

The role of the headspace in hydrogen sulfide removal during microaerobic digestion of sludge

I. Ramos, I. Díaz and M. Fdz-Polanco

ABSTRACT

The role of the headspace (HS) in the microaerobic removal of hydrogen sulfide from biogas produced during sludge digestion was studied. Research was carried out in a pilot reactor with a total volume of 265 L, under mesophilic conditions. Biogas was successfully desulfurized (99%) by introducing pure oxygen (0.46 NL/L_{fed}) into the recirculation stream when the HS volume was both 50.0 and 9.5 L. The removal efficacy dropped sharply to ≈15% when the HS was reduced to 1.5 L. The system responded quickly to the operational changes imposed: micro-oxygenation stops and variations in supply, as well as HS volume reductions and increases. As the final result, the microaerobic process required a minimum surface into the gas space to occur, which along with the elemental sulfur deposition in this area indicated that the oxidation took place there. Additionally, the pattern of sulfur accumulation suggested that the removal occurred preferentially on certain materials, and pointed to a significant biological contribution.

Key words | anaerobic digestion, biogas desulfurization, headspace, hydrogen sulfide removal, microaerobic conditions

I. Ramos

I. Díaz

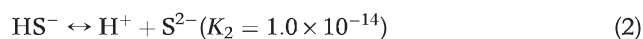
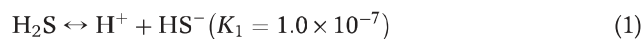
M. Fdz-Polanco (corresponding author)
Department of Chemical Engineering and
Environmental Technology,
Escuela de Ingenierías Industriales,
Sede Dr. Mergelina,
University of Valladolid,
Dr. Mergelina s/n,
47011 Valladolid,
Spain
E-mail: maria@iq.uva.es

INTRODUCTION

The energy sector accounts for 64% of the world's greenhouse-gas emissions (IEA 2009). Biogas is a versatile and renewable energy source that can be used for the replacement of fossil fuels in several applications (Weiland 2010). Consequently, anaerobic digestion (AD) is gaining increasing attention worldwide as one of the most promising biotechnologies to produce it (Jagadabhi *et al.* 2010).

AD is considered an essential part in a wastewater treatment plant (WWTP), as it reduces the sludge volume, improves its character, and reduces the associated health problems (Appels *et al.* 2008). Many industrial wastewaters have high concentrations of sulfur compounds, such as sulfates (Zhou *et al.* 2007). This anion is not a direct threat to the treatment process; however, sulfate-reducing bacteria (SRB) use it for the oxidation of organic compounds and hydrogen under anaerobic conditions, thereby producing sulfide (Hulshoff Pol *et al.* 1998). As shown in equilibriums 1 and 2, dissolved sulfide exists in undissociated and dissociated form according to pH (Deublein & Steinhauser 2007). At pH characteristic of methanogenic systems, between 20 and 50% of the dissolved sulfide is in the undissociated form (Colleran *et al.* 1995), which is released to the

gas phase according to a coefficient α (Hulshoff Pol *et al.* 1998). As the final result, this biogas component is in waste gases, wastewaters and sewage sludge:



Gaseous hydrogen sulfide causes malodour, contamination, energy performance deterioration, toxicity, and corrosion. Therefore, biogas desulfurization is required in order to prevent damage and standardize its quality according to the final biogas application (Appels *et al.* 2008). Physicochemical methods are widely employed for this purpose. Nonetheless, biological processes such as bioscrubbers, biotrickling filters, and biofilters are gaining attention as a result of their competitive performance and lower operational costs. These methods are based on the biological sulfur cycle; specifically, on the dissolved sulfide oxidation (Kleinjan 2005).

Among the biodesulfurization techniques, the direct micro-oxygenation (or micro-aeration) of anaerobic reactors can be a more interesting alternative. Sulfide oxidation takes place both biologically and chemically, and the end product formation depends on the oxygen availability (van der Zee *et al.* 2007). Sulfate production involves the production of intermediate compounds such as polysulfide, thiosulfate, tetrathionate, and sulfur, which is the final product under oxygen limited conditions (Kleinjan 2005).

Under microaerobic conditions, sulfide removal competes effectively for oxygen versus other processes, and is faster than the re-reduction of oxidized sulfur compounds (van der Zee *et al.* 2007; Fdz-Polanco *et al.* 2009). So, biogas desulfurization efficiencies higher than 97% have been achieved by both oxygen and air at equivalent rates with none impact on digestion performance (Díaz *et al.* 2010a). Jenicek *et al.* (2010), in contrast, reported that methane production could decrease because of aerobic substrate consumption. Nonetheless, that could be compensated by improved hydrolysis and increased biogas production (Johansen & Bakke 2006; Jenicek *et al.* 2008). Other oxygen benefits have been reported: sulfide toxicity suppression (Khanal & Huang 2003), improved degradation of recalcitrant organics (Jenicek *et al.* 2008), and reduction of volatile fatty acid (VFA) (Botheju *et al.* 2010).

Díaz *et al.* (2010b) demonstrated that oxygen transfer to the liquid phase was not required to achieve sulfide-free biogas, and observed elemental sulfur deposition in the walls and ceiling of the reactor headspace (HS), where different sulfide oxidizing bacteria (SOB) were found. Obviously, the contact between the oxygen and the liquid media is really restricted when it is injected into the HS, therefore almost all the oxygen is only accessible to microorganisms present in the gas space. However, Díaz *et al.* (2010b) achieved similar desulfurization efficiencies by supplying oxygen into the HS, the recirculation stream and with the feed sludge. Thus, they deduced that the hydrogen sulfide removal took place in the HS. This is consistent with Fdz-Polanco *et al.* (2009), who suggested an oxidation mechanism in the liquid–gas interface. They reported similar biogas desulfurization performances when oxygen was injected into the recirculation stream and the feed stream, independently of the mixing method. Nevertheless, dissolved sulfide removal occurred only with biogas recirculation. It certainly resulted in larger contact area between the oxygen and the liquid phase, as the size of bubbles that entered into the digester rose. That led to increased oxygen flow across the gas–liquid interface and consequent higher intake by microorganisms. Accordingly, the oxygen mass

transfer was indicated as the limiting step for hydrogen sulfide removal. In contrast, Jenicek *et al.* (2011) reported sulfur accumulation in the sludge as a result of hydrogen sulfide removal by introducing limited amount of air into the liquid media. Furthermore, that increase was consistent with the biogas desulfurization efficacy observed. Therefore, the oxidation seemed to occur in the liquid phase.

Considering the inconclusive results relative to the oxidation place, it is of interest to explore where the biogas desulfurization is carried out really. The aim of this study is to investigate the role of the HS in the microaerobic removal of hydrogen sulfide.

MATERIALS AND METHODS

Digester

Research was performed in a continuous stirred-tank reactor (CSTR) with a total volume of 265 L, whose top consisted of a conical cover with a detachable and transparent cylinder in the uppermost part (Figure 1). Mesophilic conditions were applied by an electric resistance. The bio-reactor was operated under variable hydraulic retention time (HRT) because of the changes in the HS volume (20–26d). It was fed with sewage sludge from a WWTP. The liquid phase was recirculated at a constant rate of 50 L/h by a peristaltic pump. Oxygen from a cylinder was supplied by a mass flow controller into the recirculation. Due to the variability of the feeding in terms of organic matter content, the organic loading rate (OLR) fluctuated throughout the study.

Monitoring and experimental analysis

Pressure and temperature were monitored on-line by probes. Tygon tubing led the biogas produced to an inverted cylinder, where it was measured by a fixed liquid volume displacement (550 ± 5 mL), and then released by an electro-valve. A gas chromatograph (VARIAN CP-4900 MicroGC) was used for on-line analysis of biogas composition, as described by Díaz *et al.* (2010b).

Digestion performance was evaluated by conventional parameter analysis according to the standard methods (APHA 1998): total and soluble chemical oxygen demand (COD), total solids (TS) and volatile solids (VS).

Sulfate concentration was measured by ion chromatography. Thiosulfate was analyzed by high performance

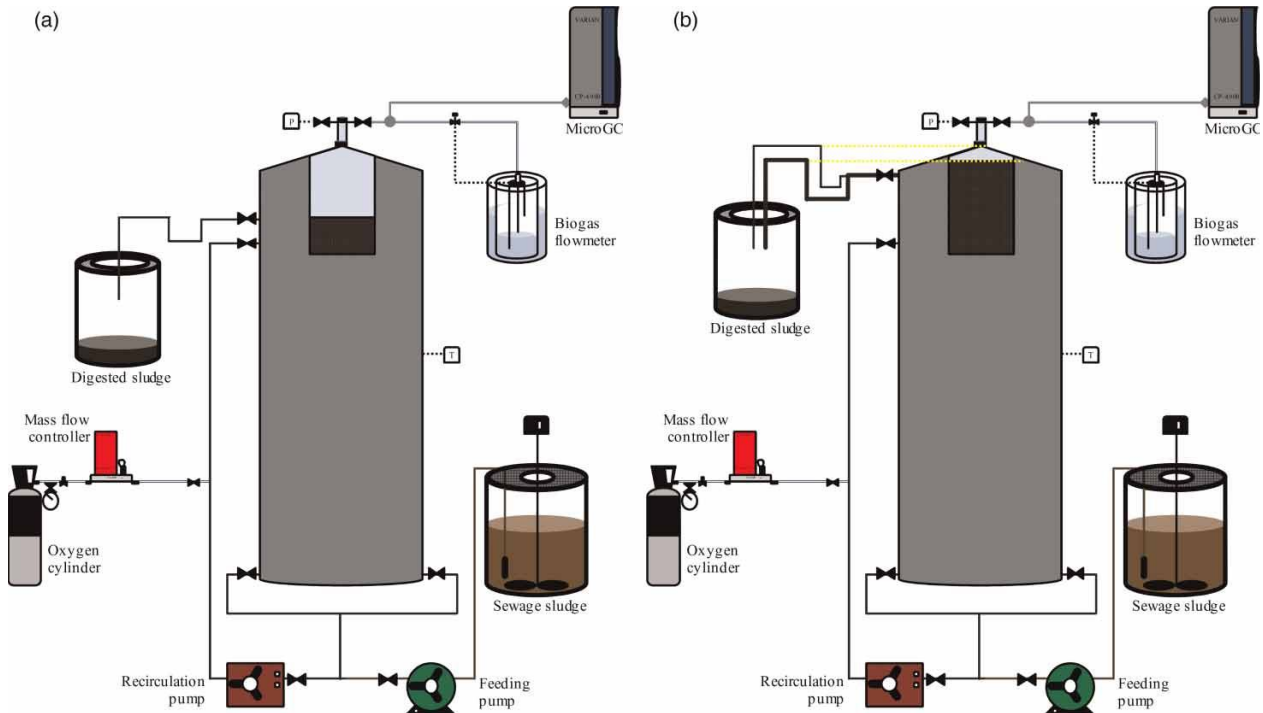


Figure 1 | Digester diagram with HS of 50.0 (a) 9.5 and 1.5 L (b) effluent represented by a thick and thin line, respectively; liquid level indicated by a yellow dotted line. (The full colour version of this figure is available in the online version of this paper, at <http://www.iwaponline.com/wst/toc.htm>.)

liquid chromatography (HPLC), according to the procedure described by van der Zee *et al.* (2007). Sulfide was measured by potentiometry with selective electrode according to the standard method (APHA 1998).

Experimental procedure

The study was divided into two phases (Table 1). At the beginning of the first phase, the digester operated under anaerobic conditions with a HS volume of 50.0 L (AN0). Once the hydrogen sulfide concentration remained stationary, the micro-oxygenation was started (MA0) according to

Figure 1(a). Supply was raised gradually until the pollutant was removed.

At the beginning of phase 2, the reactor was operated under anaerobic conditions with a HS volume of 9.5 L (AN1). Microaerobic conditions were implemented at day 3 (MA1). As in the previous phase, oxygen was injected into the recirculation stream (Figure 1(b)). Once the residual hydrogen sulfide concentration was negligible (MA2), the liquid level of the reactor was increased until the HS was reduced to ≈ 1.5 L. After almost two days under such conditions (MA3), the HS volume was raised again to 9.5 L (MA4). Finally, the reactor worked under anaerobic conditions (AN2).

Table 1 | Sequence of variations applied during the study, and digester response

	Phase 1		Phase 2					
	AN0	MA0	AN1	MA1	MA2	MA3	MA4	AN2
Time (d)	0–2	2–14	0–3	3–4	4–5	5–6	6–7	7–8
HS volume	50.0	50.0	9.5	9.5	9.5	1.5	9.5	9.5
Oxygen flow (NL/ L_{fed})	0	0.16–0.46	0	0.43	0.46	0.46	0.46	0
VS_{fed} (g/L)	29.6	32.0	39.0	29.7	29.7	31.6	31.6	31.6
Biogas production (NL/d)	158.2	169.0	207.5	166.4	157.0	173.8	179.0	174.2
Methane yield (NmL/ g_{VS})	337.1	325.5	329.4	353.9	335.4	352.0	353.9	341.6

RESULTS AND DISCUSSION

Phase 1

In AN0, the average hydrogen sulfide concentration was $0.35 \pm 0.01\%$ ov/v (Figure 2). As a result of the first oxygen flow introduced to the reactor, the biogas sulfide content dropped to 0.15% ov/v. Subsequently, the micro-oxygenation was increased by 50%, and the removal efficacy was 88%. Thereafter, the supply continued being raised to $0.27 \text{ NL/L}_{\text{fed}}$, $0.32 \text{ NL/L}_{\text{fed}}$, $0.36 \text{ NL/L}_{\text{fed}}$, $0.39 \text{ NL/L}_{\text{fed}}$, $0.43 \text{ NL/L}_{\text{fed}}$, and finally, $0.46 \text{ NL/L}_{\text{fed}}$. At $0.46 \text{ NL/L}_{\text{fed}}$, 99% of the pollutant produced was removed from the biogas. Therefore, as the stepwise supply adjustment assured the minimum biogas dilution, that value was considered the optimum micro-oxygenation level.

The desulfurization performance decreased slightly between the fifth and seventh day despite the increasing oxygen flow; it was raised at the beginning of 5th and 6th day (Figure 2). The efficacy loss recorded on the 5th day was attributed to a momentary increase in the OLR to the digester due to the sewage sludge variability (whose VS concentration varied widely throughout the study, as shown in Table 1). It also explained the biogas production peak recorded on the fifth day; it rose from 169.8 NL/d on fourth day to 201.2 NL/d , and decreased on the sixth day (161.8 NL/d). That is, the larger the amount of VS fed, the higher the release of sulfur compounds and biogas production. As a consequence, hydrogen sulfide generation and oxygen demand increased. Nevertheless, the biogas production fell on the next day and, remarkably, the biogas sulfide content continued rising. This suggested higher feeding sulfate content, which was detected shortly afterwards

(data not shown). Note that the rise in the hydrogen sulfide production was verified in MA1.

Phase 2

The first oxygen flow supplied removed 96% of the hydrogen sulfide produced (Figure 2). Then, it was raised to $0.46 \text{ NL/L}_{\text{fed}}$ (the optimum value in MA0), and the removal efficacy increased (99%). As in phase 1, the micro-oxygenation level reached by stepwise adjustment in phase 2 was considered the optimum. Furthermore, it was estimated that the hydrogen sulfide flow oxidized in MA0 and MA2 at $0.46 \text{ NL/L}_{\text{fed}}$ of oxygen supply was almost equal. Therefore, the microaerobic performance was not affected by the substantial reduction of the HS volume. The determination of the minimum HS needed to perform efficiently the biogas desulfurization could be interesting.

The higher working volume in phase 2 could result in poorer mixing (as recirculation rate was maintained constant) and longer contact time between the oxygen and the liquid phase. Furthermore, it is noteworthy that mixing was especially deficient in the upper part of the bioreactor because of the large distance between the liquid surface inside the reactor and both the exit point of digested sludge and the recirculation stream (Figure 1(b)). Whereas less efficient mixing could lower the oxygen transfer across the gas-liquid interface, higher contact time between both phases could improve it. However, as presented, the oxygen required for similar flows of hydrogen sulfide from biogas did not change from phase 1 to 2. This could mean that either the biogas desulfurization efficiency did not depend on the oxygen transfer to the liquid media, as Díaz *et al.* (2010b) suggested, or the reactor configuration set in phase

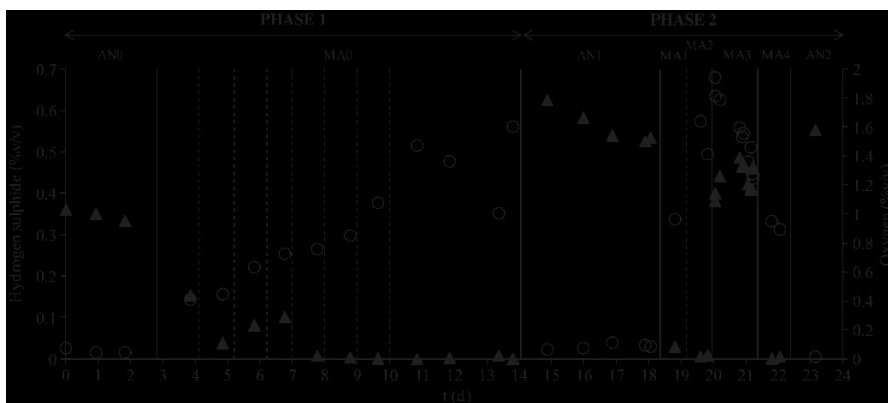


Figure 2 | Hydrogen sulfide (▲) and oxygen (○) concentrations in biogas during the study. Vertical continuous lines indicate transition periods between anaerobic and microaerobic conditions and/or changes in HS volume; vertical discontinuous lines indicate changes in oxygen supply.

2 led to the same oxygen transfer rate as in phase 1. This will be clarified by estimating how oxygen was distributed into the digester in both phases (see below).

At day 5, the HS volume was reduced to 1.5 L, while the same oxygen flow was maintained. Shortly before, an increase of 0.37%v/v in the biogas sulfide content was recorded. The average pollutant concentration in MA3 was $0.44 \pm 0.03\%v/v$, which resulted in a removal performance of $\approx 15\%$. This is consistent with the observations made during that experimental period relative to elemental sulfur deposition in HS (see below). Due to imminent clogging risks of the biogas outlet from the digester with sulfur, the liquid level was lowered. As a result, biogas was effectively desulfurized again (99%). The available surface area of the gas space seemed the limiting factor of the microaerobic process in MA3.

Although MA2 and MA4 were operated under the same conditions, oxygen contained in biogas was significantly different. Likewise, despite the low removal efficacy recorded in MA3, the oxygen concentration remained close to the values obtained in the previous period. Those oxygen responses resulted from the continuous changes in the biogas production due to the variable OLR to the digester (Table 1).

It must be emphasized that changes in the micro-oxygenation level and hydrogen sulfide flow are rapidly reflected in the biogas composition. Furthermore, the operating times to reach the stationary state at low biogas residence times (such as those fixed in this research) are very short. However, further research is being carried out in order to reduce safely the gas space (and as much as possible in an equivalent period to MA3) so that the response of the digester can be observed over a longer period of time.

Sulfur deposition

During MA3, elemental sulfur accumulating on the sludge deposited inside the transparent cylinder of the cover could be seen (Figure 3(b)). One momentary liquid level rise above the level set just at the beginning of that stage was the cause of the sludge deposition. Meantime, though to a much lesser extent, sulfur accumulated in the valve of the biogas outflow (made of rigid polyvinyl chloride, PVC-U) and in the tygon tubing (Figure 3(a)). Whereas its deposition covering the sludge clearly pointed to biological biogas desulfurization, the possibility of chemical hydrogen sulfide oxidation in those areas free of sludge could not be ruled out. However, may be the affinity of SOB for transparent PVC (PVC-GLAS) was lower, and thus it was not

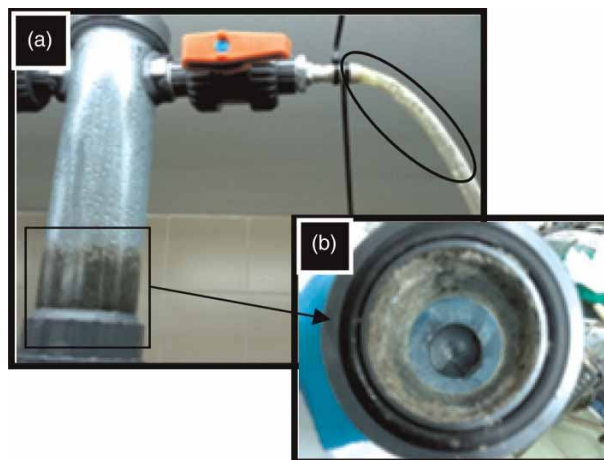


Figure 3 | Elemental sulfur accumulated in the tygon tubing (delimited by an ellipse), sludge deposited in the transparent cylinder of the HS (delimited by a square) in MA3 (a), and sulfur accumulated on it from MA3 to MA4 (b).

deposited wherever sludge did not cover the cylinder, despite the shorter distance to the liquid surface and consequent higher accessibility to water and nutrients (and carbon sources to heterotrophic SOB). Overall, the preferential distribution of sulfur highlighted the predominance of the biological reactions of sulfide oxidation over the chemical ones.

When the transparent cylinder was removed for cleaning on 23rd day, sulfur was observed on those areas of the conical cover which were exposed to biogas after MA3 (Figure 1(b)). So, it was specifically deposited over the sludge that remained there after lowering the liquid level, which covered sulfur and sludge accumulated presumably in the preceding stages. Obviously, SOB could be more frequently provided by nutrients and water there when the HS volume was 9.5 L. Considering the short duration of MA4, that observation indicated that most of the sulfur shown in Figure 3(b) accumulated during MA3. Noteworthy is also that sulfur was not seen covering the surface of the liquid media on 23rd day; this was considered to be possibly due to the poor mixing conditions maintained around that area in phase 2. Moreover, it was not seen in the effluent either, which was examined daily. Along with the resulting removal performances, these observations confirmed that the hydrogen sulfide oxidation occurred in the HS.

Accordingly, the hypothesis is that SOB carried out the biogas desulfurization in the walls and/or the conical cover of the HS (both made of polypropylene homopolymer, PPH), during MA0, MA1 and MA2. SOB were carried along to those surfaces by biogas and sludge (due to splashes and even momentary liquid level rises), and once there, they

oxidized the gaseous sulfide that dissolved in the water deposited by condensation (droplets can be seen indeed in Figure 3(a)). Hence, certainly the oxidation process took place predominantly in the areas of the walls nearest the liquid media, where the growth conditions stimulated SOB. It is consistent with Kobayashi *et al.* (2012), who found that the shorter the distance from the liquid level of digested sludge, the higher the sulfide oxidizing activity. They also reported that SOB proliferated all over HS, including ceiling, walls, as well as components made of plastic, stainless and wooden placed around the middle of it.

Oxygen utilization

The estimation of oxygen utilization into the reactor through the periods operated at 0.46 NL/L_{fed} of oxygen supply is illustrated in Figure 4 (MA0 includes the results obtained from the 10th day). Note that neither sulfate nor thiosulfate were detected; so, elemental sulfur was the sole oxidation product. On the other hand, according to previous observations, it was assumed that the biogas sulfide content in MA0 was 0.5%. Likewise, it was considered constant from the 3th day of the second phase.

Figure 4 illustrates that the amount of oxygen employed to oxidize hydrogen sulfide in both MA0 and MA2 was almost equal ($\approx 9\%$), which is in accordance with the optimum oxygen flows reached. However, it also shows a modest decrease in the oxygen consumed in unidentified processes (from 43 to 39%), which could be the final result of the poorer mixing and the longer contact time between phases (gas and liquid). This would imply that the mixing impact on the oxygen mass transfer was higher and, more importantly, that it was irrelevant to the desulfurization performance. The trend of the percentage of oxygen consumed in other processes over the study is indeed consistent with that. It must be noted, however, that it was the highest in MA4. Inexplicably, it rose by 14% over the

equivalent period (MA2), and in the meantime, a 2% increase in the percentage of oxygen invested in partial hydrogen sulfide oxidation was estimated. Nevertheless, the higher surface providing favorable growth conditions for SOB as a result of the sludge deposition in most of the HS area could explain that slight rise.

Only a small amount of the oxygen supply was employed to remove hydrogen sulfide and, more importantly, it was the lowest in MA3 (2%). This is consistent with the low desulfurization efficacy recorded. The oxygen which ceased to be utilized for that end from MA2 left the digester with biogas instead of being utilized for other processes, which also pointed to hydrogen sulfide oxidation in HS. That is, there was no competition between other oxidizing microorganisms present in the liquid phase and SOB due to sulfide oxidizers only being able to consume the remaining oxygen that reached the HS, where they developed.

As noted, most of the oxygen left the reactor in biogas or was consumed in unidentified processes in all the periods evaluated. Among these processes, aerobic oxidation of readily available organic substrates hardly contributed to that result, as a correlation between microaerobic conditions and lower methane yield was not found (Table 1).

CONCLUSIONS

Biogas was effectively desulfurized into the bioreactor at 0.46 NL/L_{fed} of oxygen supply when the HS volume was 50.0 and 9.5 L. The removal performance dropped rapidly when the HS volume was lowered to 1.5 L, thereby showing that it strongly depended on the available surface area in the gas space. The deposition of elemental sulfur confirmed it. Moreover, the pattern of sulfur accumulation indicated that the oxidation occurred preferentially on certain materials, and suggested a significant biological contribution to the microaerobic process.

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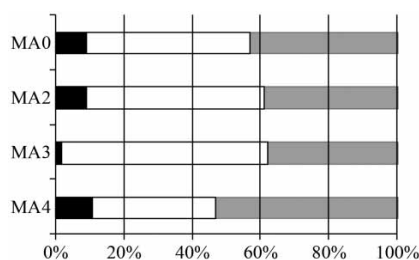


Figure 4 | Oxygen utilization in the digester. Oxygen employed to produce elemental sulfur (■), oxygen consumed in other processes (■), and oxygen in biogas (□).

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