57% with a 58% reduction in VS. Sulphate was totally transformed during digestion, and the effluent contained an average of ~86 mg/L of total sulphide and ~10 mg/L of thiosulphate.

On day 15, an air flow of 1.27 N m³/m³ feed sludge was introduced in the headspace of the biodigester, with sludge 6828recirculation as the mixing method (Table 1). The hydrogen sulphide content of the biogas declined sharply to an average of 55 ± 97 mg/N m³, as shown in Fig. 2b, despite oxygen solubility being slightly lower due to nitrogen dilution of the biogas according to Henry's Law. A small amount of oxygen was not employed in the treatment and left the digester, representing 1 (v/v)% of the produced biogas.

The biogas productivity increased to 537 ± 83 mLbiogas/VSfed due to nitrogen presence in the biogas. The average biogas composition in Table 3 shows how methane and carbon dioxide concentrations decreased in comparison to the anaerobic period as a result of the aforementioned dilution when air was supplied.

The methane yield remained stable at 226 ± 35 mg/gVSfed. As a result, no effect of microaerobic removal on methanogenic activity was observed. A similar production yield was maintained under both microaerobic and anaerobic conditions. COD removal during this stage (61%) was slightly higher in relation to the anaerobic stage, while VS solid reduction was 52%.

Total sulphide in the digester remained stable at ~99 mg/L compared to the anaerobic period, while more oxidised forms of thiosulphate (~100 mg/L) and sulphate (~30 mg/L) appeared, probably as a result of further oxidation of sulphide, which is energetically more favourable for sulphide-oxidising bacteria (see Eqs. (1)–(3)).

The hydrogen sulphide concentration during this period was below most of the manufacturers' specifications. Therefore, to optimise air flow and achieve a smaller decrease in methane concentration in the biogas, a lower flow of 0.97 N m³/m³ feed was applied to the digester starting on day 57.

Under these conditions, the average hydrogen sulphide concentration of treated biogas was 349 ± 276 mg/N m³. Oxygen, which was not employed during the process, represented 0.7 (v/v)% of the produced biogas in this case.

Nitrogen content was reduced by 1 (v/v)% compared to the previous period, and the methane concentration recovered by approximately 1 (v/v)% as well. The methane content of the biogas

increased at the expense of lower hydrogen sulphide removal, even when it was below 400 mg/N m³ in most cases. Biogas productivity was 555 ± 52 mL/V_Sfed, and the methane yield slightly increased to 242 ± 23 mg/gV_Sfed when the air flow was reduced. As shown in Table 2, variations in the organic load (higher VS concentration) of the feed sludge seemed to be more responsible for these variations than the introduction of air into the headspace.

The removal of COD and VS were 56% and 54%, respectively, in this last period. The total sulphide concentration (~107 mg/L) was similar to that observed in the anaerobic and previous microaerobic stages. The thiosulphate concentration was ~37 mg/L, while the sulphate concentration was ~11 mg/L.

During the experiment, the pH was maintained between 7.2 and 7.4, while ORP was stable in the range of –510 to –480 mV.

In summary, microaerobic oxidation successfully removed more than 99% of the hydrogen sulphide produced during AD when 1.27 N m³ air/m³ feed (97% for 0.94 N m³ air/m³ feed) was employed. Methane yield was not affected by the introduction of air, as its value in microaerobic conditions was similar or higher than the yield in anaerobic conditions.

Biogas productivity slightly increased during microaerobic oxidation with air as a result of nitrogen dilution in the biogas. The methane concentration in the biogas was lowered by 2–4 (v/v)%.

3.1.3. Comparison of oxygen/air as oxidant reactives

Neither of the reactives examined in the present research have shown an effect on digestion performance under the conditions studied. Similar methane yields, in terms of mLCH₄/gV_Sfed, were found; this result implies that methanogens were not inhibited by the presence of limited amounts of oxygen, and oxygen is mainly used as an electron acceptor for sulphide oxidation and is not directed to the aerobic oxidation of organic matter. COD removal and VS reduction were similar in both the microaerobic and anaerobic conditions when similar OLRs were applied.

In terms of hydrogen sulphide removal, both reactives were effective with quite similar performance. Removal efficiencies were higher than 97% in all cases, and a concentration below 500 mg/N m³ was reached, guaranteeing an adequate CHP operation in which biogas is majorly employed. As a result, a slight decrease in the solubility when air is employed (due to biogas dilution by nitrogen) seems to not affect the removal process significantly.

Regarding the energetic use of biogas, when pure oxygen was supplied, methane production and methane concentration in the biogas were maintained; however, a reduction in engine efficiency might be expected when burning biogas produced under microaerobic conditions with air due to nitrogen dilution, despite methane production being similar to that observed in anaerobic conditions. As a first approach to examining the economical savings/expenses from the utilisation of air or pure oxygen for hydrogen sulphide removal, Porpatham et al. (2007) found that a decrease in methane concentration from 70% to 59% only reduced the spark-ignition engine energetic performance by 0.9% for the same mass flow of methane.

Therefore, the utilisation of air, which is a costless oxygen source, seems to be more profitable when applied to a new plant in which the engine design takes into account the expected lowered methane concentration, or in working plants where small decreases in methane concentration did not show significant variations in energetic efficiencies. In contrast, the advantages of pure oxygen supply are as follows: methane content is not lowered under microaerobic operation; biogas productivity is not affected by limited oxygen introduction; and there is no need for additional equipment for hydrogen sulphide treatment when employed for CHP.

3.1.4. Sulphur and oxygen balances during microaerobic operation

Compounds resulting from the biological oxidation of hydrogen sulphide under microaerobic conditions can be mostly described by a sulphur balance, as shown in Fig. 3. The digester was fed with 6500 and 7200 mg/d of sulphur, mainly as sulphate and organic sulphur-containing compounds.

In the anaerobic period, S-sulphate and part of the organic sulphur in the feed sludge were mostly converted to hydrogen sulphide and thiosulphate (between 30% and 40% of total S in outputs), while the total dissolved sulphide concentration increased according to the gas–liquid equilibrium. A higher amount of total sulphide was found in the outputs of the experiment with oxygen compared to the experiment with air, probably as a result of a slightly lower pH during that digestion period (7.0–7.2) compared to the experiment with air (7.2–7.4). A small part of the sulphur appears as thiosulphate in the effluent.

Sulphate was found to be easily accessible for sulphate-reducing microorganisms, while organic sulphur in the form of proteins, or cell constituents, was only partly reduced, and a large portion left the bioreactor unchanged.

Under microaerobic operation with air or oxygen, hydrogen sulphide was removed from the biogas. This “lost” sulphur, comparing inputs and outputs, corresponded to the elemental sulphur not analysed in this research but observed in the condensations, effluent and headspace of the biodigester. Furthermore, S-sulphide remained practically constant, independent of the introduction of oxygen/air within the digester. This fact suggests a mechanism of hydrogen sulphide removal in the headspace as the chemical equilibrium is not displaced because only the sludge surface in the digester is in direct contact with the gas in the headspace.

More oxidised sulphur species, such as thiosulphate and sulphate, slightly increased as a result of energetically more favourable reactions in the microaerobic operation. When lower oxygen/air ratios were applied, S-thiosulphate was reduced when compared to the previous rates, and S-sulphate was negligible for the lower oxygen/air ratio.

From the sulphur balance, an estimation of oxygen utilised in the digester was performed according to the stoichiometric reactions, as shown in Fig. 4.

Both air (oxygen) and pure oxygen were employed as electron acceptors for sulphide oxidation instead of for other oxidative processes. The oxygen fraction related to sulphide oxidation, and the formation of elemental sulphur, sulphate and thiosulphate, was fairly constant in all cases and accounted for 30–40% of the total oxygen supplied. The oxygen employed for oxidised sulphur species formation, sulphate and thiosulphate decreased when the ratio of N m³ reactive/N m³ feed was reduced.

The amount of oxygen employed for other processes was negligible except for the case of 0.20 N m³ O₂/N m³ feed. This exception is probably a result of a considerably lower OLR to the biodigester than for the other cases; this fact implies a lower biogas production and the subsequent higher residence time of oxygen in the headspace, which might lead to a higher amount of oxygen dissolved in mixed liquor and utilised in other processes. This effect would presumably be different from VFA aerobic oxidation, as methane yield was not reduced. It is probable that hydrolytic facultative bacteria utilise this oxygen, leading to a methane yield increase under microaerobic conditions because of higher hydrolytic activity in the presence of oxygen. This fact is in agreement with the observations of Johansen and Bakke (2006), who found an enhanced hydrolysis of primary sludge as a result of microaeration.

According to the stoichiometric reactions, only 30–40% of the total oxygen introduced in the system as pure oxygen/air was employed for hydrogen sulphide oxidation. The rest (60–70%) left the bioreactor with the produced biogas, suggesting that reducing the

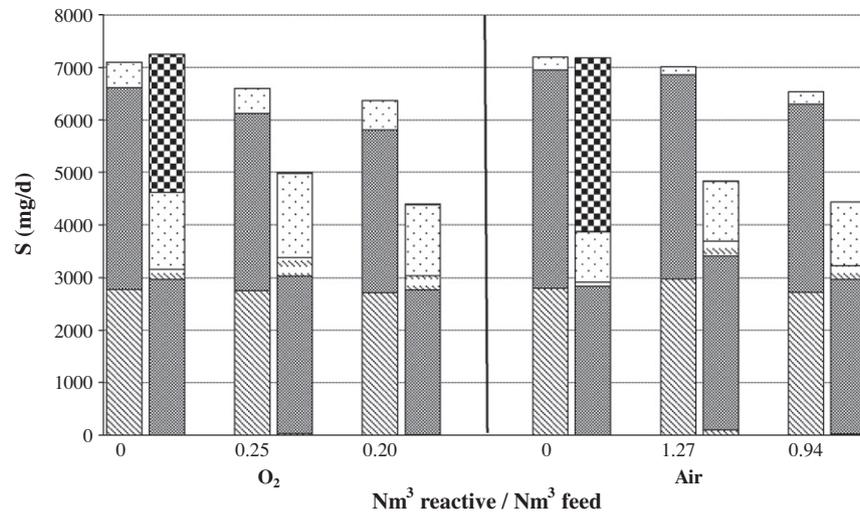


Fig. 3. Sulphur balance for the studied conditions with oxygen/air supply. For every rate of reactive: Inputs: left column and outputs: right column. Sulphur species: ■ S – organic; ▨ S – sulphate; ▤ S – total dissolved sulphide; ▩ S – thiosulphate; and ▩ S – H₂S gas.

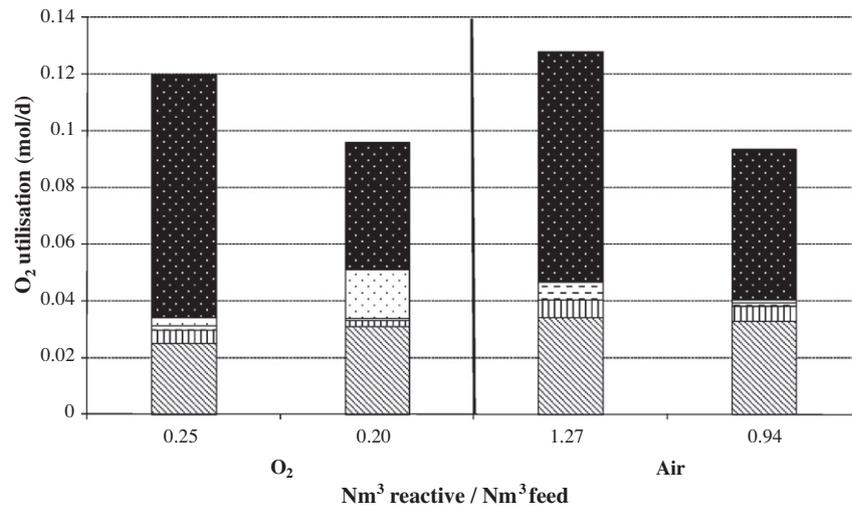


Fig. 4. Estimated oxygen utilisation in the biogas. ▨ O₂ consumed to form elemental sulphur; ▩ O₂ consumed to form thiosulphate; ▨ O₂ consumed to form sulphate; ▩ O₂ leaving the biogas; and ▩ O₂ consumed in other non-identified processes.

mass transfer resistance for oxygen may improve the oxygen intake.

3.2. Supply of nitrate

Nitrate was batch-added four times, every five days, to the digester during an anaerobic period; 200 mL of a solution containing 8.5 g/L of nitrate were added to the sludge recirculation. This value represents two times the stoichiometric amount for the average daily production of hydrogen sulphide in the biogas to the reactor, corresponding to 1.1 (v/v)% in biogas concentration.

Biogas analysis after injections showed, after 12 h, an increase in nitrogen from 0.3 to 3.0 (v/v)%, a decrease in methane concentration from 64.3 to 61.9 (v/v)%, while hydrogen sulphide remained around 1.0%; ORP increased from –508 to –380 mV. After 24 h, these compounds represented 0.6, 64.3, and 1.1 (v/v)% of the biogas, respectively, with a similar biogas production to previous days; the total dissolved sulphide concentration in the digester was ~107 mg/L. The deviation in concentrations for different injections was lower than 10%, suggesting uniform behaviour across the injections.

During this experiment, TKN was ~2.9 g/L for the feed and digested sludge. Ammonium in the digested sludge was ~1.4 g/L. These values showed no variation with respect to the conventional anaerobic conditions.

Addition of nitrate did not reduce the sulphide concentration in the biogas or the digester liquor; the observed values were similar to previous anaerobic periods. Instead, nitrogen concentration in the biogas increased as a consequence of heterotrophic denitrification, which competed with methanogenesis and decreased methane concentration. As a result, nitrate is not a good alternative for the removal of sulphide in this type of waste, as the availability of organic matter for denitrification prevents convenient hydrogen sulphide removal by the autotrophic process.

4. Conclusions

Hydrogen sulphide in biogas was removed under microaerobic conditions with oxygen/air without any influence on biogas production, methane yield or COD removal. Similar removal efficiencies were found when using oxygen and air; however, air slightly lowered methane concentration in the biogas as a consequence

of nitrogen dilution. Between 30% and 40% of the oxygen supplied under microaerobic conditions was employed for sulphide oxidation, while the rest left the bioreactor with the biogas. Finally, nitrate was found to be not feasible for treating sulphide in sludge digestion (heterotrophic denitrification outcompeted desulphurisation) because available organic matter was the primary electron donor for denitrification.

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