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Transport properties of CO₂ and CH₄ in hollow fiber membrane contactor for the recovery of biogas from anaerobic membrane bioreactor effluent

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Abstract

A significant amount of methane (CH_4) produced from anaerobic digestions of wastewater is dissolved in liquid effluent and discharged. The recovery of dissolved CH_4 is therefore essential in ensuring an enhanced energy production of the anaerobic processes, and minimizing environmental impacts of the greenhouse gas. In this work, a membrane contactor is employed as a mass transfer equipment for the CH_4 recovery. A mathematical model considering simultaneous desorption of CH_4 and carbon dioxide (CO_2) is developed using a resistance-in-series model to calculate the overall mass transfer coefficients. The simulations were validated with experimental results obtained using an in-house fabricated hollow fiber membrane as well as a real effluent from Anaerobic Membrane Bioreactor (AnMBR) and synthetic effluent made of water saturated with biogas. Results showed that the CO_2 fluxes were higher than those of CH_4 fluxes due to its higher concentration in liquid phase. A decrease of liquid phase mass transfer resistance by an increase in liquid velocity significantly enhanced both CH_4 and CO_2 fluxes. While, an increase in gas velocity slightly affected the CH_4 flux but enhanced the CO_2 flux considerably. It was also found that the CO_2 desorption increased the CH_4 recovery rate. The desorbed CO_2 helped to increase the mass transfer driving force by reducing the partial pressure of CH_4 in the gas side, and enhancing the gas phase mass transfer coefficient to facilitate CH_4 desorption. The increase of liquid velocity increased mole fraction of CH_4 in the gas outlet but decreased the rate of CH_4 recovery. On the other hand, applying vacuum conditions to decrease gas pressure enhanced the rate of CH_4 recovery but lower the CH_4 mole fraction in the product gas.

1. Introduction

Anaerobic membrane bioreactor (AnMBR) is one of the promising technologies for wastewater treatment with biodegradable organic substances. The treatments of several types of wastewater have been successfully tested, both high-strength (food or textile processing wastes) and low-strength wastewater (municipal and domestic wastewater) [1]. Major advantages of AnMBR compared to aerobic treatment processes include better effluent quality and the potential to be a net energy producer by recovering energy from the methane (CH_4) produced [2]. To realize this, membranes for separation of biomass and effluent is instrumental as they allow higher concentrations of biomass in reactors, low sludge production, and high production rate of biogas [1, 3].

In AnMBR, CH_4 is produced by anaerobic digestion of organic matters by a process called methanization and presented in the gas phase as biogas (a gas mixture contains mostly CH_4 and carbon dioxide, CO_2). However, as a liquid phase is involved in the process, there is also a significant amount of CH_4 dissolved in this liquid phase. Liu et al. [4] reported that about 45% of CH_4 produced from anaerobic treatment of a municipal waste water (200 mg/L of Chemical Oxygen Demand, COD, at 303K) is in the dissolved form. The dissolved CH_4 , when discharged from the AnMBR system, is a potential safety hazard given its highly explosive nature. A typical effluent leaving from AnMBR can reach full saturation with 50-75 vol% CH_4 or contains around 11-17 mg of dissolved CH_4 per liter of effluent at 25 °C, which can further increase under a super saturation situation [5]. However, the lower explosion limit (LEL) for CH_4 in air is only 5 vol% which is in equilibrium with 1.1 mg/L of dissolved CH_4 present in the effluent at

atmospheric pressure and 25 °C. Hence, the methane-rich effluent should be treated to reduce dissolved CH₄ concentration to before discharging to the environment or storing in containers to avoid fire hazard environment. In addition, leakage of CH₄ to the atmosphere is undesirable as it is a major greenhouse gas and has a global warming potential 21 times more powerful than CO₂. In this regard, treatment to remove dissolved CH₄ is critical for a carbon neutral process [6].

Dissolved CH₄ in AnMBR effluent can be removed using techniques, such as biological oxidation, aeration, or gas stripping [5]. Methane oxidizing bacteria can be added into the effluent to convert CH₄ to a less dangerous chemical. In the aeration and gas stripping, air can be employed using conventional mass transfer equipment, such as bubble columns or packed towers. Unfortunately, in these techniques, the CH₄ concentration in the gas outlet would be too low for further use. Rather than releasing the CH₄ gas, it is more desirable to feed the dissolved CH₄ back into the process as a potential energy resource to achieve a net energy production of the waste treatment process. Pretel et al [2] showed that the recovery of CH₄ from anaerobic effluent is necessary for AnMBR processes to realize a net energy production. Crone et al [5] published a review article on the significance of dissolved methane in anaerobic effluents and reported that the dissolved methane in effluent could be in a range between 11 to 100 % of the produced methane depending on types of wastewater as well as operation conditions of anaerobic processes. Therefore, recovery of dissolved CH₄ from anaerobic effluent is becoming increasingly compelling for exploiting the energy of the biomass present in the wastewater.

Membrane contactors have demonstrated their potential utility for CH₄ recovery from anaerobic effluent. By employing hydrophobic membranes to create a barrier, membrane contactors enable two phases to contact each other without the dispersion of one phase into the other. This allows both the liquid and gas phases coexist independently without any flooding or foaming issues. In

addition, other advantages of membrane contactors include great versatility in tuning parameters of the liquid and gas phase, high specific surface area as compared to conventional contactors [7], and easy retrofitting to existing anaerobic wastewater treatment plants. Up to date, there are only eight published research articles on using membrane contactors for the recovery of CH₄ from anaerobic effluents. The pioneering work was conducted by Bandara et al. [8] using a hollow fiber membrane module to recover CH₄ from an effluent of upflow anaerobic sludge blanket (UASB) reactor. The average removal efficiency was up to 77% at the dissolved CH₄ concentration of 15 ± 5 mg/L. In the later work of Bandara et al. [9], performances of the hollow fiber membrane contactor were monitored over seven months. They reported that the membrane fouling was insignificant to the CH₄ removal performance during the operation. Luo et al. [10] also used a vacuum membrane contactor to simultaneously remove CO₂ and CH₄ from an effluent of UASB reactor and achieved about 86% of CH₄ removal efficiency. Three research articles were published from Canfield Water Science Institute, UK. In their first work, Cookney et al. [11] employed polydimethylsiloxane (PDMS) dense hollow fiber membrane contactors for the recovery of CH₄ from the effluent of expanded granular sludge blanket (EGSB) reactor that is used for treating sewage wastewater. The results showed that, with 72% CH₄ recovery efficiency achieved, the net electrical output from the waste treatment process increased by 0.043 kWhr/m³. In the second work [12], hollow fiber PDMS and PP membranes were selected for CH₄ recovery from effluents of UASB reactor and anaerobic membrane bioreactor (AnMBR), respectively. They suggested that high organic concentrations of effluents could promote pore wetting of PP membranes and a combination between vacuum and sweep gas was necessary to obtain a high purity CH₄ product gas. In the final work, McLeod et al. [6] investigated a tradeoff phenomenon between CH₄ removal efficiency and purity of CH₄ in the gas outlet of a membrane

contactor under a wide range of gas per liquid (G/L) flow rate ratios. A high purity CH_4 in the gas outlet could be obtained by either increase of liquid velocity or reduction of sweep gas flow rate.

Although extensive studies have been carried out, most of them choose to focus only on single gas desorption which is CH_4 . At present, little is known about the effects of other dissolved gases on the recovery efficiency of CH_4 in a membrane contactor process. CO_2 as a major bulk component of biogas is 40-60 times more soluble in water than CH_4 therefore its effects on the CH_4 recovery should not be neglected. In addition, its desorption could also affect quality of product gas from the membrane contactor. A study on simultaneous CH_4 and CO_2 desorption would be beneficial for addressing this gap and providing a better understanding of the effects of all operating parameters involved. Herein, we embark on the development of a mathematical model for membrane contacting process to estimate the CH_4 recovery from AnMBR effluents. The resistance-in-series model was used to estimated overall mass transfer coefficients for both CH_4 and CO_2 desorption. The model is validated with a lab-scale gas desorption experiment operating in a counter-current mode where the gas and liquid phase flow in the shell and tube side, respectively. An in-house hollow fiber membrane that is surface-modified with fluorinated silica nanoparticles is used to eliminate membrane wetting problem. Effects of operating parameters on process efficiencies and qualities of gas outlet are also discussed.

2. Model development

The main objectives of the developed mathematical model for the membrane contactor are to predict the separation performance of dissolved gases from liquid to gas phases and to

investigate the effect of relevant parameters, such as Henry's constants, gas diffusivities on the mass transfer.

2.1 Gas desorption in membrane contactor

The schematic diagram of the mass transfer for the gas desorption membrane contactor is shown in Fig. 1. The gas which is physically dissolved will be desorbed from the solution into the membrane and diffuse towards the gas phase. Sweeping gases or vacuum condition can be applied on the opposite side of the membrane to trap the desorbed gases and thereby maintain the driving force for mass transfer. The liquid is fed to the lumen side of hollow fiber so that the liquid is forced to fully contact with the membrane surface. The relation between the individual gas, membrane, and liquid phase resistances as well as the overall mass transfer resistances can be expressed in the following resistance-in-series model:

$$\frac{1}{K_{OV,L}} = \frac{d_o}{k_L d_i} + \frac{RT_G H d_o}{k_M d_{ln}} + \frac{RT_G H}{k_G} \quad (1)$$

where K_{OV} (m/s) is the overall mass transfer coefficient based on liquid phase and k_L, k_M and k_G (m/s) are the mass transfer coefficients in the liquid, the membrane and the gas phases, respectively. H is the Henry's constant (kmol/atm.m³) and d_o, d_{ln} , and d_i (m) are the outer, log mean and inside diameter of the membranes, respectively. R is the gas constant (kmol.K/m³.atm) and T_G (K) is the temperature in the gas side. The left side of Eq. 1 represents the total mass transfer resistance (s/m), while the first, second, and third terms on the right hand side of the equation are the mass transfer resistances in the liquid, membrane, and gas phases, respectively. The correlations for calculations of individual mass transfer coefficients are shown in Table 1.

Table 1. Correlations for liquid, gas, and membrane mass transfer coefficients in membrane contactors.

Correlations	Ref.
Liquid side mass transfer: $Sh_{i,L} = \frac{k_{i,L}d_i}{D_{i,L}} = 1.62 \left(\frac{d_i}{L} Re_L Sc_{i,L} \right)^{1/3}$	[13]
Gas side mass transfer: $Sh_{i,G} = \frac{k_{i,G}d_e}{D_{i,G}} = 1.25 \left(\frac{d_e}{L} Re_G \right)^{0.93} Sc_G^{0.33}$	[14]
Membrane mass transfer: $k_{i,M} = \frac{D_{i,eff}\varepsilon_M}{\tau_M\delta_M}$	[15]

where $\frac{1}{D_{i,eff}} = \frac{1}{D_{i,M}} + \frac{1}{D_{i,Kn}}$

i = CH₄ or CO₂

Fig. 1. The schematic diagram of the membrane contactor for CH₄ desorption.

2.2 Mass balance equations

The mass balance of species i leaving and entering the liquid or gas phase of a small segment in the z direction of the membrane contactor (Fig. 2) can be written as:

$$F_{i,G(orL),Z+\Delta Z} = F_{i,G(orL),Z} + N_i n_f \pi d_o \Delta Z \quad (2)$$

where, F_i is the molar flow rate of gas i in the gas phase or dissolved gas i in the liquid phase (kmol/s), N_i and n_f are the flux of component i and number of fiber, respectively. Dividing Eq. (2) by ΔZ and approximating ΔZ to zero result in a differential equation as follows:

$$\frac{dF_{i,G(orL)}}{dz} = n_f \pi d_o N_i \quad (3)$$

The mass transfer flux of a dissolved gas (N_i , kmol/m².s) from the liquid to gas bulk can be expressed using fugacity difference as the driving force as follows:

$$N_i = K_{OV,f} (f_{i,L} - f_{i,G}) \quad (4)$$

where $K_{OV,f}$ is the overall mass transfer coefficient based on fugacity potential (kmol/m².s.atm), $f_{i,L}$ and $f_{i,G}$ are bulk liquid and gas fugacity, respectively (atm). The $f_{i,L}$ and $f_{i,G}$ can be converted to measureable parameters using the following equations:

$$f_{i,L} = C_i \gamma_i / H_i \quad (5)$$

$$f_{i,G} = p_i \varphi_i \quad (6)$$

where γ_i and φ_i are activity and fugacity coefficients, respectively (dimensionless), which are equal to one under the assumption of ideal gas and liquid behaviors. C_i (kmol/m³) and p_i (atm) are concentration and partial pressure of CH₄ or CO₂ in the liquid and gas phases, respectively.

Combining Eq. 5 and 6 into Eq. 4 yield:

$$N_i = K_{OV,f} \left(C_i / H_i - p_i \right) \quad (7)$$

where $K_{OV,f}$ can be regarded as the overall mass transfer coefficient based on the gas phase ($K_{OV,G}$, kmol/m².s.atm) as indicated by the driving force. It can be converted to $K_{OV,L}$ in Eq. 1, where the unit, m/s, is in a more common form by dividing with the Henry's constant and rearranging Eq. 7 give:

$$N_i = K_{OV,L} (C_i - p_i H_i) \quad (8)$$

Two major gases in biogas dissolved in AnMBR effluents are CH₄ and CO₂ and. Based on this information, Eq. 3 for the gas and liquid phases can be written as:

Gas phase

$$\frac{dF_{CH_4,G}}{dZ} = n_f \pi d_o K_{OV,CH_4} (C_{CH_4,L} - H_{CH_4} p_{CH_4}) \quad (9)$$

$$\frac{dF_{CO_2,G}}{dZ} = n_f \pi d_o K_{OV,CO_2} (C_{CO_2,L} - H_{CO_2} p_{CO_2}) \quad (10)$$

Liquid phase

$$\frac{dF_{CH_4,L}}{dZ} = n_f \pi d_o K_{OV,CH_4} (C_{CH_4,L} - H_{CH_4} p_{CH_4}) \quad (11)$$

$$\frac{dF_{CO_2,L}}{dZ} = n_f \pi d_o K_{OV,CO_2} (C_{CO_2,L} - H_{CO_2} p_{CO_2}) \quad (12)$$

C_i as the function of liquid flow rate (L_m , m³/s) and p_i of CH₄ and CO₂ are calculated as follows:

$$p_i = \left(\frac{F_{iG}}{F_{CH_4,G} + F_{CO_2,G} + F_{N_2,G}} \right) P_g \quad (13)$$

$$C_{i,L} = F_{i,L} / L_m \quad (14)$$

Eq. 4-7 are derived based on the following assumptions:

- 1) Ideal gas and liquid behaviors;
- 2) Steady state, isothermal and isobaric conditions in both gas and liquid sides;
- 3) No axial mixing;
- 4) Only physically dissolved gases are transferred to the gas phase.
- 5) Reaction between CO₂ and water is neglected.

In this work, only physically dissolved CO₂ was considered in the modelling. At the room temperature (25 °C), the hydration equilibrium constant of reaction between CO₂ and water is only at 2.6×10^{-3} [16] indicating that almost all of CO₂ in the system is not converted to the carbonic species but remained in a physically dissolved form. Therefore, there was no reaction term present in the liquid phase and an enhancement factor was not included in the calculations of CO₂ mass transfer coefficient. The same assumptions were previously made for a

mathematical modelling study on CO₂ desorption from water in a membrane contactor [17] and an experimental study using a wetted wall column [18] as described in the literature.

Fig. 2. Mass balance of species i in a small segment in the z direction of a hollow fiber.

2.3 Numerical method

Codes for calculations of the above Eq. 9-12 were written using the Visual Basic for Applications function in Microsoft Excel 2016. The membrane fiber is divided into many small elements (ΔZ) along the length of the absorber. The mass balance equations of CH₄ and CO₂ in each element are calculated with their local values of driving forces and overall mass transfer coefficients calculated by the resistance-in-series model (Eq. 1). In this study, the membrane contactor was operated in a counter-current condition and so the shooting method was applied into the simulation for solving problems of unknown boundary values [19]. The simulation started from

the gas inlet where the liquid outlet concentrations required for the calculation of driving force are unknown ($Z=0$). Therefore, the unknowns were guessed initially and the mass balances of each species were computed along the length of membrane module to obtain the calculated gas outlet and liquid inlet concentrations at $Z=L$. The calculated results were compared with actual values and the discrepancies were used to estimate the next guessed liquid outlet concentrations. The calculation was repeated again from $Z=0$ and continued in loops until the difference between the calculated and actual values was lower than 0.1%. For the simultaneous desorption of CH_4 and CO_2 , two loops were required for the two unknown outlet concentration as shown in the computational flow chart (Fig. 3). It should be noted that a simulation of single gas desorption was also conducted before the simulation of simultaneous desorption to obtain a reasonable first guessed value of the outlet dissolved concentration. All the physical properties of the liquid phase (densities, viscosities, and Henry's constants) were calculated using correlations for water in literature (Table 2). The diffusivity of CH_4 in water loaded biogas was obtained from a separate set of experiment (Appendix A), while the diffusivity of CO_2 was selected to best represent all the relevant experimental data. Examples of these physical values are presented in Table 3.

Fig. 3. Computational flow chart adopted in this work.

Table 2. Correlations for physical parameters.

Parameters	Systems	Equations	Ref.
Density (Den_l) (kg/m ³)	Water	$10^3(0.863559 + 1.21494 \times 10^{-3}T_L - 2.5708 \times 10^{-6}T_L^2)$	[20]
	Gas mixtures	$(y_{CH_4}Mw_{CH_4} + y_{CO_2}Mw_{CO_2} + y_{N_2}Mw_{N_2}) \times P_G / (0.080206T_G)$	Ideal gas law
Viscosity (kg/m.s)	Water	$10^{-6}(Den_L \exp(-3.28285 + \frac{456.029}{T_L - 154.576}))$	[20]
	CH ₄	$10^{-6}(0.447304 + 0.03886T_G - 1.1902 \times 10^{-5}T_G^2)$	[21]
	CO ₂	$10^{-6}(0.603234 + 0.051851T_G - 1.0976 \times 10^{-5}T_G^2)$	
	N ₂	$10^{-6}(4.50847 + 0.048209T_G - 1.2976 \times 10^{-5}T_G^2)$	
	Gas mixtures	$Vis_G = \sum_{i=1}^3 \frac{y_i Vis_i}{\sum_{j=1}^3 y_i \phi_{ij}}$ $\phi_{ij} = (Mw_j/Mw_i)^{0.5} \text{ and } \phi_{ji} = 1/\phi_{ij},$	[22]
Gas diffusivity (m ² /s)	CH ₄	$D_{1-mix} = \frac{1}{(y_2' D_{1-2} + y_3' D_{1-3})}$ $y_2' = y_2/(1 - y_1)$ $D_{1-2} = \frac{0.00266T_G^{3/2}}{P_G[(1/Mw_1) + (1/Mw_2)]^{-1}\sigma_{1-2}^2\phi_D}$	[23]
Henry's constant	CH ₄ (bar)	$\ln(H_{CH_4}) = -7.037 + 0.1017T_L - 1.426 \times 10^{-4}T_L^2$ $+ \frac{100}{83.15T_L}P_L \frac{0.338}{83.15}P_L + \frac{2.457 \times 10^{-3}}{2 \times 83.15T_L}P_L^2$ $P_L \text{ in bar}$	[24]
	CO ₂ (kPa.m ³ /kmol)	$H_{CO_2} = 2.8210^6 \exp\left(\frac{-2044}{T_L}\right)$	[25]

1= CH₄, 2 = CO₂, 3 = N₂**Table 3.** Example values of the physical properties of the gas and liquid phase used in the simulations.

Phase	Temp (°C)	Density (kg/m ³)	Viscosity (kg/m.s)	Henry's constant (kmol/atm.m ³)	D_{CH_4} (m ² /s)	D_{CO_2} (m ² /s)
Gas	23.5	1.15	1.767×10^{-5}		2.175×10^{-5} (D _{CH₄-gas mixture})	1.51×10^{-5} (D _{CO₂-gas mixture})
Liquid	23.5	997.74	9.275×10^{-4}	1.422×10^{-3} for CH ₄ -water, 3.531×10^{-2} for CO ₂ -water	1.104×10^{-8} (D _{CH₄-water})	4.72×10^{-9} (D _{CO₂-water})

3. Experimental set up

The effluents used in the gas desorption experiments were obtained from a hollow fiber anaerobic bioreactor pilot plant located at the Ulu Pandan water reclamation plant operated by Public Utilities Board (PUB) of Singapore. The properties of the AnMBR effluent are shown in Table 4. Prior to use, the effluent was bubbled with a simulated biogas (60 vol% CH₄ in balance of CO₂, Singapore Oxygen Air Liquid Pte Ltd) until an equilibrium was reached in a liquid feed tank. The concentration of the dissolved CH₄ was measured by a dissolved CH₄ sensor (Pro-Oceanus Digital Mini CH₄, Pro-Oceanus System Inc, Canada). It uses an infrared-based detector to monitor partial pressure of dissolved CH₄ together with total dissolved gas pressure of the surrounding water which data can be converted to the dissolved gas concentration reported in this work (kmol/m³) using the Henry's constant. The saturation of biogas was confirmed by monitoring the overhead gas concentrations of the feed tank and the dissolved CH₄ concentration. The apparatus for the gas desorption tests using hollow fiber membrane is shown in Fig. 4. During the experiment, the feed solution was delivered to the tube side of the hollow fiber membranes by a liquid digital gear pump (Cole-Parmer, USA) while the nitrogen sweep gas was fed to the shell side of the membrane modules. The counter-current mode of operation was selected for all experiments. The flow rates of nitrogen and the simulated biogas to the liquid tank were controlled by two mass flow controllers (Cole-Parmer, USA). The concentrations of CH₄, CO₂ and N₂ in the gas outlet were monitored by a gas chromatography (Agilent 490 Micro GC biogas analyzer, Agilent Technologies, USA) and the gas inlet and outlet flow rates were measured by a gas flow meter (Bios DefenderTM 530, Drycal USA). The pressure gauges, number one and two, were used to monitor the liquid inlet and outlet pressures, respectively,

while pressure gauges, number three and four, were for the gas inlet and outlet pressures, respectively.

Table 4. Properties of AnMBR effluent used in this work.

Parameters	Parameters
Turbidity (NTU)	23.7
total organic compound (mg/L)	7.3
total nitrogen (mg/L)	36.8

In this study, desorption fluxes (J) of CH_4 and CO_2 used to indicate process efficiency are calculated by the following equation:

$$J = \frac{G(Y_{i,out} - Y_{i,in})}{A_T} \quad (15)$$

where G is the inert gas flow rate (kmol/s), A_T is the mass transfer area calculated from the outer membrane radius (m^2), Y_{out} and Y_{in} are the mole ratios between CH_4 or CO_2 and the inert gas in the gas phase which can be calculated as follows:

$$Y_{\text{CH}_4} = \frac{y_{\text{CH}_4}}{1 - y_{\text{CH}_4} - y_{\text{CO}_2}} \quad (16)$$

$$Y_{\text{CO}_2} = \frac{y_{\text{CO}_2}}{1 - y_{\text{CH}_4} - y_{\text{CO}_2}} \quad (17)$$

where y_{CH_4} and y_{CO_2} are mole fractions of CH_4 and CO_2 in the gas phase, respectively.

The experimental K_{OV} of CH_4 desorption was calculated by the following equation [26]:

$$K_{OV,CH_4} = \frac{G(Y_B - Y_T)}{A_T(C_{CH_4,L} - C_{CH_4,G}^*)_{\log mean}} \quad (18)$$

$$(C_{CH_4,L} - C_{CH_4,G}^*)_{\log mean} = \frac{(C_{CH_4,L} - C_{CH_4,G}^*)_B - (C_{CH_4,L} - C_{CH_4,G}^*)_T}{\ln\left(\frac{(C_{CH_4,L} - C_{CH_4,G}^*)_B}{(C_{CH_4,L} - C_{CH_4,G}^*)_T}\right)} \quad (19)$$

where $C_{CH_4,L}$ and $C_{CH_4,G}^*$ are the CH_4 concentration in the liquid phase and equilibrium concentration in the gas phase, respectively (kmol/m^3). B and T denote bottom (gas outlet) and top (gas inlet) of the membrane module, respectively.

Fig. 4. Experimental set up of a membrane contactor unit for recovery of CH_4 from liquid solutions

3.1 Membranes

Membrane wetting has been a major problem in the membrane contactors processes, preventing their large-scale applications. Therefore, in this work, a highly hydrophobic microporous

membrane made in our lab was employed to prevent this problem. The hollow fiber membrane was fabricated and surface-modified based on our previous work [27]. Briefly, porous polyimide (Matrimid[®], MT) substrate was prepared using a non-solvent induced phase inversion and subsequently fluorinated silica nanoparticles were anchored on the membrane surfaces via a cyclic imide ring-opening reaction. The membrane properties and module specification are summarized in Table 5.

Table 5. In-house hollow fiber membrane properties and module specifications.

Parameters	Values
Fiber o.d./i.d. (μm)	945/670
Pore size (nm)	46.5
Contact angle with water ($^{\circ}$)	121.6
Porosity (%)	66
Number of fiber, n_f	6
Module length (cm)	18.5
Module diameter (cm)	0.62
Membrane area (m^2)	3.3×10^{-3}

4. Results and discussion

4.1 Model validation

Fig. 5 shows the experimental and simulated CH_4 and CO_2 desorption fluxes as a function of liquid velocity from both water and real effluent of AnMBR process. The liquids were fully saturated with a biogas containing 60 vol% of CH_4 in the balance of CO_2 while the utilized sweeping gas flow rate was 20 mL/min. The gas and liquid temperatures were maintained at 23.5 $^{\circ}\text{C}$ during the testing. The process was operated at atmospheric pressure for both gas and liquid sides. Our proposed model (Eq. 9-12) successfully predicts both the CH_4 and CO_2 desorption

fluxes from the synthetic and real effluents. The close agreement between experimental fluxes of the water and real effluent implies that our calculations using physical properties of water can be applied to estimate the desorption fluxes from real effluent of AnMBR (Fig. 5). The results also showed that the CO₂ fluxes were higher than those of CH₄ fluxes in this system. This is due to a higher concentration of CO₂ dissolved in liquid phase compared to CH₄. At 23.5 °C, Henry's constants of CO₂ is much higher than that of CH₄ as shown in Table 3. Therefore, when the solution is saturated with 40 vol% of CO₂ and 60 vol% of CH₄, the dissolved CO₂ and CH₄ concentrations are calculated as 0.014 and 0.00085 mol/L, respectively. The reason is due to water which is a polar molecule allows CO₂ which has a higher polarity compared to CH₄ to be more dissolved. The effect of liquid velocity on the desorption fluxes is also shown in Fig. 5. An increase in liquid velocity reduced the mass transfer resistance, and enhanced both the CH₄ and CO₂ fluxes. This same phenomenon is also found in the study by Cookney et al. [12] for the CH₄ flux. The overall mass transfer coefficients of CH₄ desorption (K_{OV,CH_4}) obtained from this work are compared with those reported from Cookney et al. [12] using a micro porous PP membrane for the recovery of CH₄ as shown in Table 6. The K_{OV,CH_4} are in the same range indicating that the mass transfers are both in a range of liquid phase controlled operation. The higher K_{OV,CH_4} obtained in this work is likely due to the higher range of liquid velocity used in the experiments.

Table 6. Comparison of K_{OV,CH_4} obtained from this work to those reported by Cookney et al. [12]

System	Liquid	
	velocity (m/s)	K_{OV,CH_4} (m/s)
Real effluent	0.19-0.35	$6.72-8.02 \times 10^{-5}$
Water	0.09-0.315	$4.84-7.83 \times 10^{-5}$

The effect of gas flow rate on the desorption fluxes is displayed in Fig. 6. The gas and liquid temperatures were 27 °C and 24 °C, respectively with a liquid flow rate of 20 mL/min (0.16 m/s). An increase in the gas flow rate enhanced the CO₂ flux. However, it seems to have little effect on the CH₄ flux. The percentage contributions of individual mass transfer resistances in the membrane contactor calculated based on the resistance-in-series model (Eq. 1) are summarized in Table 7. The mass transfer resistances in the liquid, membrane, and gas phases were calculated from the first, second and third terms on the right hand side of the resistance-in-series model (Eq. 1), respectively. The G/L flow rate ratio at 0.45 is from our experiments at the gas and liquid flow rates of 20 and 44 ml/min, respectively. The low G/L ratios at 0.1 and 0.01 were also included for the comparison since it could provide higher CH₄ purities in the product gas [6]. As shown, the liquid phase is the main mass transfer resistance for both the CH₄ and CO₂ desorption. This is due to the much smaller gas diffusivities in the liquid phase than in the gas phase as shown in Table 3. The percentage contributions of the gas phase mass transfer resistance (% R_g) for the CO₂ desorption are higher than those for CH₄. This indicates that the changes in the operating parameters of the gas phase have a stronger effect on the CO₂ desorption than the CH₄ desorption. Such higher % R_g for the CO₂ desorption is due to the higher value of its Henry's constant as compared to CH₄ (Table 3). A higher CO₂ concentration can be then found at the gas-liquid interface. As a result, a larger CO₂ concentration gradient exists between the gas-liquid interface and the bulk of the sweeping gas. This increases the contribution of the gas phase resistance to the overall mass transfer coefficient. Sherwood numbers for the CH₄ desorption of gas and liquid phases calculated from the correlations in

Table 1 at G/L ratio of 0.45 are 0.05 and 6.87, respectively. The Sherwood number is a ratio between the rate of convective mass transfer to the rate of gas diffusion. Therefore, it indicates that the diffusion and convection mass transfers are the main mechanisms in the gas and liquid phases, respectively. This corresponds with the experimental results that showed a strong dependency of CH₄ and CO₂ fluxes with the liquid velocity but a weaker correlation to the gas flow rate.

Table 7. The percentage contributions of the respective mass transfer resistances in the membrane contactor.

Phase	G/L = 0.45		G/L = 0.1		G/L = 0.01	
	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
% R _l	99.27	88.33	98.81	82.16	97.46	68.15
% R _m	0.0064	0.146	0.011	0.224	0.022	0.4
% R _g	0.71	11.52	1.18	17.62	2.5	31.46

Gas flow rate was fixed at 20 ml/min and the liquid flow rate was varied to obtain the reported G/L flow rate ratio.

Fig. 5. Experimental and simulated CH₄ and CO₂ desorption fluxes from a real effluent of AnMBR process and water as a function of the liquid velocity. **The sweeping gas flow rate was fixed at 20 mL/min.**

Fig. 6. Effect of gas flow rate on the simulated and experimental CH₄ and CO₂ fluxes from effluent of AnMBR. The liquid flow rate was fixed at 20 mL/min.

4.2 Effect of CO₂ desorption on the CH₄ recovery

To get more insights into the effects of CO₂ desorption on the CH₄ recovery, the validated mathematical model was used to predict the concentration profiles and the CH₄ recovery of the membrane contactor treating the AnMBR effluent saturated with a biogas contains 60 vol% CH₄ in balance of CO₂ in a real-scale operation. The effluent flow rate was set at 1.39 L/min (2 m³/day). The number of fibers are fixed at 650 while the module length, and module diameter are specified at 0.7 and 0.065 m, respectively (to give a total membrane area of 1.33 m²). This number of fibers was selected in order to obtain a liquid velocity of 0.1 m/s which is within the range of our experimental model validation. In addition, the Gratez numbers ($Gz, v_L d_i^2 / D_{i-water} L$) at 4.43 and 11.42 for the CH₄ and CO₂ desorptions, respectively, are within the range for accurate prediction of the liquid phase mass transfer coefficients ($k_{i,L}$) [13], which is a major mass transfer coefficient in this process. The low G/L flow rate ratio is selected and the gas flow rate (pure N₂) is set at 20 mL/min to obtain a high CH₄ composition in the gas outlet and to give a clear effect of simultaneous desorption of the two gases. The operating gas and liquid pressures were set at atmospheric pressure. At this simulation condition and using the sweep gas mode, the CH₄ removal efficiency obtained is 65%. However, higher removal efficiencies can be achieved by applying vacuum conditions in the gas phase, which its effect will be discussed in detail in section 4.3.

The gas phase concentration profiles of CH_4 and CO_2 of the membrane contactor are displayed in Fig. 7. The arrows indicate the direction of the gas flows. The x-axis is a dimensionless length of the membrane contactor from the simulation starting point to the endpoint in which the gas inlet and liquid outlet are at $Z=0$ and the gas outlet and liquid inlet are at $Z=L$. The CO_2 concentration profile shows that a large portion of CO_2 is quickly transferred to the gas phase and the CO_2 concentration profile in the gas phase almost reaches the equilibrium with its dissolved concentration in the liquid phase due to a higher mass transfer driving force as explained in the previous section. However, after that, the CO_2 mass transfer did not stop completely as can be seen from the slight changes in the concentration profile (Fig. 7). This is because the desorbed CH_4 reduces the CO_2 concentration in the gas phase as it is continuously transferred into the gas phase along the module length. In the same way, the CH_4 mass transfer is also favored by the CO_2 desorption.

Fig. 7. Concentration profile of CH₄ and CO₂ in the gas phase of a membrane contactor. The liquid velocity is at 0.1 m/s and saturated with biogas contains 60 vol% CH₄ in balance with CO₂. The number of fiber, module length, and module diameter are at 650, 0.7 and 0.065 m, respectively

Fig. 8. Concentration profiles of dissolved CH₄ in liquid phase from the simulations with and without CO₂ desorption. The simulations were performed at the same conditions, except that Eq. 10 and 12 were not included in the simulation for the case of without CO₂ desorption. The operating gas and liquid pressure are 1 atm.

Fig. 8 shows the simulated profile of dissolved CH₄ molar flow rate (kmol/s) in the liquid phase ($F_{CH_4,L}$) with and without CO₂ desorption. The simulation conditions of both cases are similar to those in Fig. 6, except that the mass balance of CO₂ desorption (Eq. 10 and 12) was not included in the simulation for the case of without CO₂ desorption. From Fig. 8, it is clear that the

dissolved CH₄ molar flow rate as well as the CH₄ concentrations ($F_{i,L}/L_m$) along the length of module were lower for the model with CO₂ desorption as compared to the one without CO₂ desorption. This is because more dissolved CH₄ can be transferred to the gas phase with a simultaneous desorption of CO₂. Without CO₂ desorption, the percentage of CH₄ recovery is only 50.5 % while it increases to 65% with CO₂ desorption. The desorbed CO₂ into the gas phase will lower the gas phase partial pressure of CH₄ as it increases the total gas molar flow rate (Eq. 13). Hence, driving force for mass transfer increases. In addition, the increase of total gas molar flow rate from the simultaneous CH₄ and CO₂ desorption will result in a significant increase in gas phase mass transfer coefficient of CH₄ ($k_{CH_4,G}$) along the module length as shown in Fig. 9.

Fig. 9. Total gas flow rate and gas phase mass transfer coefficient along the length of a membrane module. The operating gas and liquid pressures are 1 atm.

The effect of composition of biogas that determines dissolved CO_2 and CH_4 concentrations in the liquid phase on the CH_4 recovery performance is shown in Fig. 10. The membrane length (L) represents the length of membrane module required to remove 65% of the CH_4 from the liquid phase that is saturated with biogas comprising of CH_4 and CO_2 in the ratio illustrated in the x-axis. The operating gas and liquid pressures are set at 1 atm. The number of fiber, and module diameter are fixed at 650 and 0.065 m, respectively. The membrane contactor is operated in the sweep gas mode which both gas and liquid phases are at the atmospheric pressure. It can be seen that the increase in membrane length is not linear to the increase of CH_4 mole fraction in the biogas. The required membrane length increases to 16.67 % when CH_4 mole fraction in biogas increases from 0.3 to 0.45. However, when the CH_4 mole fraction increased from 0.45 to 0.6, it would require an increase of 18.57% in membrane length to achieve the same removal efficiency. This is because a higher dissolved CO_2 concentration in the liquid phase is present when the solution is saturated with a biogas of low CH_4 mole fraction. With more dissolved CO_2 , a higher CO_2 desorption can facilitate the CH_4 desorption by increasing the driving force for CH_4 mass transfer. However as expected, the CH_4 mole fraction of the gas outlet from the membrane contactor was decreased and the CO_2 mole fraction was increased with the reduction of CH_4 mole fraction in the biogas.

Fig. 10. Effects of biogas composition on the height of membrane modules required to remove 65% of CH_4 in the liquid phase and CH_4 , and CO_2 mole fractions in the gas outlet. The liquid flow rate is $2 \text{ m}^3/\text{day}$ (1.39 L/min), gas and liquid operating pressure are 1 atm.

4.3 Effects of operating parameters on the CH_4 recovery and the quality of gas outlets.

In this section, the same operating parameters (except studied parameter), membrane area, and module size of the membrane contactor as the previous section are used in the simulation to investigate the effects of operating parameters on the process performance in the terms of the CH_4 removal efficiency from the liquid effluent and CH_4 and CO_2 mole fractions in the gas outlet from the membrane contactor. The effect of liquid velocity on these parameters is shown in Fig. 11. Even though the increase in liquid velocity can increase both CH_4 and CO_2 fluxes as mentioned in the section 4.1, it reduces the CH_4 recovery efficiency. This is because the increase in liquid velocity also increases the initial CH_4 molar flow rate (kmol/s) entering the system.

Therefore, even with an increase of mass transfer rate which increases the CH_4 desorption, the higher resultant CH_4 molar flow rate correspondingly cause a decrease in the percentage of CH_4 removal. This result agrees with an experimental study performed by McLeod et al [7]. The increase of CH_4 concentration in the gas outlet with liquid velocity can also be observed from Fig. 11. The CH_4 desorption is controlled by the liquid phase resistance as previously discussed in the section 4.1. Therefore, the increase in liquid velocity can significantly enhance the CH_4 mole fraction in the gas outlet. However, increase in liquid velocity only slightly increase the CO_2 mole fraction in the gas outlet. As previously discussed in Fig.7, the CO_2 desorption is limited at the early stage of the membrane contactor due to an equilibrium concentration between two phase. Therefore, although the increase of liquid velocity can increase the CO_2 mass transfer rate, the impact on the gas outlet CO_2 mole fraction was insignificant since it is almost in equilibrium with the dissolved CO_2 concentration.

Fig. 11. Effect of liquid velocity on the percentage of CH₄ recovery from effluent and CH₄ mole fraction in the gas outlet of the membrane contactor.

The effect of gas velocity was investigated in this section by varying the packing density of membrane module. The increase in gas velocity with the packing density is achieved by decreasing the volume of the shell side of the membrane module. This parameter is selected, as opposed to a direct change in the gas flow rate, so that the compositions of the gas outlet from the membrane contactor is not be influenced by the additional gas inlet. Both operating gas and liquid pressures were set at 1 atm. Fig. 12 reveals that the increase of packing density slightly increase the rate of CH₄ recovery. This was expected since the investigation of resistance-in-series model (Table 7) shows that the gas phase resistance had a minor impact to this process and both CH₄ and CO₂ mass transfers are controlled by the resistance in the liquid phase. Therefore, the increase in gas velocity that reduce mass transfer resistance in the gas phase only causes a

small change in the rate of CH₄ recovery. Furthermore, the increase in gas velocity with the packing density would favor CO₂ desorption more than the CH₄ because the mass transfer resistance in the gas phase of CO₂ desorption had more impact on the overall mass transfer resistance. The CH₄ mole fraction in the gas outlet changes only 0.5% while the CO₂ mole fraction increased 2.1% when the packing density increases from 0.05-0.4.

Fig. 12. Effect of packing density on the percentage of CH₄ recovery from effluent and CH₄ mole fraction in the gas outlet of the membrane contactor.

Fig. 13 presents the effect of gas pressure on the CH₄ recovery efficiency and the concentration of CH₄ and CO₂ in the gas outlet. The operating liquid pressures was set at 1 atm. The decrease in gas pressure would increase the driving forces for CH₄ and CO₂ transports and thereby result in an increase in the CH₄ recovery efficiency. However, at the same time, it reduces the CH₄ concentration in the gas phase, even though the mass transfer driving forces increases for both gases in the same ratio. This can be explained by the concentration profiles as shown in Fig. 7.

As observed, the mass transfer of CO_2 is limited at an early stage of the membrane module as the CO_2 concentration in the gas phase is at equilibrium with its dissolved concentration in the solution. On the contrary, CH_4 can be continuously desorbed throughout the module. The decrease in gas pressure would lower the equilibrium concentration of CO_2 in the gas phase, thus more CO_2 can be desorbed to reduce the CH_4 concentration in the gas phase.

Fig. 13. Effect of pressure in the gas side of the membrane contactor on the percentage of CH_4 recovery from effluent and CH_4 mole fraction in the gas outlet of the membrane contactor

4.4 Effect of vacuum condition on the process performance.

Fig. 14 shows the effect of gas pressure on the required height of a membrane module for removal of 65% CH_4 from the effluent. Unlike the simulations in section 4.3, only vacuum conditions are applied to the shell side of the module so that the gas outlet contains only CH_4 and

CO₂. The liquid flow rate is fixed at 1.39 L/min (2 m³/day) and the solution is saturated with 60 vol% CH₄ biogas. Number of fiber and packing density are 650 and 0.14, respectively while the gas and liquid temperature is maintained at 25 °C and the operating liquid pressure is at 1 atm. The result shows an exponential decrease in the required membrane height with a reduction of shell side pressure. This is because the CO₂ flux is low at high gas pressure (or low vacuum conditions). Thus, the shell side contains high concentration of CH₄ and this results in a low mass transfer driving force for the CH₄ desorption. In addition, the CH₄ concentrations in the shell side along the length of membrane module are almost at its equilibrium concentrations. Therefore, a large membrane area is required to remove the dissolved CH₄ when the driving force is small. The decrease of gas pressure will significantly increase the CO₂ desorption, lower the partial pressure of CH₄ in the gas phase and result in an increase in the CH₄ recovery efficiency.

Fig. 14. Effect of gas pressure on the height of membrane contactor required to remove 95% of CH₄ from effluent.

5. Conclusion

A mathematical model of the membrane contactor was developed to investigate simultaneous desorption of CH₄ and CO₂ from effluent of AnMBR process. The predicted desorption fluxes were validated with experimental data operating at different gas and liquid velocities. The experimental and calculation results showed that the liquid phase is the main mass transfer resistance for both CO₂ and CH₄ desorption. However, the change in gas velocity influenced the CO₂ flux significantly but created relatively little impact on CH₄ flux. The study of concentration profiles also revealed that CO₂ desorption improves CH₄ recovery performance. The CH₄ desorption was increased in the presence of CO₂ desorption as the desorbed CO₂ could reduce its partial pressure in the gas phase. This in turn increased the gas phase mass transfer coefficient of CH₄ by increasing the gas flow rate. The effects of operating parameters on the CH₄ recovery efficiency and mole fraction of CH₄ in the gas outlet were also studied. The increase of liquid velocity increased the mole fraction of CH₄ in the gas outlet, but decreased the percentage of CH₄ recovery. While the gas pressure had a strong effect on the performance of membrane contactor, an increase in gas flow rate by increasing packing density of the membrane module increased the percentage of CH₄ recovery only to a small extent.

Appendix A Diffusivity of CH₄ in biogas saturated solution.

In this work, the diffusivity of CH₄ in solutions saturated with biogas contains 60 vol%CH₄ in the balance of CO₂ was obtained from the gas desorption experiment in membrane contactor. It can be seen from experimental results reported in section 4.1 that the gas phase mass transfer resistance did not influence the CH₄ flux and its overall mass transfer coefficient was significantly changed with liquid velocity. Therefore, it can be said that the overall mass transfer coefficient is nearly same as to the liquid mass transfer coefficient and can be written as only the function of liquid velocity as follows:

$$K_{OV} \approx k_L = \left(\frac{D_{CH_4,L}}{d_i} \right) 1.62 \left(\frac{d_i}{Z} ReSc \right)^{1/3} = D_{CH_4,L}^{2/3} \left(\frac{1.62}{Z^{1/3} d_i^{1/3}} \right) V_L^{1/3} \quad (A1)$$

By plotting between K_{OV} and $\left(\frac{1.62}{Z^{1/3} d_i^{1/3}} \right) V_L^{1/3}$, the $D_{CH_4,L}$ can be obtained from the slope as show in figure A.1. It should be note that the experimental results in this part were not the same set as in section 4.1. The membrane module comprised only one hollow fiber, the membrane length was 24 cm. and module diameter was 0.76 cm.

Figure A1. $D_{CH_4,L}^{2/3}$ as the slope between K_{OV} and $\left(\frac{1.62}{Z^{1/3}d_i^{1/3}}\right)V_L^{1/3}$

Nomenclature

A_T	Membrane mass transfer area (m ²)
C_i	Concentration of gas i dissolved in liquid phase (kmol/m ³)
COD	Chemical Oxygen Demand (mg/L)
Den	Density (kg/m ³)
$D_{G,eff}$	Effective gas diffusion coefficient in membrane pores (m ² /s)
D_i	Diffusion coefficient of gas i (m ² /s)

D_{Kn}	Knudsen diffusion coefficient (m ² /s)
D_M	Molecular diffusion coefficient (m ² /s)
F_i	Molar gas flow rate (kmol/s)
f_i	Fugacity (atm)
G	Inert gas flow rate (N ₂) (kmol/s)
d_e	Hydraulic diameter ($n_f \left(d_o / d_m \right)^2$, m)
d_i	Inside membrane diameter (m)
d_{ln}	Log mean membrane diameter (m)
d_m	Membrane module diameter (m)
d_o	Outside membrane diameter (m)
H	Henry's constant (kmol/m ³ .atm)
J	Experimental desorption flux (kmol/m ² .atm)
k_G	Gas phase mass transfer coefficient (m/s)
k_L	Liquid phase mass transfer coefficient (m/s)
k_M	Membrane phase mass transfer coefficient (m/s)
$K_{OV,f}$	Overall mass transfer coefficient based on fugacity potential (kmol/m ² .s.atm)

$K_{OV,L}$	Overall mass transfer coefficient based on liquid phase(m/s)
M_w	Molecular weight (g/mol)
LEL	Lower explosion limit
L	Length of hollow fiber membrane (m)
L_m	Liquid flow rate (m ³ /s)
N_i	Desorption flux (kmol/m ² .s)
n_f	Number of fiber (dimensionless)
P	Pressure (atm)
p_i	Partial pressure of gas i (m)
R	Gas constant (kmol.K/m ³ .atm)
R_g, R_L and R_M	Mass transfer resistances in gas, liquid, membrane phases, respectively (s/m ²)
Re	Reynold number (dimensionless)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
T	Temperature (K)
V_G and V_L	Gas and liquid velocities, respectively (m/s)

Y_i Mole ration between gas i and inert gas (dimensionless)

y_i Mole fraction of gas i in gas phase (dimensionless)

Z Distance along membrane length (m)

Greek letters

ε_M Membrane porosity (dimensionless)

τ_M Tortuosity (dimensionless)

δ_M Thickness of membrane (m)

ϕ Polar correction term for the viscosity (dimensionless)

σ Collision diameter (A °)

ϕ_D Collision integral for diffusion (dimensionless)

γ_i Activity coefficient (dimensionless)

φ_i Fugacity coefficients (dimensionless)

Subscript

B Bottom of a membrane module

G Gas phase

<i>i</i>	CH ₄ or CO ₂
<i>L</i>	Liquid phase
<i>M</i>	Membrane phase
<i>T</i>	Top of a membrane module
<i>tot</i>	Total gas flow rate

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