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Biogas purification using membrane micro-aeration: A mass transfer analysis

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Abstract
When sulfur containing organic feedstocks undergo anaerobic digestion, sulfides are formed due to the biological activities of sulfur reducing bacteria. Presence of hydrogen sulfide (H_2S) negatively affects the usage of biogas and needs to be reduced to levels that depend on the intended biogas application. Conversion of sulfide to its oxidized forms can be carried out by aerobic chemolithotrophic bacteria consuming oxygen as the electron acceptor. Membrane micro-aeration is a recently developed reliable method of safely supplying oxygen into anaerobic digesters. In this study, mass transfer models are developed to represent diffusion and back diffusion of gases through tubular polydimethylsiloxane (PDMS) membranes. The models are utilized to determine the required membrane area and length in order to supply the stoichiometric amount of oxygen for biologically oxidizing a given amount of sulfide feed into elemental sulfur. Penetration of oxygen and nitrogen into the digester and transfer of methane, carbon dioxide and hydrogen sulfide back into the membrane tube are analyzed using these mass transfer models. Circulating air or aerated water inside the membrane tube is considered as two alternatives for supplying micro-aeration to the digester. Literature digester performance and sulfide data are used for example calculations. The required membrane length depends on circulating water flow rates and dissolved oxygen concentrations when water is used inside the membrane. A considerable fraction of CO_2 can also be removed from the biogas in this case. Circulating air inside the membrane is, however, more promising solution as it requires much less membrane area and thereby also causes insignificant methane loss. The proposed membrane micro-aeration technique cuts N_2 biogas dilution in half compared to direct air purging for in-situ sulfide oxidation.

Keywords: Biogas; Hydrogen sulfide; Mass transfer; Micro-aeration; PDMS membrane; Sulfide oxidation.

1. Introduction
Significant amounts of hydrogen sulfide can be formed inside anaerobic digesters when sulfur containing organic substrates such as, paper mill effluents [1], seafood processing wastes [2], animal manures [3], food wastes [4], are fed into digesters. The reduction of S containing compounds is performed by sulfur reducing bacteria growing inside the digester. Depending on the pH these reduced sulfides can be present in three different forms, i.e. HS^-, S^{2-} and H_2S [5]. H_2S transfers into the gas phase as part of the biogas, restricting the direct use of raw biogas as a fuel. Accelerated corrosion of utilities (combustors,

compressors, engines, boilers, etc.) and reduced lifespan of pipe work and other installations are among the major impacts of H_2S presence in biogas. Presence of high sulfide concentrations in digesters can also lead to inhibition of the methanogenesis stage of digestion [6]. Heat production boilers require H_2S concentration to be less than 1000 ppmv and electricity production using internal combustion engines require it to be less than 100 ppmv [7]. Cleaning of raw biogas is thus often essential to achieve such purity levels.

Chemical, physicochemical and biological methods can be used to remove sulfides from biogas [8, 9]. Biological methods are assumed to have the advantages of low cost and the environmental sustainability.

Photoautotrophic or chemolithotrophic microorganisms are involved in biological sulfide removal methods [10]. Photoautotrophs use CO_2 as the terminal electron acceptor in an anaerobic process carried out by purple and green sulfur bacteria [10]. Biological sulfide oxidation is most commonly applied with colorless chemolithotrophic bacteria such as Thiobascillus sp. Reduced inorganic sulfur compounds like S^{2-}, S^o, $S_2O_3^{2-}$ and organic sulfur compounds like methanethiol are suitable substrates for these types of bacteria [10]. Aerobic chemolithotrophic species use oxygen as the terminal electron acceptor and anaerobic species can use nitrate and nitrite as electron acceptors [10]. According to [10], most of the chemolithotrophic bacteria thrive under mesophilic conditions while Thiobascillus genera can survive both in thermophilic and mesophilic conditions.

Aerobic chemolithotrophs obtain energy by the following reactions where the final product depends on the amount of oxygen available [10].

$$H_2S + 1/2O_2 \rightarrow H_2O + S^0 \qquad \Delta G^0 = -209.4 \text{kJ/reaction} \tag{1}$$

$$S^0 + 2H_2O + 3/2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad \Delta G^0 = -587.1 \text{kJ/reaction} \tag{2}$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad \Delta G^0 = -798.2 \text{kJ/reaction} \tag{3}$$

$$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad \Delta G^0 = -818.3 \text{kJ/reaction} \tag{4}$$

Anaerobic digesters can be provided with limited amounts of oxygen (micro-aeration) to have beneficial effects (e.g. enhanced hydrolysis) without inhibiting the anaerobic biochemical pathways leading to methane generation [8, 11, 12]. Micro-aeration can be applied either to the head space or to the liquid phase of the anaerobic digester. Supply of pure oxygen for this purpose, in order to avoid biogas dilution by nitrogen in air, can appear to be advantageous but air as an oxygen source is much less expensive. The direct introduction of air or oxygen into anaerobic digesters is, however, not approved by the safety regulations in Scandinavian countries, due to the explosion risk of methane and oxygen mixtures. Oxygen transfer using dense membrane tubes can be considered as a safer and more controllable mean of supplying micro-aeration into anaerobic digesters, to comply with such regulation restrictions.

In this analysis, micro-aeration circulating aerated water or air in a dense tubular poly-dimethylsiloxane (PDMS) membrane placed inside the headspace of the anaerobic digester is studied. O_2 and N_2 diffuse into the headspace while CH_4, CO_2, and H_2S can diffuse the other way into the membrane tube from the biogas containing headspace. The aim is to quantify and model these transports in order to evaluate the practical potential of such solutions. The analysis is based primarily on the knowledge that transport of gases through dense polymeric membranes can be described by the solution-diffusion mechanism [13]. First, the gas is dissolved into the polymer membrane from the feed side and then diffuses through the membrane according to the direction of the concentration driving force. The rate of gas transfer across the membrane depends on the mass transfer resistance and the extent of driving force. Mass transfer resistance is caused by the membrane material itself and the liquid and/or gas films on the membrane surfaces.

2. Model development

Two models are developed to analyze the mass transfer of gases across a tubular PDMS membrane. One is when water is circulated inside the membrane and the other is when air is circulated. The membrane is placed in the biogas containing digester headspace in both cases.

2.1 Water circulation

Mass transfer of gases into and out of the PDMS tube is derived conceptualizing the resistances in series model. Accordingly, water flows inside the membrane tube and biogas exists outside the membrane tube within the headspace. Figure 1 illustrates the suggested placement of the membrane tube loop inside the headspace of the reactor and one way of aerating the water that flows inside the membrane tube. Both the outward diffusion and the backward diffusion are analyzed here. The following assumptions are made for the model development.

- Water inside the membrane is completely mixed because of the high water circulation rate.
- Flow inside the membrane tube is a fully developed laminar flow.
- Biogas in the head space of the anaerobic digester is completely mixed.
- Diffusion through the membrane follows Fick's first law of diffusion.
- Gas phase temperature is constant and uniform; and equal to the reactor liquid phase temperature.
- Biogas behaves as an ideal gas under the given conditions.

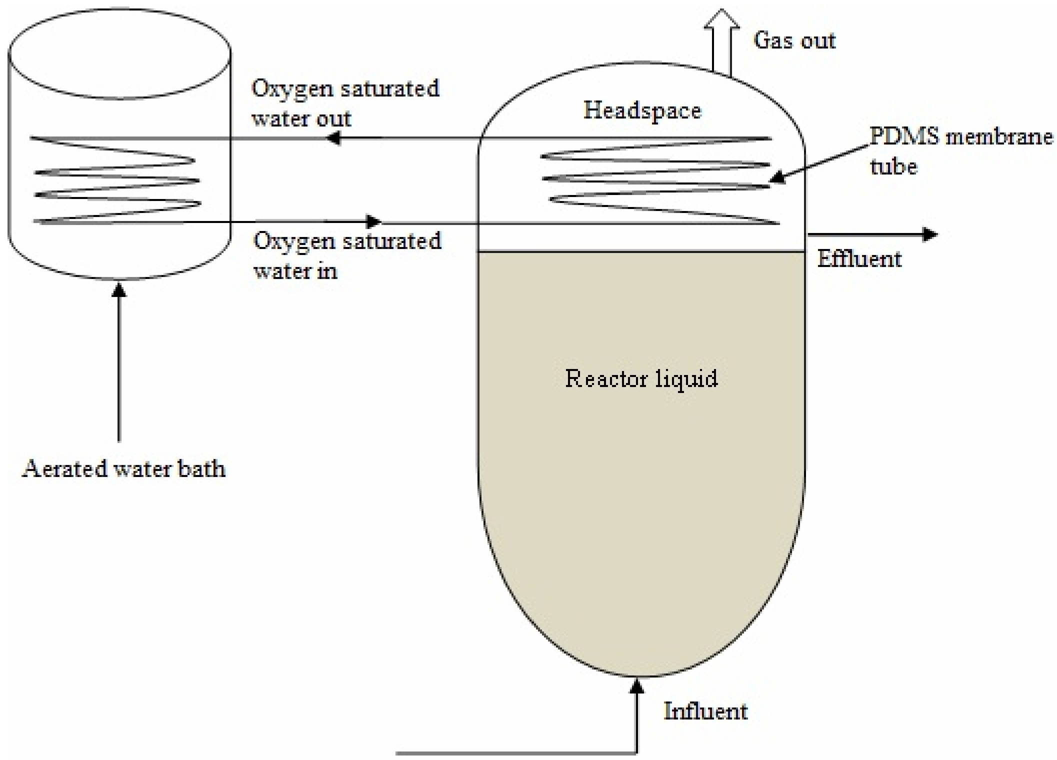

Figure 1. Arrangement of the mass transfer membrane loop inside the digester using an aerated water bath to supply oxygen to the circulating water

Outward Diffusion

Dissolved oxygen and nitrogen gases are diffused into the head space of the anaerobic digester. Figure 2 represents the distribution of concentration gradients.

Mass transfer rate of oxygen and nitrogen across the water film boundary layer inside the membrane tube is given by Eq. 5.

$$J_i = k_{i,in} 2\pi r_i L (C_{i,in} - C_{i,in,eq}) \tag{5}$$

Transfer of gases across the membrane is given by the Fick's first law (Eq.s 6 and 7).

$$J_i = -D_{i,m} A_{lm} \frac{dc}{dr} \tag{6}$$

$$J_i = D_{i,m} 2\pi L \frac{(C_{i,m,in} - C_{i,m,out})}{In\left(\frac{r_o}{r_i}\right)} \quad (7)$$

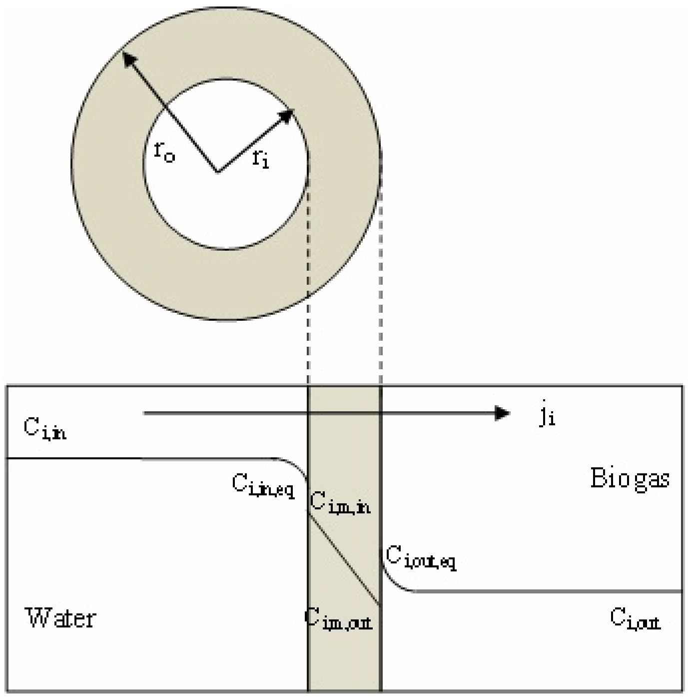

Figure 2. Distribution of oxygen and nitrogen concentration gradients

Equilibrium partition coefficient for water side is given by $S_{i,mle}$ (Eq. 8).

$$\frac{C_{i,m,in}}{C_{i,in,eq}} = S_{i,mle} \quad (8)$$

Equilibrium partition coefficient for gas side is given by $S_{i,mge}$ (Eq. 9).

$$\frac{C_{i,m,out}}{C_{i,out,eq}} = S_{i,mge} \quad (9)$$

The concentrations on the membrane can be substituted with the water and gas phase partition coefficients as given by Eq.s 8 and 9 to obtain Eq. 10.

$$J_i = \frac{D_{i,m} 2\pi L S_{i,mle}\left(C_{i,in,eq} - C_{i,out,eq}\frac{S_{i,mge}}{S_{i,mle}}\right)}{\ln\left(\frac{r_o}{r_i}\right)} \quad (10)$$

Mass transfer rate across the boundary layer outside the membrane tube is given by Eq. 11.

$$J_i = k_{i,out} 2\pi r_o L (C_{i,out,eq} - C_{i,out}) \quad (11)$$

Equation 12 is the mass transfer rate of oxygen and nitrogen from water side to gas side and is obtained by solving equation 5, 10 and 11.

$$J_i = \frac{\left(C_{i,in} - \frac{S_{i,mge}}{S_{i,mle}} C_{i,out}\right)}{\frac{1}{k_{i,in} 2\pi r_i L} + \frac{\ln(r_o / r_i)}{D_{i,m} 2\pi L S_{i,mle}} + \frac{S_{i,mge} / S_{i,mle}}{k_{i,out} 2\pi r_o L}} \tag{12}$$

Back diffusion

Methane, carbon dioxide and hydrogen sulfide gases diffuse from the biogas headspace into the membrane tube as illustrated in Figure 3.

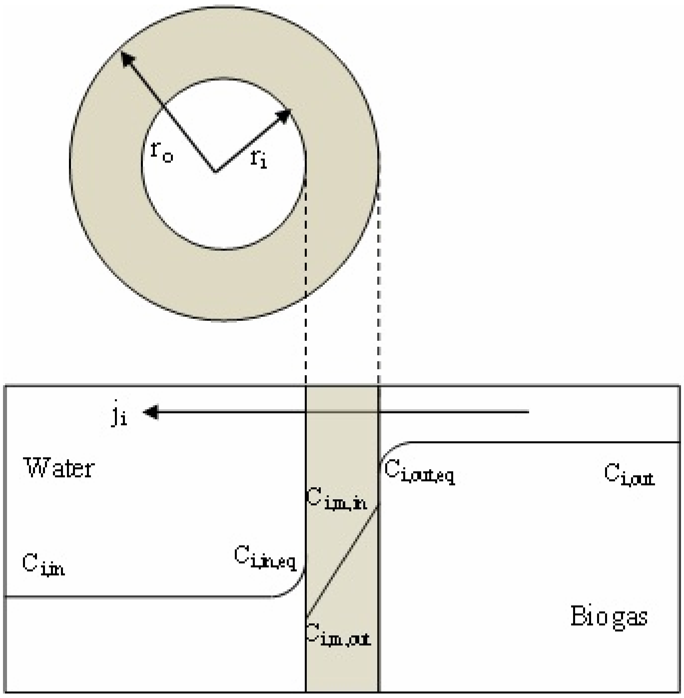

Figure 3. Distribution of methane, carbon dioxide and hydrogen sulfide concentration gradients

Mass transfer rate across the boundary layer in the gas side is given by Eq. 13.

$$J_i = k_{i,out} 2\pi r_o L (C_{i,out} - C_{i,out,eq}) \tag{13}$$

Back diffusion of gases across the membrane is, again, given by the Fick's first law (Eq. 14).

$$J_i = -D_{i,m} 2\pi L \frac{(C_{i,m,in} - C_{i,m,out})}{\ln\left(\frac{r_o}{r_i}\right)} \tag{14}$$

Substitution of membrane concentrations with equilibrium partition coefficients gives Eq. 15.

$$J_i = \frac{-D_{i,m} 2\pi L S_{i,mge} (C_{i,in,eq} \frac{S_{i,mle}}{S_{i,mge}} - C_{i,out,eq})}{\ln(r_o / r_i)} \tag{15}$$

Mass transfer rate of methane, carbon dioxide, and hydrogen sulfide across the water side boundary layer inside the membrane tube is given by Eq 16.

$$J_i = k_{i,in} 2\pi r_i L (C_{i,in,eq} - C_{i,in}) \tag{16}$$

Solving Eq.s 13, 15 and 16 lead to Eq. 17 which describes the back diffusion of gases.

$$J_i = \frac{\left(C_{i,out} - \dfrac{S_{i,mle} C_{i,in}}{S_{i,mge}} \right)}{\dfrac{S_{i,mle}}{k_{i,in} 2\pi r_i L S_{i,mge}} + \dfrac{\ln(r_o / r_i)}{D_{i,m} 2\pi L S_{i,mge}} + \dfrac{1}{k_{i,out} 2\pi r_o L}} \tag{17}$$

2.1.1 Equilibrium Partition coefficient

Partition coefficient is the ratio of concentrations of a compound in the two phases of a mixture of two immiscible solvents at equilibrium. Relations for equilibrium partition coefficients are derived using Eq.s 18 - 21.

Solubility of a gas in a liquid can be expressed as in Eq. 18.

$$C_{i,liquid} = S_{i,liquid} P_{i,gas} \tag{18}$$

Applying Henry's law leads to Eq.s 19 and 20.

$$P_{i,gas} = H_{i,membrane} C_{i,membrane} \tag{19}$$

$$P_{i,gas} = H_{i,liquid} C_{i,liquid} \tag{20}$$

Applying ideal gas law leads to Eq. 21.

$$P_{i,gas} = C_{i,gas} RT \tag{21}$$

Now, considering the gas side of the membrane, we can express,

$$C_{i,out} = \frac{P_{i,out}}{RT} \tag{22}$$

Using Eq. 19:

$$C_{i,out} = \frac{H_{i,mg} C_{i,m,out}}{RT} \tag{23}$$

$$\frac{C_{i,m,out}}{C_{i,out}} = \frac{RT}{H_{i,mg}} \tag{24}$$

$C_{i,out}$ is replaced with $C_{i,out,eq}$ and the relation for $S_{i,mge}$ can be written as Eq. 25.

$$S_{i,mge} = \frac{RT}{H_{i,mg}} \tag{25}$$

Relation for $S_{i,mle}$ is obtained in a similar manner from Eq.s 18 and 20 to yield Eq.s 26-28.

$$C_{i,in} = S_{i,in} P_{i,in} \tag{26}$$

$$P_{i,in} = H_{i,gl} C_{i,in} \tag{27}$$

$$S_{i,in} = \frac{1}{H_{i,gl}} \tag{28}$$

Applying Henry's law according to Eq.19 leads to Eq. 29.

$$P_{i,in} = H_{i,mg} C_{i,m,in} \tag{29}$$

Eq.s 26 and 28 give Eq. 30 and 31.

$$\frac{C_{i,in}}{S_{i,in}} = H_{i,mg} C_{i,m,in} \tag{30}$$

$$\frac{C_{i,m,in}}{C_{i,in}} = \frac{1}{S_{i,in} H_{i,mg}} \tag{31}$$

By substituting $C_{i,in}$ with $C_{i,in,eq}$ in Eq. 28 leads to Eq. 32.

$$S_{i,mle} = \frac{H_{i,gl}}{H_{i,mg}} \tag{32}$$

2.1.2 Mass transfer coefficients

Mass transfer coefficients of the inside liquid and outside gas films are calculated using Sherwood number (Sh) correlations.

$$Sh = \frac{k_{i,in} d_h}{D_{i,l}} \tag{33}$$

For inside water film:

$$Sh = 3.66 + \frac{0.0668(\frac{Pe.d_h}{L})}{(1 + 0.04(Pe.d_h / L)^{2/3})} \tag{34}$$

This is valid $\frac{x / d_h}{\mathrm{Re}.Sc} < 0.10$, and $10^4 > \frac{\pi d_h}{4x} \mathrm{Re}.Sc > 10$ for a fully developed parabolic velocity profile and laminar flow conditions in a tube [14].

Water side mass transfer coefficient can be calculated using Eq.s 33 and 34.

$$k_{i,in} = \left[3.66 + \frac{0.0668(\frac{Pe.d_h}{L})}{(1 + 0.04(Pe.d_h / L)^{2/3})} \right] \frac{D_{i,l}}{d_h} \tag{35}$$

For outside gas film:
According to the derivations presented by [15], if the membrane tube can be assumed to be in a region of free convection, Equation 36 is found to fit with mass transfer data for tubular rings within the range $5.5\times10^{5} < Sc.Gr < 9.4\times10^{8}$. Deviations from the single ring data at the outer surface of helical coils depend on the number of turns per coil. The maximum deviation is found to be 12 %.

$$Sh = 0.55(Sc.Gr)^{0.25} \tag{36}$$

Mass transfer coefficient is given by:

$$k_{i,out} = 0.55\left[\frac{\mu}{\rho D_{i,g}}\frac{g\beta\rho^{2}(C_{i,out,eq}-C_{i,out})L^{3}}{\mu^{2}}\right]^{0.25}\frac{D_{i,g}}{d_{h}} \tag{37}$$

For the mass transfer rate calculations below, resistance to mass transfer in the gas film is neglected since its contribution to the total resistance is very low.

2.1.3 Parameters
Table 1 summarizes the values of diffusivity, solubility, Henry's coefficients and partition coefficients related to the gases of relevance here. Parameters are evaluated assuming a water temperature of 20^{0}C. The anaerobic digester is, however, considered to operate under mesophilic conditions (close to 35 ^{0}C). Diffusion coefficients of gases in water are estimated using Eq. 38 [16].

$$D = \frac{7.4x10^{-8}(\phi\overline{M}_{H2O})^{1/2}T}{\mu_{H2O}\overline{V}^{0.6}_{gas}} \tag{38}$$

D is the diffusion coefficient in cm^2/sec. V_{gas} can be calculated using Eq. 39 [17].

$$\overline{V}_{gas} = 0.285V_{c}^{1.048} \tag{39}$$

According to [18], "solubility and diffusivity in polydimethylsiloxane membranes show very small variations in the temperature range 25-65 ^{0}C". Therefore, the diffusion coefficients and the Henry's law coefficients used in this analysis are assumed approximately constant for the temperature range of 20-55 ^{0}C.

Table 1. Parameters related to gas transfer

Parameter	Oxygen	Nitrogen	Methane	Carbon dioxide	Hydrogen sulfide	Reference
$D_{i,m}$(m^2/s)	1.6E-09	1.5E-09	1.3E-09	1.1E-09	1.55E-09	[19] [20]
$D_{i,l}$(m^2/s)	2.1E-09	1.88E-09	1.77E-09	1.81E-09	1.91E-09	Estimated
[1]H_{mg}(Pa.m^3/mol)	7321.7	15131.5	3982	1031.7	[2]2694	[19]
H_{gL}(Pa.m^3/mol)	74879.7	146561.8	68527.2	2590.8	881.5	[21]
$S_{i,mle}$	10.23	9.68	17.21	2.51	0.33	Estimated
$S_{i,mge}$	0.33	0.16	0.64	2.48	0.95	Estimated

[1]Estimated from solubility data, [2] [22]

Mass transfer rates of the gases are calculated for 3 different sizes of silicone membrane tubes commonly available. Different water velocities in the laminar flow range are considered. Several dissolved oxygen concentrations, saturated and sub-saturated, are also tested in calculations. Table 2 gives data on different sizes of membrane tubes used in the calculations.

Table 2. Three membrane tube sizes used in the analysis

r_i (mm)	1	1.5	4
r_o (mm)	1.5	2.5	5
Log mean radius, r_{lm} (mm)	1.2	1.9	4.5

2.2 Air circulation

The case of air instead of water circulating inside the membrane is analyzed as a simplified version of the water case described above. The gas film mass transfer resistance (Eq.37) is determined to be insignificant compared to the membrane resistance so that both inside and outside gas film resistances are assumed negligible for this case. Eq. 40 therefore describes the outward diffusion of gases and Eq. 41 describes the back diffusion of gases in this case.

$$J_i = \frac{S_{i,mge,in}C_{i,in} - S_{i,mge,out}C_{i,out}}{\dfrac{\ln\left(r_o/r_i\right)}{D_{i,m}2\pi L}} \tag{40}$$

$$J_i = \frac{S_{i,mge,out}C_{i,out} - S_{i,mge,in}C_{i,in}}{\dfrac{\ln\left(r_o/r_i\right)}{D_{i,m}2\pi L}} \tag{41}$$

3. Results and discussion

The above developed mass transfer models are used to calculate the required PDMS membrane area and also the length of the membrane tube for a specific level of sulfide removal in a given case. Two published AD studies, representing high and moderate sulfide situations, were selected as case studies for our analysis. Table 3 summarizes some parameters characterizing these studies. Membrane requirements and mass transfer are first calculated for the option of using water inside the tube and next using air.

Table 3. Operating conditions for the two case studies selected

Case no.	1	2
Reference	[12]	[23]
Feed source	Waste water +Sodium sulfate	Municipal organic waste
Working volume of the reactor (m^3)	0.2	0.538
Operating temperature (K)	308.15	296.15
Avg. total sulfur input (mg-S/day)	7890	Not given
Avg. inlet COD Concentration (g/l)	71	Not given
Avg. daily biogas production (l/day)	200	*960
Avg. H_2S conc. in biogas under anaerobic conditions (ppmv)	14400	1100
Avg. CH_4 concentration in biogas (% v/v)	62	65
*Required O_2 flow rate to oxidize total sulfide(kg/s)	2.11E-08	8.05E-09

* Estimated from given data

3.1 Use of water inside the membrane

For the above two cases, membrane lengths required to induce the necessary amount of oxygen are calculated using the developed mass transfer models given by Eq.s 12 and 17. Table 4 summarizes the results for different membrane sizes.

Table 4. Estimated membrane requirement for different membrane sizes in the two cases

Case	r_{lm} (mm)	U (m/s)	$C_{O2,in}$ (mg/l) (Saturated)	Liquid film resistance to O_2 transfer (s/m^3)	Membrane resistance to O_2 transfer (s/m^3)	L (m)	A_{lm} (m^2)
1	1.2	0.016	7.26	308330	34970	90	0.7
	1.9	0.028	7.26	299910	43350	91.5	1.1
	4.5	0.1	7.26	315285	27990	62	1.7
2	1.2	0.016	8.67	984770	93020	40.5	0.3
	1.9	0.028	8.67	959375	118300	40	0.5
	4.5	0.1	8.67	960150	117560	17.5	0.5

Case 1: Reactor temperature = 35^0C and water temperature = 35^0C
Case 2: Reactor temperature = 23^0C and water temperature = 23^0C

The required length of the membrane is higher in Case 1 due to higher biogas H_2S concentration compared to the other case. Increase in tube diameter decreases the required length while the required area increases. There is a small effect of membrane thickness on the mass transfer. Most of the resistance to mass transfer is in the liquid film (~90 %) and the membrane resistance only accounts for 10 % of the total resistance. A turbulent water flow would decrease the liquid film resistance but may not be practical.

Gas penetration rates across the membrane calculated for both cases are given in Table 5. Oxygen and nitrogen diffuse into the headspace of the anaerobic digester while other gaseous components back diffuse into the membrane tube from the headspace. Diffusion rate of carbon dioxide is considerably higher compared to the other gases. Some of the hydrogen sulfide back diffuses into the membrane tube, so that the actual oxygen requirement will be lower than the calculated value. This is a significant factor for case 1 because it has a high H_2S concentration. Back diffusion of some methane can negatively impact the process performance.

Table 5. Mass flow rates through the membrane (r_{lm} = 4.481 mm)

Gas	Case 1 Water Temperature: 35^0C Reactor Temperature: 35^0C		Case 2 Water Temperature: 23^0C Reactor Temperature: 23^0C	
	Mass flow rate (mg/day)	Gas flow rate (l/day)	Mass flow rate (mg/day)	Gas flow rate (l/day)
Oxygen	1832	1.44	696	0.53
Nitrogen	2851	2.57	1080	0.94
Methane	2670	4.22	1071	1.69
Carbon dioxide	73958	42.48	24538	14.12
Hydrogen sulfide	3024	2.25	73	0.05

Membrane lengths required for different water velocities are estimated considering the largest tube diameter assuming that oxygen concentration is kept at saturation level (Figure 4). The observed relation is close to a second order polynomial showing that less membrane is required at higher velocities.

Calculated required membrane length for different concentrations of oxygen in the circulating water (for the same conditions as in Figure 4) are shown in Figure 5. Oxygen saturated condition demands a less membrane length, as can be expected, compared to sub-saturated cases since the highest driving force is available when the water is saturated with oxygen.

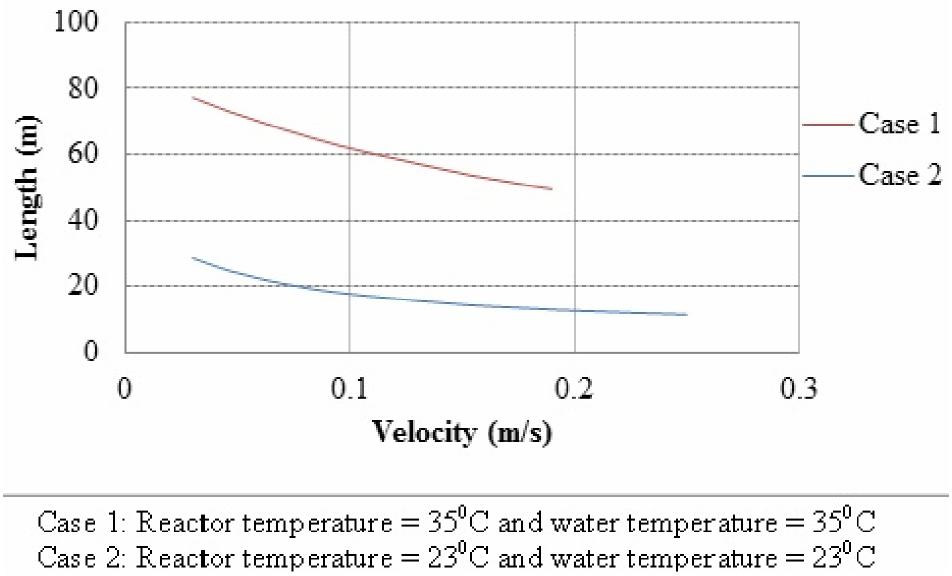

Figure 4. Calculated required membrane length vs. Velocity for the two cases (r_{lm} = 4.5 mm)

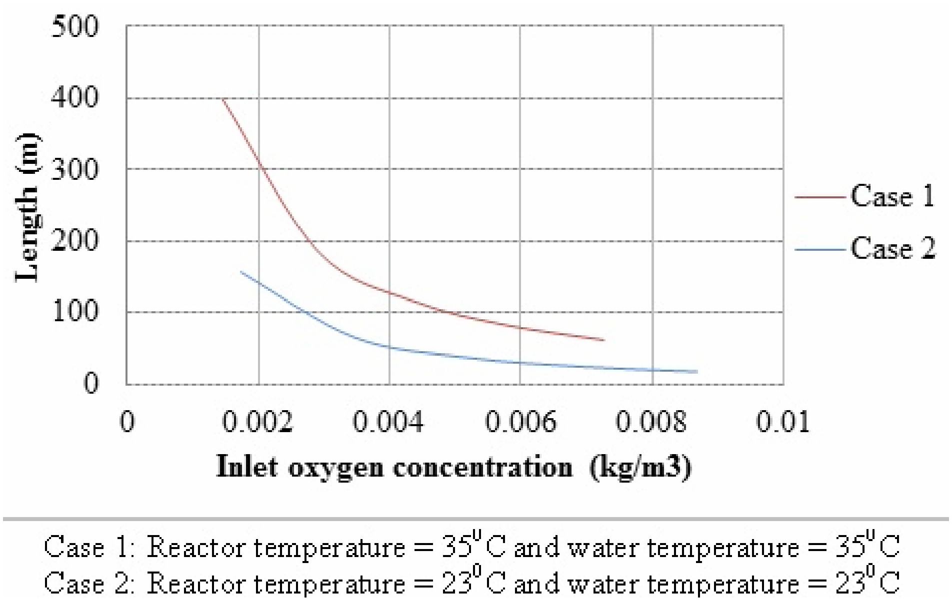

Figure 5. Calculated required membrane length vs. Oxygen concentration (r_{lm} = 4.5 mm)

Digester temperatures and inlet water temperature can also influence the required membrane length, but, according to Table 6, the temperature influence is not that significant. Membrane tube log mean radius is 4.5 mm. Increasing the digester temperature decreases the required memebrane length, mainly due to the higher values of diffusion coefficients at increased temperatures.

Table 6. Effect of temperature on the required membrane length

Case 1			Case 2		
Reactor temperature (K)	Water temperature (K)	Length of the membrane (m)	Reactor temperature (K)	Water temperature (K)	Length of the membrane (m)
35^{0}C	20^{0}C	66.5	23^{0}C	23^{0}C	17.6
35^{0}C	35^{0}C	61.8	35^{0}C	35^{0}C	16.4
55^{0}C	55^{0}C	58.2	55^{0}C	55^{0}C	16.3

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3.1.1 Different configurations of membrane micro-aeration for water circulation
Water bath vs. open air aeration of the membrane tube

Water flowing through the membrane tube mainly carries oxygen and nitrogen into the anaerobic digester and absorbs methane, carbon dioxide and hydrogen sulfide from the biogas. These absorbed gases need to be released from the circulating water. Two options for this purpose evaluated are:

1. Submerging the membrane section outside the anaerobic digester in an aerated water bath (as illustrated in Figure 1).
2. Placing the membrane section outside the anaerobic digester in open air.

Reduced nitrogen transfer into the membrane tube and less methane loss from the biogas are advantages of the first option. Low solubility of nitrogen in water decreases the diffusion of nitrogen into the membrane and hence penetration of nitrogen into the digester is kept at a low level. Methane also has low solubility in water and accordingly the amount of methane diffused into the water bath through the membrane tube is low. Therefore most of the methane, diffused from the biogas to the membrane remains inside the membrane tube which leads to a smaller methane concentration gradient between anaerobic digester gas and the membrane tube; so that the methane loss is reduced (compared to results in Table 5).

Nitrogen diffusion into the biogas headspace will be higher and the methane loss from the biogas will be higher in option 2 than the first option. Option 2 is, however an easier and more efficient way to supply the required oxygen, thus the required membrane length outside the AD will be shorter.

3.2 Use of air inside the membrane

Air consists of 78.1 % nitrogen, 20.9 % oxygen, 0.033 % carbon dioxide, and other trace gases including argon. Effect of trace gases such as argon is not considered in the following calculations. Both mass transfer resistances inside and outside of the membrane is considered insignificant, according to argument in Chapter 2.1.2 that gas phase mass transfer resistance is much less than liquid film and membrane resistance. Only the membrane resistance is therefore accounted for in the calculations for this case. The calculated required lengths of the different sizes of membranes for Cases 1 and 2 for both the water and air circulation scenarios are compared in Table 7. Water as circulating fluid requires more than one hundred times larger membrane than air as oxygen supply gas.

Table 7. Comparison of required membrane lengths when water or air is circulated inside the membrane tube

Case		1						2					
Circulating fluid		Water			Air			Water			Air		
Temperature in the reactor & fluid (^{0}C)		23	35	55	23	35	55	23	35	55	23	35	55
L (m)	r_{lm} 1.2 mm	100.66	88.35	77.94	0.30	0.30	0.30	38.20	32.55	29.00	0.11	0.11	0.11
	r_{lm} 1.9 mm	102.12	88.50	78.90	0.37	0.37	0.37	36.25	31.50	28.50	0.14	0.14	0.14
	r_{lm} 4.5 mm	65.73	61.86	58.16	0.16	0.16	0.16	17.60	16.36	16.27	0.06	0.06	0.06

No effect of temperature on the membrane length is noticeable when air is circulated instead of water. Increase in tube diameter reduces the required membrane length, as for the water flow case. A larger effect from membrane thickness on the required membrane length is observed for the air than for the water option. E.g.: The membrane tube having a log mean radius of 1.9 mm and a thickness of 1 mm requires a longer membrane than the 1.2 mm option with a thickness of 0.5 mm.

The estimated gas penetration rates through the membrane for air circulation cases are shown in Table 8. For a fixed amount of oxygen supply; penetration of methane, carbon dioxide and hydrogen sulfide is less compared to when water is used inside the membrane because of the reduced membrane length. It was hypothesized that water was advantageous to avoid loss of methane due to low methane solubility in water, but these calculations refute this hypothesis. Nitrogen, similarly, that has a higher diffusion rate per length through the membrane for the air circulation case, which can be understood based on the water solubility of N_2 and the higher concentration of nitrogen in air, but the overall transfer is less than in the water case. The nitrogen to oxygen ratio supplied (~2) is, thereby, half of the ratio in air (~4), implying another significant advantage compared to directly adding air to headspace.

Back diffusion of gases is minimal for this air circulation case, due to the far shorter membrane length compared to water circulation cases. Hydrogen sulfide diffusion is negligible and methane also has a very low back diffusion, making this option potentially very attractive. The only possible disadvantage of air compared to water circulation is the reduced capability of carbon dioxide removal from biogas.

Table 8. Gas penetration rates (mg/day) with air inside the membrane

Case		1			2		
Circulating fluid		Air			Air		
Temperature in the reactor & fluid		23	35	55	23	35	55
r_{lm} 1.2 mm	O_2	1833	1833	1833	696	696	696
	N_2	3099	3099	3099	1177	1177	1177
	CH_4	130	135	144	51	53	57
	CO_2	686	714	762	243	253	270
	H_2S	11	11	12	0	0	0
r_{lm} 1.9 mm	O_2	1829	1829	1829	700	700	700
	N_2	3094	3094	3094	1184	1184	1184
	CH_4	130	135	144	52	54	57
	CO_2	685	713	760	244	254	271
	H_2S	11	11	12	0	0	0
r_{lm} 4.5 mm	O_2	1829	1829	1829	700	700	700
	N_2	3092	3092	3092	1183	1183	1183
	CH_4	130	135	144	52	54	57
	CO_2	684	713	760	244	254	271
	H_2S	11	11	12	0	0	0

3.3 Membrane aeration vs. direct air purging

Composition of the biogas for the two cases where (i) the reactor is membrane aerated and (ii) the reactor is directly air purged, are presented in Table 9. The following assumptions were made for the calculations.

All the oxygen supplied to the reactor is consumed.

1. Hydrogen sulfide is totally removed from biogas due to oxidation and back diffusion.

Approximately the same amounts of nitrogen gas are diffused into the reactor headspace in the air and water circulation scenario, which is approximately half the amount of nitrogen dilution caused by direct air purging. The membrane aeration techniques suggested here maintain the biogas nitrogen dilution within the limits for vehicle fuel quality as opposed to the direct air injection method for high sulfide situations (Case 1).

Table 9. Calculated composition of biogas before and after aeration by membrane and by air purging (r_{lm}= 4.5 mm)

Description	Case 1 (35^0C)				Case 2 (23^0C)			
	Without aeration	After Membrane Aeration (Water)	After Membrane Aeration (Air)	After Air purging	Without aeration	After Membrane Aeration (Water)	After Membrane Aeration (Air)	After Air purging
Daily biogas production (l/day)	200	200	200	200	960	960	960	960
O_2 (%)	0	0	0	0	0	0	0	0
N_2 (%)	0	1.7	1.4	2.7	0	0.1	0.1	0.2
CH_4 (%)	62.5	78.9	61.7	61.7	65	65.9	64.9	65
H_2S (%)	1.5	0	0	0	0.1	0	0	0
CO_2 (%)	36	19.4	36.8	35.6	34.9	34	36.8	34.8
CH_4/CO_2 Ratio	1.73	4	1.67	1.73	1.86	1.94	1.67	1.86

4. Conclusions

Membrane micro-aeration appears as a sound technique for oxygen supply to AD headspace for in situ aerobic microbial oxidation of hydrogen sulfide in raw biogas. Diffusion through a dense membrane gives the ability of supplying a precise amount of oxygen in a safe manner without mixing air and biogas directly.

Preferential transfer of relevant gasses (Methane, oxygen, hydrogen sulfide, nitrogen and carbon dioxide) for alternative scenarios can be studied and understood based on the mass transfer models presented. The mass transfer analysis conducted here can be utilized to design and evaluate appropriate practical configurations for experimental and on-field anaerobic digesters.

Comparing the use of air and water inside the membrane tube to supply the required oxygen shows that air is the most promising option because it requires little membrane area and cause insignificant loss of methane. The main advantage of using water is that it can remove a considerable fraction of carbon dioxide from the biogas.

The main mass transfer advantage of the proposed membrane micro-aeration technique compared to direct air purging for in-situ sulfide oxidation is the reduced biogas dilution by N2, to a level that is acceptable for vehicle fuel quality, even in the high sulfide case studied.

Nomenclature

J_i	Flow rate of solute i (kg/s)
r_i	Inside radius of membrane tube (m)
r_o	Outside radius of membrane tube (m)
L	Length of the membrane tube (m)
A_{lm}	Log mean area of the membrane (m^2)
$C_{i,in}$	Concentration of solute in water (kg/m^3)
$C_{i,out}$	Concentration of solute in biogas (kg/m^3)
$C_{i,in,eq}$	Equilibrium solute concentration in water side (kg/m^3)
$C_{i,out,eq}$	Equilibrium solute concentration in gas side (kg/m^3)
$C_{i,m,in}$	Concentration of solute in membrane in liquid side (kg/m^3)
$C_{i,m,out}$	Concentration of solute in membrane in gas side (kg/m^3)
$C_{i,liquid}$	Concentration of solute in a liquid (kg/m^3)
$C_{i,gas}$	Concentration of solute in a gas (kg/m^3)
$P_{i,gas}$	Partial pressure of i in the gas (Pa)
$S_{i,liquid}$	Solubility of i in a liquid ($kg/m^3.Pa$)
$D_{i,m}$	Diffusion coefficient for diffusion of solute in membrane (m^2/s)
$S_{i,mle}$	Equilibrium partition coefficient at the liquid membrane interface (-)
$S_{i,mg}$	Equilibrium partition coefficient at the gas membrane interface (-)
$S_{i,mge,in}$	Equilibrium partition coefficient at the gas membrane interface inside the membrane when air is circulated (-)

$S_{i,mge,in}$ Equilibrium partition coefficient at the gas membrane interface outside the membrane when air is circulated (-)
$H_{i,gl}$ Henry's Law constant for solute in gas liquid system (Pa.m^3/mol)
$H_{i,mg}$ Henry's Law constant for solute in gas-membrane system (Pa.m^3/mol)
$H_{i,membrane}$ Henry's Law constant for solute in membrane (Pa.m^3/m
$H_{i,liquid}$ Henry's Law constant for solute in liquid (Pa.m^3/mol)
R Gas constant (Pa.m^3.K^{-1} mol^{-1})
T Temperature (K)
$k_{i,in}$ Mass transfer coefficient water side (m/s)
$k_{i,out}$ Mass transfer coefficientgas side (m/s)
x Distance from entrance (m)
d_h Hydraulic diameter(m)
Re Reynolds number (-)
Sc Schmidt number (-)
Sh Sherwood number (-)
Pe Peclet number (-)
$D_{i,l}$ Diffusion coefficient for diffusion of solute in liquid (m^2/s)
μ Dynamic viscosity of water (Pa.s)
ρ Density of fluid (kg/m^3)
u Velocity of water inside the membrane tube (m/s)
Gr Grashof Number (-)
g Acceleration due to gravity (m/s^2)
β Volumetric thermal expansion coefficient (equal to approximately 1/T, for ideal fluids, where T is absolute temperature)
$D_{i,g}$ Diffusion coefficient for diffusion of solute in gas (m^2/s)
Φ Empirical parameter (For water it is 2.6)
$\widetilde{M}_{H_2O}$ Molecular weight of water (Daltons)
μ_{H_2O} Viscosity of water (Centipoise)
$\widetilde{V}_{gas}$ Molecular volume of gas (cm^3/mol)

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