Hollow fiber membrane contactors for dissolved methane recovery from anaerobic reactor effluents

Godakooru Sethunga Mudiyanseilage Dilhara Prebhashwari Sethunga

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**HOLLOW FIBER MEMBRANE CONTACTORS FOR
DISSOLVED METHANE RECOVERY FROM ANAEROBIC
REACTOR EFFLUENTS**

G.S.M. DILHARA P. SETHUNGA
Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute
Singapore Membrane Technology Center

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G.S.M. DILHARA P. SETHUNGA 2019

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A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

27th June 2019

Date

Godakooru Sethunga Mudiyansele

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27th June 2019

Date

Asst./Prof. Bae Tae-Hyun

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 3 is published as Sethunga, G.S.M.D.P., Rongwong, W., Wang, R., & Bae, T. H., Optimization of hydrophobic modification parameters of microporous polyvinylidene fluoride hollow-fiber membrane for biogas recovery from anaerobic membrane bioreactor effluent, *Journal of Membrane Science*, 548 (2018) 510-518. DOI: <https://doi.org/10.1016/j.memsci.2017.11.059>

The contributions of the co-authors are as follows:

- A/Prof T-H Bae provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr W. Rongwong, Prof. Wang Rong and A/Prof T-H Bae
- I designed the study and performed all the laboratory work at the Singapore Membrane Technology center. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing.
- Dr. W. Rongwong helped me to collect anaerobic effluents from the Singapore Public Utility Board facility.

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- A/Prof T-H Bae provided the initial project direction and edited the manuscript drafts.
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- I performed all the membrane fabrication, modification, and testing in the set-up.

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- [2] **Sethunga, G. S. M. D. P.**, Karahan, H. E., Wang, R., & Bae, T. H., PDMS-coated porous PVDF hollow fiber membranes for efficient recovery of dissolved biomethane from anaerobic effluents. **J Membr Sci**. 584(2019) 333-342.

- [3] **Sethunga, G. S. M. D. P.**, Jaewoo Lee, Wang, R., & Bae, T. H., The influence of membrane characteristics and operating parameters on the performance of a membrane contactor for recovering dissolved methane from anaerobic effluents; **J Membr Sci**. 589(2019) 117263.

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LIST OF ABBREVIATIONS

AFM	atomic force microscope
AGMD	air gap membrane distillation
AnMBR	anaerobic membrane bioreactor
ATR	attenuated total reflection
BFM	bubble flow meter
BM	bulk modified
CEP	critical entry pressure
COD	chemical oxygen demand
D-CH ₄	dissolved methane
DHS	down-flow hanging sponge reactor
DLS	dynamic light scattering
DOE	degree of freedom
DSMD	direct contact membrane distillation
EDS	energy dispersive X-ray spectroscopy
EEM-FS	emission-excitation matrix fluorescence spectroscopy
EGSB	expanded granular sludge bed reactor
EPS	extra cellulose polymeric substances
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared spectrophotometer
GHG	green-house gas
G-L MC	gas-liquid membrane contactors

GWP	global warming potential
HOGV	hand operated gate valve
HRT	hydraulic retention time
LC-OCD	liquid chromatography-organic carbon detection
LEP	liquid entry pressure
LM	lumen modified
MCRy	membrane crystallization
MD	membrane distillation
ME	membrane emulsification
MFC	mass flow controller
MicrobFC	microbial fuel cell
Micro-GC	micro gas chromatography
MPTC	membrane phase transfer catalysis
MWCO	molecular weight cut-off
NIPS	non-solvent induced phase separation
OA	orthogonal array
OMD	Osmotic membrane distillation
PDMS	Polydimethylsiloxane
PFPE	polyfluoropolyether
PT	pressure transducer
PTC	phase transfer catalysis
PVDF	poly vinylidene difluoride
PWP	pure water permeability
S/N	signal to noise

SGMD	sweep gas membrane distillation
SSP	surface streaming potential
TN	total nitrogen
TOC	total organic carbon
UASB	up-flow anaerobic sludge blanket
VMD	vacuum membrane distillation
WCA	water contact angle

NOMENCLATURE

Δ	difference
A_T	membrane mass transfer area (m^2)
C	species concentration (mol m^{-3})
d	membrane diameter
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
G	gas flowrate ($\text{m}^3 \text{s}^{-1}$)
H	dimensionless henry constant
J	CH_4 recovery flux ($\text{mol m}^{-2} \text{s}^{-1}$)
K	overall Mass Transfer Coefficient (m s^{-1})
k	individual mass transfer coefficients (m s^{-1})
L	liquid flowrate ($\text{m}^3 \text{s}^{-1}$)
N	number of
P	pressure (Pa)
RE	the percentage recovery of the gases (%)
u	liquid velocity (m s^{-1})
Z	effective module length (m)

Subscripts

a	constant
b	constant
E	energy per 1 m^3 effluent treated (MJ m^{-3})
f	fibers
G	gas phase
GP	gas blower
i	in
in	fluid inlet
L	liquid phase
lm	log-mean value
LP	liquid pump
M	membrane

motor	motor
MT	micro-turbine
o	out
OL	overall value
out	fluid outlet
Pump	pump
ts	transmission system

Superscripts

d	dense
P	porous
Water	water

Greek letters

Δ	difference
α	constant
δ	membrane thickness (m)
ε	porosity
η	efficiency
μ	dynamic viscosity (Pa s)
τ	membrane tortuosity
ω	heating value (J mol ⁻¹)

SUMMARY

Methane dissolution and lost in the liquid effluent during anaerobic digestion of wastewater causes not only substantial environmental and safety complications but also a hurdle in process intensification. In this context, gas-liquid membrane contactors deem to be a promising alternative over conventional degassing devices owing to its attractive features, especially the higher achievable overall productivity and the potential cost reduction during operation. Yet, membrane degassing contactor technology shows sluggish development on the way to commercialization due to membrane wetting and fouling during prolonged operation. Besides, the shortage of the available number of studies to mitigate simultaneous wetting and fouling in membranes plus the knowledge gap to firmly understand the process parameters that affect the overall productivity and net energy production hinders the effective utilization of membrane contactors in the recovery of dissolved methane. Thus, this work aims at contributing fundamental knowledge of efficient recovery of dissolved methane from anaerobic effluents by developing better performing membranes to overcome both wetting and fouling.

As the basic approach to understanding the behavior of membrane contactors in methane recovery, a highly porous polyvinylidene fluoride (PVDF) membrane (~83%) was hydrophobically modified using amphiphilic block copolymer (Fluorolink S10). The contact angle of the PVDF membrane was improved by 32% after the surface modification. This membrane showed better methane recovery performance than the commercial polypropylene (PP) degassing membrane and a very stable flux without pore wetting during 10 days of operation with synthetic effluent. In addition, the membrane prepared in this study could be operated without significant fouling (7% flux drop during 8 days of

operation) with real anaerobic membrane bioreactor (AnMBR) effluent. Even though higher hydrophobicity can effectively restrict membrane wetting, the water vapor passage due to the capillary effect on the membrane surface is unavoidable.

Thus, in the next study, it was suggested to incorporate a thin dense film (polydimethylsiloxane (PDMS)), which is highly permeable to gas but can avoid water penetration on the porous membrane mass transfer boundary. Despite their denser skin layers, the modified membranes demonstrated superior dissolved CH₄ recovery flux. The long-term performance tests performed using actual anaerobic effluents suggested that the PDMS coating did not accelerate fouling, such that the lumen-modified membranes showed an almost steady flux for 8 days with an anaerobic membrane bioreactor effluent. A high-strength effluent, obtained from an up-flow anaerobic sludge blanket reactor (UASB), induced faster fouling. However, ~25% flux decline was observed in a 10-day operation.

To tackle the fouling issue, in the subsequent study two PDMS-based amphiphilic copolymers with short (147 Da) and long (~1.57 kDa) side chains were incorporated on previously developed thin composite layer. Both types of post-treated membranes exhibited an improved performance when tested against not only a low-strength effluent but also a high-strength effluent from UASB. The membrane treated with the short-side-chain copolymer could sustain 7 days of continuous operation with UASB effluent with a performance loss of < ~10%. It was observed that the fouling layer compositions of the post-treated membranes were less abundant in organic and cellular components, which can be easily clean with water.

Not limiting to that, to the best of my knowledge, no studies have comprehensively investigated the synergistic effect of membranes' physicochemical characteristics and

various operating parameters on biogas recovery encompassing a wide range of variables such as hydrophobicity, pore size, porosity, several physical characteristics (e.g., inner diameter, membrane area, and module length) of hollow fibers, and operating parameters (e.g., liquid flow rate). Also evident is the lack of theoretical guidance for the enhancement of CH₄ recovery in this area. In this regard, I was motivated to analyze the CH₄ recovery performance of the three membranes as mentioned above types (i.e porous, non-porous, and composite membranes) under various operating conditions along with theoretical studies to provide criteria for achieving the optimal CH₄ recovery efficiency. Moreover, the electrical power generation from recovered biogas is of the highest importance and rarely reported in the literature. In this thesis, I also have demonstrated the energy efficiency of the MC-based CH₄ recovery process based on the best membrane, which is promising for industrial practices.

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1 GENERAL BACKGROUND and THESIS OVERVIEW

1.1 Water-energy nexus and environmental sustainability

Escalating demands for water and energy as a consequence of expanding the population, burgeoning economies, changing consumption patterns and dynamic lifestyles result in a depletion of resources to humankind [1, 2]. Almost 10% of the global freshwater withdrawals are accounted for the utilization in the energy sector for primary energy production plus power generation [3, 4]. At any type of energy production process (*i.e.*, hydro-power generation, power plant cooling, refineries, production of biofuels), water is heavily used [4, 5]. Likewise, ~4% of the global electricity supply is used for the extraction, treatment, collection, and distribution of both water and wastewater [3, 4]. Thus, “water” and “energy” demand are strongly intertwined. Accordingly, the interdependence of water and energy leads to the notion of “water-energy nexus” (**Figure 1.1**)

Apart from the depletion of natural water and energy resources, the damage caused by the environmental emissions put an extra burden to the environment (including and beyond the global warming). Currently, over 35% of municipal wastewater directly goes to the environment without treatment, which causes severe complications for the health of the environment as well as humankind [4]. One reason behind this picture is the fact that wastewater treatment processes are often energy consuming [6]. However, on the flip side, wastewater holds a promise to serve as an energy resource, including methane (CH₄) production [7]. Thus, the wastewater treatment processes have a central role in water-energy nexus.

Wastewater treatment processes take up ~1% of the global energy consumption, and almost 9% of global environmental CH₄ emissions arise from the wastewater treatment-related activities, which include collection, treatment, and discharge [4, 8]. Moreover, the secondary wastewater treatment processes (that involve the biological processes) require a tremendous amount of energy due to aeration and filtration steps mainly. As a result, we need to enhance the energy-efficient and eco-friendliness of wastewater treatment processes urgently.

Figure 1.1 The conceptual illustration of the “water-energy nexus.” (Note that water-energy nexus is also closely related to the environment, forming an even bigger web of interactions often called water-energy-environment nexus.)

1.2 The biological wastewater treatment process

1.2.1 Aerobic versus anaerobic treatments

Biological wastewater treatment processes are often advantageous over the conventional physical and chemical treatment methods in terms of operational costs, secondary pollution levels, and set up footprints [7]. In biological processes, either aerobic or anaerobic microorganisms degrade the organic matter in wastewater, thereby producing sludge and gases as by-products. In aerobic digestion, the aerobic bacteria oxidize the biodegradable substances and produce sludge along with carbon dioxide (CO_2) with high efficiency. In contrast, the anaerobic microorganism slowly consumes more complex organic substances producing biogas and sludge as by-products inside well-controlled environments (**Figure 1.2**). However, due to the stringent emission standards and the possibility of resource recovery, anaerobic digestion technology is under extensive study. **Table 1.1** provides a summarized comparison between two digestion processes.

Figure 1.2 Anaerobic digestion process

Table 1.1 Aerobic vs anaerobic digestion [7, 9, 10]

Parameter	Aerobic digestion	Anaerobic digestion
By-products	CO ₂ , water, excess biomass	Methane (CH ₄), CO ₂ , excess biomass
Start-up time	2-4 weeks	2-4 months
Degradation rate	Fast	slow
Sludge yield	High	low
Post treatments	Direct discharge or disinfection	Downstream aerobic treatment
Footprint	Large	Small and compact
Capital expenditure	High	Low
Odor	Low	High
Nutrient requirement	High	Low
Effluent quality	High	Low
Example technologies	Activated sludge process, Membrane bioreactors, tricking filters, fixed-film processes, etc.	Up-flow anaerobic sludge blanket reactor (UASB), Anaerobic membrane bioreactor (AnMBR), Expanded granular sludge bed reactor (EGSB), etc.
Greenhouse gas emission	High	Low

In agreement with **Table 1.1**, the anaerobic process is less attractive over the aerobic process, yet the energy recovery potential, low cost, and compactness outweigh the former than the latter. The biogas, as the byproduct of anaerobic digestion plus an excellent source of bioenergy, plays a critical role in the renewable energy market. Biogas can be used as a fuel for vehicles, boiler (and stoves), engines (and turbines) for producing electricity and fuel cells [11]. Although, the biogas can be used as the raw form some impurities in the such as H₂S, CO and NH₃ create unfavorable consequences in the downstream utilization

(*i.e.* human health impacts, corrosive nature, lower heating quality, *etc.*) causing additional maintenance costs. Thus, biogas upgrading is of broad and current interest.

1.2.2 Biogas upgrading and CO₂ reuse

Biogas can be upgraded *via* either removal or utilization of CO₂. According to the market analysis of those biogas upgrading technologies (*via* CO₂ removal) by Bauer *et al.* [12], water scrubbing dominates the market with a share of 40%. Pressure swing absorption and ammine absorption have quite a competitive market share of 23% and 22%, respectively, while membrane separation possesses 8%. Cryogenic separation (market share < 0.5%) is the most underutilized technique due probably due to the technology is still under development [13]. **Table 1.2** shows the available biogas upgrading technologies with obtainable CH₄ purity, CH₄ loss, and process efficiency. Most importantly, the selection of the upgrading technique should be based on the biogas utilization method since the low-cost option is not always the best due to the anticipating losses during application [11]. For instance, moderate quality of the biogas is needed for power generation, especially with mandatory H₂S and moisture removal. **Table 1.3** shows a comparison of the different stationary power generation equipment.

The waste stream of the biogas upgrading mainly consists of CO₂, which is a valuable ingredient for several applications. Besides, CO₂ being a greenhouse gas has taken much attention as the major contributor to climate change. Thus, direct emissions are not permissible; instead, carbon capture and storage technology (CCS) grab the interest. Moreover, CO₂ recycle, and reuse is another option to mitigate anthropogenic emissions while adding economic value plus environment sustainability. In this sense, the captured CO₂ from the biogas upgrading can be deployed to produce carbonated beverages, oil

extraction from ores (enhanced oil recovery), metal extraction (*e.g.*, aluminum from bauxite) and supply as a nutrient to grow plants.

Table 1.2 Biogas upgrading technologies [11]

Technology		CH ₄ purity (%)	CH ₄ loss (%)	Efficiency (%)
Biogas upgrading via CO ₂ removal	Water scrubbing	96 – 99	> 2	88.9 – 92.8
	Cryogenic separation	91 – 99	0.5 – 1	84.9 – 95.5
	Physical absorption	95 – 99	2 – 4	90 – 95.5
	Chemical absorption	97 – 99	4 – 5	88.5 – 97.7
	Pressure swing absorption	83 – 99	2 – 4	84.8 – 93.6
	Membrane separation	95 – 99	0.5 – 20	82.4 – 98.0
Biogas upgrading via CO ₂ Utilization	In-situ CH ₄ enrichment	97	8	
	Hydrate formation	84	High	
	Biological method	96		

Nevertheless, a high degree of CH₄ solubility in the liquid effluent drives the anaerobic digestion of wastewater treatment less appealing than expected [8, 14]. Moreover, low temperature and supersaturation exacerbate CH₄ dissolution in liquid effluent than in the headspace. For instance, Crone *et al.* revealed that the supersaturation levels in a UASB reactor ranged from 1.3-6.9, while 12-100% CH₄ lost in the liquid effluent at temperatures 8-35 °C [15]. Moreover, in the AnMBR reactor, the supersaturation reported was approximately 1, whereas 19-88% CH₄ dissolved in the liquid.

Table 1.3 Comparison of different biogas power generation equipment [16]

Parameter	Engine	Gas turbine	Microturbine	Stirling engine	Fuel cell
Electrical efficiency (%)	30 – 42	25 – 40	25 – 30	30 – 40	40 – 45
Thermal efficiency (%)	40 – 50	30 – 50	30 – 35	35 – 40	30 – 40
Overall system efficiency (%)	70 – 80	70 – 75	55 – 65	65 – 80	75 – 80
Biogas purification requirement	Medium	Medium	Medium (minimum 30% CH ₄ in biogas)	Low – Medium	High
NO_x emission	High	Low	Low	Very low	Extremely low
Investment cost	Low	Low	Low	Moderately high	High
Maintenance and operational costs	high	Low	Low	Low	Low

1.2.3 Dissolved methane as a risk and resource

The consequences of environmental releases of CH₄ are twofold: 1) contributing to global warming, and 2) the possibility of creating an explosive environment (in the downstream processes). According to the Environmental Protection Agency (of The United States), CH₄ is the second most critical greenhouse gas after CO₂ (*i.e.*, CO₂: 82% and CH₄: 10%) [17]. Nevertheless, the global warming potential of CH₄ (over 100 years horizon) is 28-36, which is defined according to CO₂ [18]. Moreover, the explosive limits of CH₄ in the air (at atmospheric conditions) is between 4.6–15.8 v/v%, which poses a high risk of

explosion in closed environments [19]. To avoid explosions, the discharge waters should normally have less than 0.14 mg L^{-1} dissolved CH_4 (D- CH_4), while the anaerobic effluents contain $10\text{--}25 \text{ mg L}^{-1}$ [15, 20]. Hence, the effect of CH_4 emission threatens the wellbeing of the earth, stressing the need of innovative, efficient recovery techniques.

Besides the potential environmental and safety risks, CH_4 is an invaluable energy source having a heating value of 55 MJ kg^{-1} that can be convertible to thermal and electrical energy [21]. However, in anaerobic reactors, the produced CH_4 dissolution and lost in the effluent stream are unavoidable [14, 22, 23]. Thus, harnessing CH_4 from both gas and liquid phases is necessary for making the process energy efficient. In contrast, Crone *et al.* demonstrated that anaerobic processes could be able to self-sustain with the effective recovery of the produced CH_4 from both headspace and the D- CH_4 in effluents [15]. Therefore, currently, the emergence of an efficacious D- CH_4 recovery method is vital for phasing out the potential hazards while exploiting the economic gains in turn.

Figure 1.3 Conceptual self-sufficient anaerobic digestion process. Note that the prevention of energy losses improves the energy self-sufficiency.

1.2.4 Methodologies for dissolved methane recovery

Considering the possible risks and energy losses associated with the anaerobic processes, several studies have recommended methods for the removal of D-CH₄ from effluents, which can be broadly classified as follows:

1. Destructive CH₄ removal (*e.g.*, biological oxidation)
2. Aeration-based CH₄ removal (*e.g.*, spray aeration, packed columns, tray aerators, and diffused aeration)
3. Membrane-based CH₄ removal (*e.g.*, membrane contactors)
4. Emerging techniques (*e.g.*, microbial fuel cells)

1.2.4.1 Biological oxidation

CH₄ oxidizing bacteria can transform D-CH₄ in an effluent into CO₂ as a remedy for CH₄ loss in liquid. However, this process is not attractive in terms of energy recovery since CH₄ consumption by microorganisms. Nevertheless, Adam *et al.* suggested that biological oxidation would be a promising option to treat D-CH₄ until an effective CH₄ recovery method is found; therefore, at least suppressing the emissions [24]. Preferably, subsequent ammonium oxidation will promote nitrification/denitrification which is a pre-requisite for effluent discharge. Hatamoto *et al.* confirmed that both ammonium and CH₄ oxidation simultaneously occur inside their down-flow hanging sponge reactor (DHS), howbeit soon after the CH₄ loading increased inside the reactor, CH₄ oxidation dominated over nitrification [25]. They reported a 95% D-CH₄ removal efficiency with 0.8 kg chemical oxygen demand (COD) m⁻³ day⁻¹ recovery rate and 2-hour hydraulic retention time (HRT). Later, Matsuura *et al.* introduced two-stage closed DHS reactors to treat D-CH₄ from UASB effluent as in the first reactor, CH₄ recovered as fuel, whereas the second

reactor acted as the oxidizer [26]. The efficiency in the first reactor was reported as 76.8%, while more than 99% of overall CH₄ removal. The same group in a succeeding study claimed that the 1-year duration of UASB operation coupled with two-stage DHS resulted in 57-88% overall D-CH₄ recovery efficiency due to the seasonal variations [27].

1.2.4.2 Aeration-based D-CH₄ removal

The aeration-based equipment exploits the concept of direct contact mass transfer between liquid and gas phases. Subjecting to the device configuration, different aeration categories are available, including spray aeration, packed columns, tray aerators, and diffused aerators.

In spray towers, gas loaded liquid droplets usually formed by a spray nozzle at the top of the chamber contact with the air that is supplied from the bottom. The stripped-out gas is passed through a demister to remove the moisture and then collected. The mass transfer is a function of droplet size, drop height, droplet velocity, and the type of nozzle used. Gloria *et al.* studied the effect of drop height, and gas flow rates at free drop falling conditions that they reported over 60% D-CH₄ recovery efficiency [28, 29]. However, the back mixing of liquid reduces mass transfer in a great deal in a spray tower [30]. Further, the high-pressure requirement for the formation of fine liquid droplets makes the process energy-consuming [31].

On the contrary to the spray tower, the packing tower consists of packing materials filled inside the tower that supports gas to liquid mass transfer by enhancing the effective mass transfer area. The liquid is supplied from the top of the column, ensuring a uniform distribution over the cross-section, usually by spray nozzles or drip plates. Avoiding “flooding” (*i.e.*, a phenomenon occurs at higher gas flowrates that influencing liquid

downward flow) during operation is very crucial. Thus, in packed column design, the gas velocity is set 80% of the respective flooding value [32]. Other drawbacks of the device are liquid “channeling” and “wall flow” through the column, which happens as a consequence of liquid maldistribution [33]. Therefore, proper column design is critical to achieving hassle-free separation. Scherer *et al.* recommended to use packed towers for D-CH₄ removal from groundwater if the required removal efficiencies are over 90% [34]. Hu *et al.* studied the applicability of packed towers for CO₂ removal from aquaculture water and revealed that gas to liquid ratio (G/L) strongly affects the D-CO₂ recovery efficiency [35]. They also recommended maintaining G/L ratio between 5 – 8 for effective operation in terms of energy that would result in 80 – 92% overall recovery efficiency. Besides air stripping, vacuum operation also possible in those packed towers, but higher operational cost limits the applicability [31]. Albeit degasification of ammonia, hydrogen sulfide, and CO₂ in packed column aerators are common in literature, a very limited number of studies have been reported for CH₄ degasification that restricts providing more related references [36-38].

Another type of possible D-CH₄ degassing device is tray towers. The perforated “plates” or “trays” provide different degassing stages inside the column [39]. The number of trays determines the overall gas recovery. Moreover, the pressure drop across the column is less compared to the packed towers since the length between plates provide free space for gas to diffuse. Further, the energy consumption for liquid feed is less in the tray column since the liquid distributors at the top operate under gravity. More importantly, cleaning is simple for this configuration because of limited clogging and ease of accessing the plates. Hisar *et al.* used a plate tower as an oxygenating and degassing tower for improving the water quality in salmonid hatcheries. The major findings of their investigation revealed that

the efficiency of oxygenating and CO₂ degassing process was 29% and 18%, respectively [40]. Kurella *et al.* studied H₂S scrubbing with three-stage sieve plate columns for different gas and liquid flowrates [41]. However, for their testing conditions, the maximum H₂S scrubbing efficiency they could achieve was 78.88%. The major drawback of the plate tower is the large liquid hold-up at high liquid flow rates [42].

The last type of aeration equipment in this discussion is the “bubble column.” Unlike all the other aeration devices described early, here, the column is filled with liquid, and the stripping gas pass through a diffuser to form bubbles. The mass transfer is a function of the size and rate of the bubbles formed through the gas diffuser. Alvarez *et al.* found a clear enhancement of mass transfer at higher liquid and gas flowrates for CO₂ stripping in a bubble column [43]. They attributed the observation to the enlargement of the mass transfer area and driving force with higher gas and liquid flow rates, respectively. In a different study, Anna *et al.* utilized a bubble aerator to desorb the D-CH₄ from full-scale anaerobic reactor effluent [44]. D-CH₄ recovery efficiency was reported to be 90-100% for their operating conditions. However, foaming would be problematic for liquid flowrates below 0.4 cm s⁻¹. Moreover, handling the liquids with solids negatively affects the mass transfer coefficient of bubble columns since these solids attach to the bubble surface reducing the effective mass transfer area [45].

1.2.4.3 Gas-liquid Membrane contactors (G-L MC)

In G-L MC, the membrane acts as a non-selective barrier providing a nondispersive contact between the gas and liquid phase for mass transfer [46]. Well-defined mass transfer area at the G-L interface, along with the non-dispersive contact features, the G-L MC over the aeration-based devices [47]. Thus, it provides highly efficient gas recovery even though

the overall mass transfer coefficients are almost the same or slightly lower than that of aeration-based devices [48]. Typically, for these devices, the mass transfer area available per unit device volume ranges between 500 – 1000 ft⁻¹, whereas for conventional tray or packed column, the area is only 10 – 100 ft⁻¹ [47]. Apart from that, as discussed in the previous section, the conventional separation devices often suffer from several operational drawbacks such as flooding and channeling. To highlight the importance, the advantages and disadvantages of G-L MC over the conventional devices are summarized and indicated in **Table 1.4**.

Nevertheless, studies have been carried out to investigate the feasibility of G-L MC over conventional mass transfer devices. Yeon et al., during their pilot-scale investigations of CO₂ removal from flue gas, showed that the absorption flux for unit device volume was 2.7 times better than that of the packed tower [49]. Moreover, Hoff *et al.* compared G-L MC with a packed column for CO₂ capture from flue gas and for natural gas sweetening. Their results revealed that 75% of size reduction was achievable with an MC device [50].

Also, Herzog *et al.*, through their cost-benefit analysis, revealed that by switching the CO₂ capturing technology from a conventional process to a membrane absorption, 30-40 % of installation and operational cost could be eliminated [51]. Furthermore, they highlighted that over 65% of both weight and space reduction would be possible due to the modular nature of the MCs. Most importantly, they could minimize the solvent loss in the conventional setup. Thus, switching the conventional process into membrane technology has promising economic and energy benefits. **Table 1.5** summarizes the key performance indicators (KPI) that measure the feasibility of both technologies for gas capturing. Note that the KPIs considered here is the capital cost (CAPEX), operational cost (OPEX), energy requirement, and maximum CH₄ recovery efficiency.

Table 1.4 Advantages and disadvantages of MC over conventional separation devices [47, 48, 52, 53]

Advantages	Disadvantages
High specific mass transfer area	Membrane itself exerts resistance to mass transfer
Independent fluid flow	Operational problems
No flooding at high flowrates	Shell side bypassing (Lowers the efficiency)
No unloading at low flowrates	Pressure-drop along the module
Fixed mass transfer area	Membrane-related problems
No phase dispersion	Membrane fouling
No emulsion formation	Membrane wetting
Ability of handing a wide range of fluids	Intermittent membrane replacement due to end-of-life
No density difference of fluid required	Module related problems
Possibility of aseptic operation	The deterioration of the potting adhesive because of the fluids in operation
Handing explosive solvents	
Easy operation and low energy requirement	
No mechanical parts	
Modular design	
Linear scale-up	

Since the advantages outweigh the disadvantages (**Table 1.4**) and the plausible energy gains (**Table 1.5**) of MCs over conventional mass transfer devices, currently ongoing research and development scrutinize the feasibility of these in industrial scale. In this context, G-L MC for D-CH₄ recovery is still in its infancy stage, given a very limited number of studies reported thus far. To date, depending on the membrane type used in the G-L MC device, more than 98% CH₄ recovery has been reported in the literature, which indicates the potential of this device in the field of D-CH₄ recovery from anaerobic effluents [20, 54, 55].

Table 1.5 Comparison of aeration-based devices vs. membrane contactors [30, 31, 37, 39, 42, 56].

KPI	Aeration-based devices	Membrane contactors
CAPEX	similar	similar
OPEX	high	low
Energy requirement	high	low
CH ₄ recovery efficiency	> 90%	> 99%

1.2.4.4 Microbial fuel cells (Microb.FC)

Recently, for the first time, Chen *et al.* studied the applicability of a Microb.FC for recovering D-CH₄ from anaerobic effluents for energy recovery as well as mitigation of GHG emissions [57]. They could achieve 85% D-CH₄ removal with 0.55 V generation and found that the governing parameters for improving CH₄ efficiency are the HRT and oxygen diffusion, whereas higher the value of those parameters improved the efficiency.

However, both the biological oxidation and the Microb.FC reduces the potential of CH₄ recovery and is not well- studied yet to confirm the feasibility in industrial scale. Thus, still, G-L MC holds a promising technique for D-CH₄ recovery from anaerobic effluents.

1.3 Problem statement

As per the discussion in **section 1.2.1**, anaerobic wastewater treatment contributes to low GHG emissions while producing low sludge and usable energy (*i.e.*, biogas) in turn. However, dissolving of the produced gases in the reactor liquid is inevitable owing to the gas and liquid phase equilibrium, as described by Henry's law. Additionally, the gas saturation could be below or over the equilibrium levels depending on the mass transfer rates from gas to liquid and vice versa. As reported by Souza et al., the degree of CH₄ supersaturation in an anaerobic reactor effluent can vary between 1.9 to 6.9 depending on

the reactor type and operational conditions [23]. Thus, a significant amount of CH_4 from the anaerobic process gets released to the environment with the liquid effluent, causing ineffective anaerobic operation three-fold. Firstly, CH_4 emissions contribute to environmental pollution. Secondly, CH_4 that is released might promote explosive working environments. And finally, there is a loss of highly valuable energy sources. Thus, the recovery of dissolved biogas from anaerobic effluent becomes pivotal for intensification of process sustainability. In this respect, gas-liquid (G-L) membrane contactors (MC) seems to be a promising technology over conventional gas stripping technologies. The capability of handling gas and liquid phases separately, compact designs to reduce the footprint, the higher mass transfer area to unit equipment volume, and the problem-free operation (no channeling, no flooding) allure MCs from traditional gas stripping technologies.

Bandara et al. reported the first utilization of a degassing membrane for recovering of CH_4 from bench-scale synthetic wastewater treated by UASB anaerobic reactor effluents.[22]. They investigated the temperature and HRT effects on D- CH_4 recovery efficiency. The key findings revealed that D- CH_4 efficiency is a function of effluent temperature, HRT in the degassing reactor, and the transmembrane pressure. Moreover, they explained that when the temperature of the liquid effluent dropped, the D- CH_4 concentration increased in the UASB reactor due to a higher solubility of gases at lower temperatures. Thus, this led to higher D- CH_4 recovery efficiency. The conditions, including higher HRT inside the degassing reactor and transmembrane pressures, resulted in more CH_4 being extracted. As a result of the study, they could improve the total CH_4 recovery from the UASB process in the range of 71% to 97% by retrofitting a hollow fiber degassing membrane.

Later Cookney *et al.* coupled a degassing G-L MC in the downstream of an EGSB pilot plant reactor to recover D-CH₄. They observed a 28% enhancement of the net electrical energy output under optimum operating conditions determined in the study [20]. Also, they observed that maximizing CH₄ recovery of the overall process caused a significant reduction in the fugitive emissions, thereby producing a lower net carbon footprint. Although Bandara *et al.* (2011) presented G-L MC for D-CH₄ recovery as a viable option for maximizing the overall CH₄ recovery, Cookney *et al.* (2012) painted a positive outlook, which inspires researchers to look into this application.

In subsequent studies, investigators focused more on the parameters that affect the gas stripping process using microporous and dense hollow fiber MCs using different anaerobic reactor effluents. Most of the results agreed with a typical gas stripping process using degassing membranes. Particularly, Cookney *et al.* (2016) and Henares *et al.* (2016) explored the feasibility of both porous and non-porous membranes in D-CH₄ recovery using different anaerobic effluents. Both studies arrived at the same conclusions: 1) the lower the liquid flowrate, the higher the CH₄ recovery, 2) microporous membrane show higher efficiency compared to the dense membranes, 3) lumen side operation is ideal for achieving higher recovery efficiencies but pore wetting limits microporous membrane, 4) the membrane mass transfer resistance control the overall mass transfer in dense membrane while in microporous membrane liquid phase mass transfer is dominant, and 5) vacuum mode promotes the mass transfer coefficient compared to the sweep gas operation, however, it is less effective for microporous membrane due to pore wetting [54, 55]. As these studies are short-term, it is difficult to predict the long-term applicability. Thus, Henares *et al.*, in their subsequent studies, showed that membrane fouling and wetting limit the efficacy of the process [55, 58]. They observed membrane fouling is severe for shell

side operation compared to the lumen operation and recommended the intermittent cleaning.

To this end, most of the tested membranes are limited to commercial PP and PDMS degassing membranes. However, these membranes suffer from wetting and fouling during long-term operations. Hence, there is a need for robust membranes for D-CH₄ recovery. In such a context, Wongchitphimon *et al.* successfully fabricated a highly hydrophobic Matrimid® membrane incorporating fluorinated silica for enhancing the wetting resistance of the membrane. The results confirmed a stable D-CH₄ recover flux over 300 hours along with very high CH₄ flux compared to the commercial PP degassing membrane [59]. Furthermore, they claimed that the higher porosity of the degassing membrane could accommodate a higher D-CH₄ recovery flux due to a lower mass transfer resistance. However, the complex modification steps and high brittleness limits this membrane in commercial production, letting space for more research on high-performance membrane fabrication.

Apart from membrane wetting, membrane fouling is the greatest challenge for this application as anaerobic effluent contains a wide range of foulants that cannot be removed only by simple pre-filtration. Currently, no membrane tested under this application exhibited proper fouling resistant capability. However, Wichitpan *et al.* (2019) showed that even for low strength, anaerobic effluent (*i.e.*, AnMBR) membrane fouling is significant, which dropped the membrane performance within a few hours [60]. Although membrane cleaning helps to recover back the membrane performance, the cleaning downtime plus chemical cleaning reduces both energy efficiency and the membrane lifespan. In this respect, there is a need of producing fouling-resistant membranes that would effectively minimize the cleaning down-times and less usage of chemical cleaning.

Moreover, the ultimate goal is to minimize energy utilization in the MC operation, thereby maximizing energy recovery. Thus, it needs comprehensive studies to investigate the parameters affecting the energy recovery from anaerobic effluents. In this sense, Rongwong *et al.* (2018) conducted the first detail energy analysis of D-CH₄ recovery from anaerobic effluent using mathematical modeling and validating with experimental results [61]. They examined the membrane module- and operation-related parameters and provided optimized parameters to achieve a higher net energy recovery. The results suggested that a combined vacuum and sweeping gas mode is ideal at near atmospheric conditions for generating higher net energy. Nevertheless, they assumed that the mass transfer solely depends on the liquid phase resistance; thus, neglecting the effects of gas-phase mass transfer resistance. Still, the validity of this assumption is questionable since many parameters that are affecting gas phase mass transfer (*i.e.*, packing density, module diameter, gas flowrate, G/L ratio) change with varying effective module length and mass transfer area. Therefore, a critical analysis of the parameters is pivotal for determining the maximum energy recovery to industrialize this application successfully.

Yet lack of study on the effect of membrane-related parameters (*i.e.*, the membrane porosity, dimensions, structure, hydrophobicity), operation parameters (*i.e.*, gas-liquid flowrates, vacuum pressure), hydrodynamics (*i.e.*, module design) plus challenges (*i.e.*, membrane wetting and fouling) dampens the commercialization potential of this application. Thus, mainly, this work contributes comprehensive studying those parameters while producing high-performance membranes to enhance the CH₄ recovery and maximizing energy production using G-L MCs by overcoming associated challenges and finally imparting commercialization of the application.

The following section is a comprehensive literature review on MC technology.

1.4 Membrane contactor technology

1.4.1 Process introduction

Figure 1.4 Schematic of hollow fiber membrane contactor

Membrane contactor technology for separation and purification is an emerging field that has promising features compared to traditional processes. Analogous to the conventional mass transfer devices, the primary objective of the MC device is to promote inter-phase mass transfer [47, 62, 63]. In an MC device (**Figure 1.4**), two streams of the same/different phases flow at the opposite sides of the membrane while one phase is allowed to immobilize within the membrane pores by carefully controlling the applied pressure [48, 62]. The membrane prevents phase mixing but exerts no selectivity on the transporting species, allowing them free passage through the membrane pores [47, 64]. Therefore, the two phases contact only at the pore of one side of the membrane, rendering the species to diffuse across the membrane pores according to their chemical potential [47, 65]. Thus, one can define an MC as a device that promotes mass transfer (gas-liquid or liquid-liquid) without inter-phase dispersion [47].

The key parameter of achieving a higher mass transfer rate is the available contacting area between the phases (the higher the contacting area higher the mass transfer rate). To attain such higher mass transfer rates, some conventional devices (*i.e.*, spray tower,

bubble columns) form bubbles or droplets small in size but high in number while a few use packing materials (*i.e.*, packed towers) [66]. However, these devices suffer several challenges due to phase mixing and scalability issues (note that the challenges are discussed in **section 1.2.3.3**). In such a context, membrane contactors are a promising approach to utilize in separation applications.

1.4.2 Membrane contactor systems

Depending on the phases besides the membrane, MC processes belong to one of the categories; gas-liquid, liquid-liquid, or gas-gas contactors [53, 62, 63, 66, 67]. The following section briefly discusses the available MC systems commonly utilized in the industry. Herein, the major focus will be given for gas-liquid MCs, while other types are discussed in general.

1.4.2.1 Gas-liquid membrane contactors (G-L MC)

The two-phase system contains gas and a liquid individually flowing through the sides of the membrane, while the concentration or the partial pressure difference drives the mass transfer between the phases. Two operational modes can be distinguished; gas-filled membrane operation (dry mode, the gas fills the membrane) and liquid-filled operation (wetted mode, the liquid partially or fully enters the membrane pores). Among these two modes, the dry operation is more effective since membrane resistance is negligible [68]. However, the critical issue associated with this process is the “membrane wetting” problem during long-term operations [69, 70]. Membrane wetting is a phenomenon where the liquid penetrates inside the membrane pores, creating a stagnant barrier that exerts additional mass transfer resistance [71]. Many studies have since attempted to improve the membrane hydrophobicity, some even to superhydrophobicity, to mitigate this issue [71-74].

G-L MCs are more attractive for industries such as chemical, energy, biomedical, and petrochemical industries. The following sections will briefly discuss the current state-of-art technology in these application areas.

Membrane based oxygenation/deoxygenation

Some industries, including those in power generation, manufacturing, medical, and biotechnology sectors, demand high-quality water or bubble-free aeration for stringent process requirements [75]. For example, the steam boilers need ultrapure water to avoid corrosion or scaling inside tubes while, in manufacturing semi-conductors, the main concerns are to avoid metal oxide and microbubble formation for obtaining clean, smooth surfaces [76, 77]. Moreover, in the medical industry during open-heart surgeries, the key requirements of blood oxygenators are avoiding serious complications such as protein denaturation, blood cell damage, and destruction while providing efficient O₂/CO₂ transport [78-80]. Due to impressive mass transfer performances along with low cost, low footprint, and modular design of G-L MC, those industries grab the advantage over conventional devices.

Many researchers studied the parameters affecting the mass oxygen transfer of the process, such as flow configuration (parallel flow, transverse flow, *etc.*), the gas/liquid flow rates, vacuum pressures, and types of membranes (dense or microporous), *etc.* [81, 82]. However, some literature reported membrane fouling and wetting during long-term operation that lowered membrane performance [77, 83-86]. Further, the studies focus on process modifications for improving mass transfer, including module design, catalytic membranes to convert O₂ into the water, tri-bore membranes fabrication, *etc.* [86-88].

Gas humidity control

Air humidity control is of great importance in a variety of air conditioning systems, including buildings, vehicles, storage, and transporting perishable products [75, 89, 90]. The conventional humidity control involves dew-point dehumidification of water vapor, literary consuming more energy [91]. Besides, absorption or adsorption of water vapor into a desiccant liquid or solid is another way of humidity control but requires a larger mass transfer area and drawbacks associated with conventional mass transfer devices, as discussed in an earlier section. In this respect, membrane contactors serve better advantages over ascribed methods.

In membrane dehumidification, the water vapor inside the warm, humid air passes through the membrane and get absorbed by the liquid at the other side of the membrane. Then in the absorbent regeneration membrane, the water vapor strips out to concentrate the liquid absorbent. Evaporative cooling occurs in the membrane humidification process, where the evaporated water vapor passes through a membrane to humidify the air flow entering the membrane contactor.

The process efficiency depends on the type of membrane, module configuration, operational parameters, and the liquid absorbent. Kneifel *et al.* pointed out that the micro-porosity in the membrane would adversely affect the contactor performance since they are prone to pore wetting and/or solute precipitation, which impart limitations in operating conditions [91]. However, composite hollow fiber membranes with a skinless membrane morphology on the gas side and higher membrane porosity facilitate water vapor permeance despite resistance from the dense layer. Later, researchers employed quasi

counter flow parallel plate configuration and tri-bore membranes to determine the effect of mass transfer of MCs [92, 93].

Paraffin-olefin separation

Olefin-paraffin separation is one of the most important processes in the petrochemical industry. The closer physical properties (*i.e.*, the boiling point) and molecular sizes of those gases make it more challenging for separation [94]. Moreover, the traditional separation techniques such as cryogenic distillation, liquid absorption, and supported liquid membranes are highly energy-intensive and/or unstable in performance. Therefore, there is a need for less energy-consuming stable technologies [94, 95]. In this context, researchers have made efforts to perform the separation utilizing G-L MCs. Herein, two consecutive G-L MCs operate as absorption and regeneration units [96]. In the absorption cycle, the feed gas and liquid absorbent (typically a solution of silver salt) flow from different sides of the membrane with one component absorbing at the G-L interface, whereas in the other unit, absorbent regeneration occurs using a sweep gas [97, 98]. Yet, membrane wetting, pore-clogging due to crystals formation and membrane degradation limit the applicability of G-L MC in this area [95, 99].

Acid gas capture

Acid gas capture from post-combustion flue gases of power plants, CO₂ removal for biogas upgrading, and natural gas sweetening are some of the most studied G-L MC industrial applications under this category. The conventional gas scrubbing devices, including packed columns, bubble columns, spray towers, impart problematic operation due to flooding, channeling, foaming, restricted gas and liquid flow rates, larger space requirement, and higher operational costs. G-L MCs have the capability of overcoming all

these respective disadvantages, which motivate many investigators to explore more and expand on existing knowledge.

In general, to obtain a better performance, the membrane pores should be completely dry, plus the adsorbent should be sufficiently reactive [100]. Both membrane and adsorbent selection are equally important. However, the most critical challenge in using G-L MCs at this stage is pore wetting, which drastically affects the prolonged membrane operation [35, 101-103]. To tackle this issue, most of the studies investigated hydrophobic modifications for membranes and new categories of adsorbents that are more compatible with membranes [104-107].

Methane recovery from anaerobic reactor effluents

Methane degassing from anaerobic reactor effluents is the most recent G-L MC application reported in the literature. Since this is the major focus application in this study, a comprehensive review was carried out in **section 1.3**.

1.4.2.2 Other MC technologies

In membrane distillation (MD), a heated aqueous feed with volatile components is in contact with a microporous hydrophobic membrane forming the vapor-liquid interface on the membrane surface. The temperature and partial pressure (or concentration) gradient across the membrane induce volatile components to evaporate across the liquid-vapor boundary, diffuse through the membrane pores and condense at the other side of the membrane [108]. A phenomenon commonly identified as “temperature polarization” is a major challenge with the MD process as the driving force will be lost over time [108]. Cooling down of the membrane temperature near the liquid-vapor boundary as a result of evaporation of the volatile component leads to this temperature polarization [108, 109].

Although improving the hydrodynamics (*i.e.*, high Reynolds number, creating turbulence using spacers/baffles, *etc.*) of the process could alleviate the issue to a certain extent, there requires a more effective solution to deal with temperature concentration [62]. Novel concepts such as thermo-plasmonics that can impart local heating by photoexcitation of plasmons are currently under study to overcome the loss in temperature due to evaporation of volatile matter [109]. When the feed solutions are very sensitive to temperature, osmotic membrane distillation (OMD) can replace MD [110]. In OMD, the driving force is the vapor pressure difference between the feed and permeate solution [111]. However, the low vapor flux limits OMD in commercial applications. At present, research is focused on the possibility of hybrid systems containing reverse osmosis and OMD in chemical and food industries [112].

Membrane crystallization (MCry) is a combination of MD and crystallization. Firstly, the MD process concentrates the liquid to near saturation level and then sends the concentrated liquid to a crystallizer for producing fine crystals. The resulting crystals from MCry is well structured with a high degree of purity that it is very difficult to achieve with conventional crystallization methods. In MCry, membrane functions not only as a separating barrier, but also heterogeneous support for nucleation starting at low saturation ratios [113].

In membrane emulsification (ME), the dispersed and continuous phase form a two-phase system. During the operation, pressurized dispersed phase spontaneously transport through the membrane pores to enter the continuous phase [114-116]. ME is useful in obtaining more stable and uniform fine emulsions without any critical issues associated with conventional emulsifiers such as high-pressure homogenizers and rotary starter systems [116].

Phase transfer catalysis (PTC) promotes reactions between the immiscible aqueous and organic phase reactants [117]. In membrane PTC (MPTC), both the aqueous and organic solutions containing reactants and catalysts pass through the sides of a porous membrane, allowing the formation of the organic-aqueous interface. The concentration gradient drives the species to the liquid-liquid boundary while the reaction takes place at the interface *via* the phase transfer catalyst that is present within the membrane pores (interfacial contactors) [62]. The ability to extract the product and catalyst streams independently through the MPTC eliminates the inconvenience caused by a down-stream separation of catalysts and products in a conventional PTC [118]. **Figure 1.5** summarizes all the MC technologies discussed above, and the place of this study fits in.

Figure 1.5 Summary of MC technology and focus of this study

1.4.3 Basic principles of gas-liquid membrane contactors

1.4.3.1 Resistance-in-series model

In line with the previous discussion, the concentration difference (or the partial pressure gradient) across the membrane drives the mass transfer in three different regions. If the MC operates as a gas absorber, the transporting component in the gaseous stream diffuses through the bulk gas phase towards the membrane surface, then pass through the

membrane pores and finally enters the liquid through the G-L interface. Since the diffusing element must overcome resistances from the gas, membrane, and liquid phases (or liquid, membrane, and gas phase) in sequence during absorption (or stripping), the mass transfer coefficient is a function of the three individual phase mass transfer coefficients. The mass transfer model that relates all the mass transfer coefficients is the well-known “resistance-in-series” model or the “film theory” [68, 100, 119].

Figure 1.6 G-L membrane contactors (a) absorption process (b) stripping process

Figure 1.6 shows the three distinguishable mass transfer regions and respective concentration profiles for gas absorption and desorption processes. Since the G-L boundary layer experiences an equilibrium in agreement with Henry’s law, the concentration profiles besides the G-L boundary has a discontinuity as clearly visible in **Figure 1.6a** and **Figure 1.6b**. The following correlation expresses the relationship of overall mass transfer coefficient (K_{OL}) to the individual mass transfer coefficients (gas phase; k_G , membrane phase; k_M , liquid phase; k_L) for a hollow fiber G-L MC with non-wetted mode operation. Note that the gas and liquid are flowing in the shell side and the lumen side respectively, in the selected case [68].

$$\frac{1}{K_{OL}} = \frac{d_i}{Ek_L} + \frac{Hd_i}{k_M d_{ln}} + \frac{Hd_i}{k_G d_o} \dots\dots\dots (1-1)$$

Where; d_i , d_o , and d_{ln} are the hollow fiber inner, outer, and the log-mean diameters, respectively. H is the Henry constant for the selected gas species. E is the enhancement factor for any reactions between the liquid and the gas species.

1.4.3.2 Individual mass transfer coefficients

Gas and liquid phase mass transfer coefficients

Determination of individual mass transfer coefficients of gas and liquid phases solely rely on the empirical correlations, because of the influence of fluid hydrodynamics, flow configuration, and module geometry on gas diffusion. Among these correlations, Leveque's equation is applicable for a wide range of applications in a lumen flow with reasonable accuracy, even though the polydispersity of membrane could limit the accuracy of the correlation [66]. Yet, none of the proposed shell-side mass transfer correlations adequately describe the mass transport in the MC shell side as fiber maldistribution boosts up localized turbulence and liquid bypassing due to a very high degree of packing density [48].

Membrane mass transfer coefficient

The membrane morphology (*i.e.*, porous, dense, or composite) and the type of fluid inside the membrane pores (*i.e.*, gas or liquid) are critical factors in determining the precise mass transfer correlations. Essentially, the MC membrane should be porous. However, there are instances where other membrane structures can be of practical use. Thus, it is sensible to discuss the membrane mass transfer coefficient of dense and composite membranes from a broad perspective.

Diffusion, being the gas transport mechanism in a gas-filled porous membrane, has two forms, “Knudsen-” and “viscous-diffusion” [120]. This classification is based on the dimensionless Knudsen number (Kn), the ratio between the mean pore radius (r_p) of the membrane, and the mean free path (λ) of the gas molecule. Given the condition that $Kn < 1$ (*i.e.*, $\lambda > r_p$), the gas molecules transport mechanism is Knudsen diffusion or viscous otherwise [119]. Generally, for gas species transport in porous membranes, diffusion is a combined Knudsen- and viscous-diffusion. In contrast, gas transport through dense membrane is via solution-diffusion, where the permeability coefficient becomes dominant in the mass transfer coefficient calculation [120]. Both dense and porous membrane mass transfer considerations must be included in the composite membranes mass transport coefficient calculations. When the liquid is inside the membrane pores (wetted mode), the gas species molecular diffusion coefficient in the liquid phase affects the mass transfer across the membrane. **Table 1.6** shows the literature coefficient for each phase.

Table 1.6 Individual mass transfer correlations for counter-current flow [43, 116, 118]

Mass transfer coefficient	Parameter
Shell side mass transfer coefficient	k_S : shell side mass transfer coefficient (m s^{-1})
$k_S = D\beta \frac{(1-\phi)}{Z} \left(\frac{d_e v \rho}{\mu Z} \right)^{0.6} \left(\frac{\mu}{\rho D} \right)^{0.33}$	k_T : lumen side mass transfer coefficient (m s^{-1})
For $0 < \text{Re} < 500$ and $0.04 < \phi < 400$	k_M : membrane mass transfer coefficient (m s^{-1})
$k_S = 8D \frac{(1-\phi)}{Z} \left(\frac{d_e v \rho}{\mu Z} \right) \left(\frac{\mu}{\rho D} \right)^{0.33}$	Re: Reynold's number
$k_S = 1.25D \frac{(1-\phi)}{Z} \left(\frac{d_e v \rho}{\mu Z} \right)^{0.93} \left(\frac{\mu}{\rho D} \right)^{0.33}$	Gz: Gratz number
For $0.5 < \text{Re} < 500$ and $\phi = 0.03$	D: diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
Lumen side mass transfer coefficient	$D_{M, \text{eff}}$: effective diffusion coefficient of the membrane ($\text{m}^2 \text{s}^{-1}$)
$k_T = 1.62 \frac{D}{d} \left(\frac{d^2 v}{ZD} \right)^{0.33}$	Z: effective module length (m)
For $Gz > 4$	d_e : hydraulic diameter (m)
Membrane mass transfer coefficient	v: velocity of the fluid (m s^{-1})
Porous membranes	β : constant (<i>i.e.</i> , 5.8, 6.1 for hydrophobic and hydrophilic membrane respectively)
$k_M = \frac{D_{M, \text{eff}} \epsilon}{\tau \delta}$	μ : dynamic viscosity of the fluid (Pa s)
Dense membranes	ρ : liquid density (kg m^{-3})
$k_M = \frac{\text{Permiability} \times \text{Partial Pressure}}{\text{Membrane thickness}}$	ϕ : packing density
	ϵ : membrane porosity
	τ : tortuosity
	δ : membrane thickness (m)

1.4.4 Challenges of G-L MC

Carefully reviewing the membrane applications discussed in **section 1.4.2.1**, evidently, “membrane wetting” is the most common challenge associated with micro-porous hollow fiber membranes whereas, “membrane fouling” caused trouble for few applications.

1.4.4.1 Membrane wetting

Membrane wetting happens in microporous membranes because of liquid intrusion into membrane pores, which fill up the voids of the membrane. Membrane wetting may be a partial or full liquid penetration, but it will drastically affect membrane performance. In fact, the intruded liquid film is stagnant, thus creating a passive G-L boundary inside the membrane pores, resulting in low mass transfer between the liquid and gas phase. Technically, at this stage, the membrane mass transfer resistance increases with the wetting distance across the membrane and correspondingly decrease the overall mass transfer coefficient. In general, causes for membrane wetting is two-fold. Firstly, exceeding the critical pressure of the membrane (**Figure 1.7a**) and secondly capillary condensation (**Figure 1.7 b**).

Figure 1.7 Membrane wetting due to (a) exceeding critical pressure of the membrane (b) capillary condensation

Transmembrane pressure effects on membrane wetting

$$\Delta P = \frac{2\gamma \cos \theta}{r} \dots\dots\dots (1-2)$$

The Laplace-young equation in **Equation 1-2** adequately describes the wettability of a membrane [121]. In accordance with the equation, the minimum transmembrane

pressure (ΔP , Pa) that a liquid needed to break through the hydrophobic forces and infiltrate into membrane pores (critical entry pressure, CEP/liquid entry pressure, LEP) is a function of liquid surface tension (γ , N m⁻¹), the maximum membrane pore radius (r , m), the contact angle (θ , °) of the membrane with the same liquid and the geometric pore coefficient. Thus, factors that foster membrane wetting can be membrane-related (*i.e.*, contact angle, membrane pore size, pore geometry, and microstructure), liquid-related (*i.e.*, surface tension), or operation-related (liquid flow rate, vacuum pressure). Hence, one should be very careful in maintaining proper pressure difference across the membrane to make sure no pore wetting during operation.

1. Membrane-related parameters

Membrane hydrophobicity is a key parameter that affects membrane wetting. If the adhesive forces between the membrane and liquid molecules are weaker than the cohesive forces of the liquid molecules, the membrane is considered as hydrophobic to the particular liquid and hydrophilic if otherwise. When the membrane is hydrophilic, the liquid molecules can climb up along the pore wall until they reach the lowest energy state and form a concave meniscus due to the capillary action. A small increment of the pressure on the liquid side would drive the meniscus to push towards the gas side. Thus, it is necessary to utilize a sufficiently hydrophobic membrane for a G-L MC to protect the membrane against membrane wetting for efficient operation. The contact angle (CA) of the membrane and the contacting liquid physically measures the membrane hydrophobicity. Generally, a CA of value $> 90^\circ$ is considered hydrophobic.

Another important parameter is the maximum membrane pore diameter. The liquid can easily penetrate larger pores as compared to smaller pores in a hydrophobic membrane

due to the lower required external force to overcome the hydrophobic force. Many studies have reported the effect of the pore size on membrane wetting. For example, Ahmad *et al.* used highly hydrophobic ($CA > 125^\circ$) flat sheet PVDF membranes with two different pore sizes for CO₂ removal using 2-Amino-2-methyl-1-propanol as the liquid absorbent [122]. Despite the hydrophobicity, the membrane module with the smaller pore diameter performed better. The authors attributed the observation to the lower degree of wetting due to the smaller membrane pore diameter. Also, Jian-Gang *et al.* reported the same observation for hollow fiber membrane modules with two different pore sizes and porosities [121]. Therefore, when fabricating a membrane for applying in G-L MC, both membrane hydrophobicity and the pore size distribution should be carefully considered.

Lastly, the membrane pore geometry and microstructure also affect membrane wetting. Typically, membranes with cylindrical geometry experience a lower degree of wetting over non-cylindrical pores. Rasha *et al.*, in their study, calculated the pore geometric coefficient (B) for three different PTFE microstructures and reported that B could vary with temperature due to structural changes at higher temperatures [123]. Moreover, the highest reported B values had larger critical entry pressures, ensuring minimum pore wettability. Also, Naim *et al.* claimed that having a sponge-like structure near the G-L interface can lead to larger CEPs, thereby achieving a lower degree of membrane wetting [124].

2. Liquid related parameters

The liquid physical properties like surface tension and the viscosity influence membrane wettability. In compliance with **Equation 1-2**, liquids with a higher surface tension have a lower liquid leaking tendency. Most of the absorbents have lower surface

tension than that of water, indicating a possibility of liquid wetting during the operation. Besides, the low viscous absorbents have higher possibility of liquid seepage through the membrane pores. Additionally, the absorbent type and concentration could aggravate membrane wetting by reducing solution surface tension. Rongwong *et al.* studied the effect of absorbent type and concentration for CO₂ absorption experiments [125]. The wettability of the membrane with three different absorbents followed the effect of surface tension (*i.e.*, higher wettability for lowest surface tension absorbent). Also, the addition of sodium glycinate to the monoethanolamine (MEA) solution showed good MC performance due to minimal pore wetting as a result of an increment in the solution viscosity rather than the surface tension. Besides, higher MEA concentrations showed improvement in the absorption flux, but the long-term stability for 12 days was deteriorated with the increasing concentration that resulted in reducing the surface tension leading to membrane wetting.

Another important aspect is the compatibility among the absorbent and the membrane material. Many studies reported that long-term contact between the absorbent and the membrane reduced the mass transfer rates, due to the alteration of membrane structure. For instance, Franco *et al.* experienced around 41% increment of membrane wetting after 69 hours of operation with MEA [126]. Reasons such as increment in membrane wettability to the morphological degradation of PP membrane that resulted in contact angle and pore size alteration were attributed.

3. Operational parameters

Gas side vacuum, high liquid flow rates, and pressure drop along the module can induce membrane wetting as they give rise to higher transmembrane pressure [127-129]. When the pump forces the liquid into the membrane module, the created pressure at the

liquid entrance can induce membrane wetting. The effect can be more severe with elevated liquid flowrates since the wetted portion can propagate along the membrane aggravating the mass transfer resistance [101, 121].

Capillary condensation effects on membrane wetting

Capillary condensation is another cause of membrane wetting. The vapor molecules that transport across the membrane can adsorb onto the pore wall; eventually, adsorbing more vapor molecules until the formation of a liquid meniscus in the pore [130]. The phenomenon of developing localized liquid-filled pores is known as the capillary condensation. Unlike the previous case, this type of membrane wetting is difficult to control, since capillary condensation can occur at any instance during the microporous membrane operation. Capillary condensation is known to degrade membrane performance in due course [131-134]. In fact, the effect is serious in smaller pores rather than in larger pores [135-138].

1.4.4.2 Membrane fouling

Apart from wetting, another anticipated long-term operational problem of G-L membrane contactor handling impure effluents is membrane fouling. In this scenario, impurities in the gas or liquid phase undesirably adhere to the membrane surface lowering its intrinsic performance over time [139]. In general, membrane fouling occurs as a consequence of convective flow across the membrane, as well as the effect of concentration polarization. Generally, fouling causes an adverse impact on membrane operations such as membrane filtration (*i.e.*, ultra-, nano-, micro-filtration, reverse osmosis, forward osmosis, pressure retarded osmosis) and membrane distillation [139-141]. In contrast to those membrane processes, G-L MCs do not experience concentration polarization or membrane

fouling stimulated by high-pressure. However, membrane fouling remains in G-L MCs that handle wastewater effluents that contain organic matter in suspended and dissolved forms and biological substances (*e.g.*, extracellular polymeric by-products (EPS), microbes) [60, 142]. The inherent hydrophobicity of those membranes eventually promotes protein-like foulants to attach and build upon the membrane surface [60]. Thus, degassing membranes are prone to membrane fouling [100].

Henares *et al.* observed membrane fouling during anaerobic wastewater degassing using commercial PP hollow fiber MC. Severe CH₄ recovery decline was related to shell side operation while lumen operation had stable recovery up to 180 hours [143]. They attributed the performance drop to both organic and inorganic foulants present in the wastewater effluent, especially polysaccharides, proteins, and EPS. The authors recommended daily water cleaning of the membrane for 30 minutes as a result of membrane fouling. Later, Rongwong *et al.* studied the fouling formation mechanism on a hydrophobic PVDF membrane using AnMBR and UASB effluents [60]. The membrane fouling layer analysis revealed that despite the complex foulant profile in the effluent. The primary foulants that are responsible for membrane fouling include protein-like substance as well as EPS. Moreover, the higher effluent velocity exacerbated membrane fouling owing to the higher foulant loading on the membrane. Those studies provide evidence that fouling limits the feasibility of G-L MC application when handling dirty liquids.

1.4.4.3 Membrane wetting and fouling prevention

There are numerous wetting and fouling preventive techniques for different membrane applications suggested in the literature. Before, focusing on both problems

together, it is advisable to look forward to the challenges individually since proper solutions can be found by careful revision of both mitigating techniques.

Membrane wetting prevention

Among the membrane wetting prevention methods, membrane related improvements are highly reported, whereas optimization of operating parameters and absorbent selection also have been utilized as wetting mitigation techniques. Nevertheless, the selection of absorbents is omitted at this stage due to the lesser significance of this thesis work.

1. Membrane related improvements

In compliance with the Laplace-Young's equation mentioned in **Equation 1.2**, higher contact angle and smaller maximum pore size of the membrane can improve the CEP, thus minimizing the effect of membrane wetting. In this view, many researchers followed membrane hydrophobic-modifications and the development of hydrophobic membranes with narrow pore size distributions. However, the most reported methods of introducing hydrophobicity to the membrane are *via* surface fluorination and improving roughness [71]. Since fluorinated substances have a strong C-F bond, they exhibit low polarity and high chemical inertness that can contribute to achieving hydrophobicity in a great deal [144].

Roughening a hydrophobic surface leads to the formation of an extremely rough surface, even a superhydrophobic surface. Several researchers have put effort into making superhydrophobic membrane surfaces by exploiting the idea mentioned above [145-148]. Superhydrophobic surfaces are extremely rough that they can mimic the so-called "lotus

effect” to lower the contact between surfaces. Typically, for membranes having contact angles over 150° are superhydrophobic, thus minimizing the solid-liquid contact leading to gain anti-wettability and fouling properties as per the Cassie-Baxter model [149, 150]. Still, membrane wetting and fouling were inevitable since the membrane is not superhydrophobic to the absorbent, thus changing the surface eventually [104, 106, 149, 151]. Moreover, super-hydrophobicity cannot cope up with surface-active substances like surfactants in the liquid feed that will eventually wet the membrane [152].

Moreover, anisotropic (or asymmetric) membrane structure, which contains a hierarchical pore structure and extremely thin skin layer, is beneficial for achieving higher CEPs. One can fabricate an anisotropic membrane *via* the phase inversion technique. For advanced readers, it is recommended to refer the critical review articles on phase inversion membrane fabrication [153-155]. Mansourizadeh *et al.* showed that having a thick sponge structure near the lumen where the liquid is in contact with membrane improved the CEP greatly but reduced the CO₂ flux across the membrane yet maintained a stable gas flux during long-term operation [156]. Such membrane morphology is possible to obtain by incorporating proper non-solvent additives into membrane dope solutions such as lithium chloride, ethanol, acetic acid, low molecular weight polyethylene glycols, etc. and maintaining suitable spinning parameters [124, 156-158].

Some studies suggested applying composite membranes containing highly permeable thin dense coating on microporous support to alleviate membrane wetting. The dense part of the composite membrane is facing to the liquid side, hence limiting the liquid passage through membrane pores. Nonetheless, partial wetting due to the capillary condensation effect could be exempted, still anticipated performance drop because of the additional membrane resistance by the dense layer is unavoidable [97, 103, 142, 159].

2. Optimizing operating parameters

The distinguished influential operating parameters for membrane wetting are the liquid side flowrate, vacuum pressure, and the operating temperature. Liquid flow rates can cause higher pressure drops across as well as along the membrane that both can induce membrane wetting.

Membrane fouling prevention

The most primitive and classical method of suppressing membrane fouling is chemical cleaning. Importantly, the proper selection of the cleaning agents is beneficial for efficient foulant removal from the membrane. Typically, for inorganic foulants membrane cleaning with citric acid, ethylenediaminetetraacetate (EDTA) and ammonium bifluoride-based solution would remove scales. Moreover, for biological foulants the cleaning agents derived from EDTA at high pH, sodium bisulfite and disinfection method will be propitious. However, membrane cleaning for organic fouling is less effective, yet cleaning with isopropanol, or proprietary solutions will work. Still, due to the intermittent chemical membrane surface would be changed leading to mechanical damages even wetting. However, it is recommended to pre-treat the feed before applying in the MC system which will be helpful to reduce membrane fouling.

Secondly, maintaining proper operational parameters such as liquid flowrate, the pressure drops across the membrane, and operating configuration will cause rather slow down the fouling formation. For instance, as per the Rongwong *et al.*, the higher liquid flowrates provoke more fouling, which was corresponded to the higher foulant loading fed into the membrane [60]. Because of the same reason, shell side operation was also not beneficial compared to the lumen operation [60, 143].

Finally, fabrication of fouling-resistant membranes for those applications might have the highest potential for fouling mitigation compared to the other two methods. It has been found that mostly surface properties like hydrophobicity and surface roughness are accountable for membrane fouling due to hydrophobic like foulants and particulate substances respectively [160, 161]. However, surface hydrophilization is a proven remedy for membrane fouling by foulants having hydrophobic properties (*i.e.*, proteins, polysaccharides) [160]. Recently, amphiphilic co-polymers having both hydrophilic and hydrophobic nature specially polyethylene glycol (PEG) segmented fluoropolymers, are widely experimented [162-164]. These components contain both anti-adhesion properties (due to non-polar fluorinated segments) and fouling resistivity of hydrophilic substances (due to PEG segments) [162]. These substances can easily form a hydration layer with water via hydrogen bonds restraining the protein adsorption due to the energy barrier between the membrane surface and the protein molecule [165]. Nevertheless, the approaches of PEG grafting on different membrane surfaces are complicated and need careful control of chemistry. For instance, several studies followed the functionalized PEG attachment after activating the membrane surface via surface-initiated atom transfer radical polymerization (ATRP) while some anchored the PEGylated substances on the membrane surface by plasma activation [166]. Besides these techniques, the simplest method of PEG coupling onto the membrane surface is by physical adsorption. The PEG cross-linked copolymers are commercially available, which can directly apply on the membrane surface as a coating. These substances have a bi-continuous structure which contains hydrophilic groups containing PEG and hydrophobic groups (*e.g.*, Pluronic materials), whereas the hydrophobic part can easily attach to hydrophobic membrane surface [167]. Not limited to the PEG like modifications, some studies used nanoparticle for improving antifouling properties of the membrane [168, 169]. Rana *et al.* performed a comprehensive review of

antifouling membrane modification that is highly recommended for interested readers [160].

Although there are numerous wetting and fouling mitigation techniques suggested in the literature, most of them are valid in the absence of one scenario. For example, improving hydrophobicity might hinder membrane wetting, but worsen fouling due to organic matter. Thus, the prevention solution should address both issues at once which might be very challenging. However, researches have investigated omniphobic-membranes for effacing those challenges at once.

Omniphobic (re-entrant) surfaces possess both hydrophobicity (water repellent) and the oleophobic (oil repellent) characteristics as a result of inherent roughness and the low surface free energy. Typically to fabricate those surfaces, the nanoparticles are immobilized in a very low surface free energy solution, usually containing fluoropolymers. Boo *et al.* fabricated re-entrant surfaces with silica nanoparticles and fluoroalkyl silanes (FAS) with different molecular lengths [170]. They claim that the membrane modified with the silica nanoparticles plus the longer chain (FAS) showed the best MD performance even for low surface tension feed waters. Moreover, Huang *et al.* developed an omniphobic membrane using Zinc nano-particles that operated 96 hours continuously in CO₂ absorption without doping the performance [171]. Li *et al.*, for the first time, deployed an omniphobic membrane for D-CH₄ recovery from anaerobic reactor effluents [172]. Although they could achieve over 90% CH₄ recovery, the lack of long-term performance provides no clue on wetting and fouling mitigation. Huang *et al.* claimed that those membranes could effectively mitigate membrane wetting and fouling simultaneously, but they only provide the long-term performance for wetting resistance in MD applications [173]. However, the underwater oleophobicity of the membrane proved that their membrane can repel oil

containing feed effectively. Lack of study under subsequent wetting and different fouling conditions create research gap that should be further investigated.

However, yet there are very few studies investigated to overcome both challenges at once because most of the liquid feed used in MCs are absorbents rather than waste effluents. Therefore, this work is aimed to study the membrane- and operational related parameters plus develop better membranes for membrane contactors in the context of recovering CH_4 from anaerobic reactor effluents. **Figure 1.8** shows the conceptual framework of this study.

Figure 1.8 Conceptual framework of the thesis work

1.5 Research objectives and Thesis overview

1.5.1 Research objective

The basic research objective of this study is maximizing energy recovery from the anaerobic process by recovering D-CH₄ from liquid effluent. The specific directives are,

- Understanding the fundamentals of G-L MCs to utilize in D-CH₄ recovery from real anaerobic effluents and the effect of membrane parameters on the recovery performance
- A comprehensive study on membrane related and operational-related parameters affecting D-CH₄ recovery performance based on theoretical estimations and experimental confirmations.
- Tailoring the membrane surface to achieve anti-wetting properties of a highly porous laboratory-made PVDF membrane, which can also withstand low-strength wastewater effluent (*i.e.*, AnMBR effluent) during D-CH₄ recovery.
- Improving both wetting and fouling resistivity of laboratory-developed PVDF membrane for long-term applicability in MC with high-strength wastewater (*i.e.*, UASB effluent) during D-CH₄ recovery using amphiphilic copolymers.
- Detailed study on the available foulants in the effluents, characterization, and determination of fouling formation during the application.
- In-depth study of the membrane- and operational-related parameters on energy recovery for D-CH₄ recovery performance based on theoretical and experimental estimations.
- Concluding the studies and benchmarking the modified membranes with commercially available degassing membranes and the literature.

1.5.2 Thesis overview

This thesis aims to achieve objectives, as mentioned above with four experimental studies. Thus, overall, the thesis encompasses seven chapters, which are summarized as follows:

Chapter 1: GENERAL BACKGROUND and THESIS OVERVIEW

This chapter covers the basic introduction of the problem definition and comprehensive review about the gas-liquid membrane contactor technology and the associated challenges and the current state of CH₄ recovery from anaerobic reactor effluents.

Chapter 2: Materials, Membrane Fabrication, and Characterizations

Herein, presents the detailed descriptions of materials used and methodologies followed in the entire work.

Chapter 3: Hydrophobic Modification of PVDF with Fluorinated Agents

This work aimed to produce a highly porous hydrophobic PVDF membrane to analyze the mass transfer behavior and long-term stability in the CH₄ recovery application using anaerobic reactor effluent and compare with the commercial microporous degassing membrane. The produced membrane showed better CH₄ recovery performance than the commercial PP membrane and a very stable flux without pore wetting during 10 days of operation with synthetic effluent (made by saturating a 60:40 CH₄/CO₂ mixture into tap

water). Further, it operated for 8 days without significant fouling (7% flux drop during 8 days of operation) with actual AnMBR effluent.

Chapter 4: The Influence of Membrane Characteristics and Operating Parameters

In this study, a comprehensive theoretical and experimental analysis of the CH₄ recovery performance of three kinds of membranes (*i.e.*, porous, nonporous, and composite membranes) under various operating conditions was performed. And, was attempted to provide the criteria to realize the best CH₄ recovery efficiency.

Chapter 5: Coating of PVDF Membranes with PDMS for Antiwetting Functionality

This chapter demonstrates the fabrication of a composite hollow fiber membrane that efficiently recovers D-CH₄ from anaerobic wastewater treatment effluents via the MC process. The long-term performance analysis using actual AnMBR and UASB reactor effluents showed that the best membrane is stable for low strength wastewater, yet applicable with high strength wastewater with proper cleaning.

Chapter 6: Antifouling Coating of PDMS-PVDF Membranes with Amphiphilic Additives

Herein presents a dual-functioned (anti-wetting and antifouling) membrane modification for effective utilization in the MC process for CH₄ stripping from anaerobic effluents. The membrane fabricated in chapter 5 was further modified with two types of commercially available PDMS copolymers with hydrophilic segments of different lengths

to accomplish the antifouling characteristics. Those developed membranes exhibited better fouling resistance capability for at least 3 days.

Chapter 7: General Conclusions and Future Prospects

The experimental evidence is summarized in this chapter. Moreover, the recommendations for future work is presented here.

Figure 1.9 Thesis overview

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2 Materials, Membrane Fabrication, and Characterization

2.1 Materials and chemicals

Unless otherwise specified, all chemicals were purchased from Sigma-Aldrich and were used without further purifications. PVDF (Kynar 740) in pellet form was used to fabricate the membranes. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck), Pluronic F-127 (PEO₁₀₀-PPO₆₅-PEO₁₀₀, CAS# 9003-11-6, Sigma), and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, Merck) were used as the solvent and non-solvent additives, respectively. To avoid shrinkage during membrane drying, *n*-hexane (CH₃(CH₂)₄CH₃, CAS# 110-54-3, Merck), and 2-propanol (C₃H₈O, IPA, CAS# 67-63-0, Merck) were used to immerse the membranes. Dextran solutions with molecular weights ranging from 6,000 to 500,000 Da ((C₆H₁₀O₅)_n, CAS#9004-54-0, Sigma) were used to determine the molecular weight cutoff (MWCO) of the fabricated membranes.

For modification of hollow-fiber membranes in **Chapter 3**, α,ω -triethoxysilane-terminated perfluoropolyether ((EtO)₃Si-PFPE-Si(OEt)₃), Fluorolink S10, Solvay) and tetraethoxyorthosilicate (TEOS, CAS# 78-10-4, Merck) was used as the fluorinated silane and silica precursor, respectively. Toluene (CAS# 108-88-3, Merck) was used as the dispersive solvent for TEOS and Fluorolink S10. Sodium hydroxide (NaOH, pellets, CAS# 1310-73-2, Merck) was selected to prepare solutions with different pH values for the membrane surface modification. All aqueous solutions were prepared with deionized water (Milli-Q, 18 M Ω ·cm).

The composite membrane fabricated in **Chapter 4** required glycerol (CAS# 56-81-5, Merck), Polydimethylsiloxane elastomer kit (SYLGARD® 184, Dow Corning),

Polyethylene glycol (CAS#25322-68-3, MW:400, Sigma) and Chloroform (CHCl_3 , CAS# 67-66-3, VWR) as the pore protector, composite polymer mixture and the dispersive solvent.

PDMS coating stated in **Chapter 5** was prepared using n-hexane (CAS# 110-54-3, Merck), and glycerol (CAS# 56-81-5, Merck) and PDMS elastomer kit (SYLGARD® 184, Dow Corning) as the dispersive solvent, pore protector, and the hydrophobic modifier. The two components of the PDMS kit was mixed at the recommended ratio (elastomer base, Part-A: 10 parts; cross-linker, Part B: 1 part) ca. 30 min before its use as prepolymer mixture.

The anti-fouling modification as mentioned in **Chapter 6** required polydimethylsiloxane-co-3-(2-(2-hydroxyethoxy)ethoxy)propylmethylsiloxane (MDL# MFCD01324299, Sigma Aldrich), poly[dimethylsiloxane-co-methyl(3-hydroxypropyl)siloxane]-graft-poly(ethylene glycol) methyl ether (CAS# 68938-54-5, Sigma Aldrich) and PDMS elastomer kit (SYLGARD® 184, Dow Corning). Chloroform (CHCl_3 , CAS# 67-66-3) was purchased from VWR and used as the dispersive solvent for the coating solution.

And, the commercial polypropylene-made hollow fiber degassing membranes (PP-DGM) and flat-sheet microporous PVDF membranes filters (47 mm, average pore size: 0.22 μm) were obtained from Edgexcross Membrane Technology Co., Ltd. and Hawach Scientific Co., Ltd., respectively for comparison purposes.

AnMBR and UASB effluents were obtained from Singapore Membrane Technology Center's (SMTC) pilot-scale plant and Singapore's Public Utilities Board's

(PUB) industrial-scale wastewater treatment facility, respectively. Collected samples were utilized within a month after collection, and all samples were kept in a cold room (at 4 °C). Tap water was used for short term studies.

2.2 Membrane characterization

The pure water permeability (PWP) and molecular weight cut-off (MWCO) of freshly fabricated PVDF membrane (prior modification) were tested using laboratory-scale hollow-fiber modules containing four fibers each. The operating pressure was kept at 34 kPa, and the permeate was collected three times, for 5 min each time, and weighed for calculation of the PWP. To obtain the MWCO, dextran solutions with molecular weights between 6,000 and 500,000 were prepared and allowed to flow through the same laboratory-scale modules that were used to determine the PWP. The operating pressure was kept at 34 kPa and the permeate was collected after 30 min. Feed and permeate were characterized using gel permeation chromatography (GPC) (PL-GPC50 Plus, Avarian, Inc.).

The diameters of the hollow fiber membranes were determined using a digital microscope (VHS-500F, KEYENCE) with the help of image analysis software provided by the manufacturer. The membrane morphology (cross-section and inner and outer surfaces) of unmodified and modified membranes were obtained using field emission scanning electron microscope (FESEM, JSM-7200F, JEOL). To obtain the cross-sectional images, the samples were fractured in liquid nitrogen, and a thin layer of platinum was sputtered on the sample surface at 20 mA for 45 sec using a JEOL JFC-1600 auto fine coater. The elemental distribution across the membrane cross-section was observed by energy-dispersive X-ray spectroscopy (EDS) equipped on the FESEM. The inner surface

morphologies of selected membranes were studied with an atomic force microscope (AFM) (Park NX10, Park Systems) using standard non-contact mode silicon tips (610-1051 Mounted PPP-NCHR, Park Systems). The raw AFM images were processed using the Gwyddion platform (Version 2.51) [174].

The surface infrared spectra of lab-made membranes before and after the modifications were recorded between 400 cm^{-1} and 4000 cm^{-1} on an IR Prestige-21 Fourier transform infrared (FTIR) spectrophotometer (SHIMADZU). The spectra were recorded at a resolution of 4 cm^{-1} in attenuated total reflection (ATR) mode after 45 scans.

Tensiometer (DCAT11 Dataphysics) was used to determine the dynamic contact angle of the membranes. After the tensiometer was set into three consecutive cycles, the hollow fiber samples in 2 cm length were fixed on the sample holder, followed by the measurement of the dynamic contact angle. The dynamic contact angle was calculated by the software based on the surface tension force, the geometry of the membrane, and water surface tension at $20\text{ }^{\circ}\text{C}$. The static water contact angle (WCA) measurements of cut-open fibers were performed on a goniometer system (OCA15, DataPhysics) using $0.7\text{ }\mu\text{L}$ of DI-water. The WCA values were taken after $\sim 30\text{--}35\text{ s}$ of membrane-water contact by analyzing the frames captured by the built-in camera of the setup. For statistical purposes, a minimum of 2 different samples was used for each membrane, and at least 5 different frames were analyzed in total per sample.

A dead-end module with one fiber was used to determine the CEP of the modified membranes. The liquid pressure was created by nitrogen gas and gradually increased in 1 psi intervals (for each pressure level, the module was pressured for 10 min) until the first water droplet appeared on the membrane surface.

The surface streaming potential (SSP) measurements of the unmodified and modified hollow fiber membranes were made on an electrokinetic analyzer (SurPASS™ 3, Anton Paar) using 10 mM sodium chloride solution as the supporting electrolyte without pH adjustment (pH ~6).

The membrane porosity was calculated based on the density measurements, as described by Khayet *et al.*[175]. Additionally, in Chapter 6 porosity measurements were estimated using a simple calculation. Firstly, the dry mass and density of using 10 cm long hollow fiber membranes were measured. Then, using the density values of PVDF (1.78 g cm⁻³) and PDMS (0.965 g cm⁻³) obtained from the literature [176, 177], the estimated pore volume was calculated. For the PDMS-modified membranes, the assumption was made that all fiber dimensions are consistent and used the average mass and density values of unmodified PVDF membranes while calculating the pore densities. Capillary flow porometer (Porous Materials Inc., model CFP-1500A) was used to determine the mean pore sizes of membranes. And a Zwick Roell Z0.5 universal testing machine was used to determine the mechanical properties of both unmodified and modified hollow-fiber samples.

The excitation-emission matrix fluorescence spectroscopy (EEM-FS) readings of the MC feeds as well as the extracts of the fouling layers formed on membranes were made on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). For the preparation of fouling layer extracts, small pieces of fouled membranes (~4.5 cm²) placed in regular glass beakers (filled with 20 mL of DI water) were subjected to bath sonication (Fisher Scientific, FB 15068) for 30 minutes.

For the characterization of the anaerobic effluents, a multitude of analyzes was performed. COD was tested using a dedicated kit as described by the manufacturer (Method 8000, Hach). Total Organic Carbon (TOC) and Total Nitrogen (TN) tests were performed using TOC-VCHS (Shimadzu) and TNM-1 (Shimadzu) devices, respectively. Besides, the liquid chromatography-organic carbon detection (LC-OCD) measurements were performed using a DOC-Labor Dr. Huber setup (Model 8), dynamic light scattering (DLS) measurements on a ZetaPALS device (Brookhaven Instruments Corp.). The anion-cation content of the anaerobic effluents was measured using Dionex™ ICS-1100 Ion Chromatography (Thermo Scientific) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima™ 8000, PerkinElmer, Inc.). The protein concentration of the anaerobic effluent samples was analyzed using a BCA bicinchoninic acid assay (Pierce™ BCA Protein Assay Kit, Thermo Fisher Scientific). **Table 2.1** shows the wastewater characteristics used in the experiments.

Table 2.1 Characteristics of the industrial anaerobic wastewater treatment effluents used

Parameter	AnMBR	UASB
TOC (ppm)	8.8 ± 1.5	78.5 ± 3.1
COD (ppm)	21 ± 0.7	190 ± 2.8
TN (ppm)	33.8 ± 1.6	71 ± 2.6
Protein concentration (ppm)	25.6 ± 1.4	64.2 ± 6.6
Ion concentrations (ppm)		
Cl⁻	80.76 ± 1.17	234.00 ± 0.15
PO₄³⁻	9.42 ± 0.05	not detected
SO₄²⁻	27.46 ± 0.09	109.86 ± 0.03
Na⁺	17.81 ± 3.93	101.15 ± 0.50
Mg²⁺	3.59 ± 0.01	19.06 ± 0.17
Ca²⁺	14.12 ± 0.01	33.34 ± 0.33
Fe³⁺	0.02 ± 0.01	0.23 ± 0.01

2.3 D-CH₄ recovery experiments

2.3.1 The experimental set-up

The membrane contactor setup used for D-CH₄ recovery experiments is depicted in

Figure 2.1.

Figure 2.1 Experimental G-L MC set-up. Note that, MFC, PT, BFM, HOGV, and Micro-GC stands for “Mass Flow Controller,” “Pressure Transducer,” “Bubble Flow Meter,” “Hand-operated Gate Valve,” and “Micro Gas Chromatograph,” respectively. And, the numbers seen inside the Saturator Tank (from 1 to 4) indicate the temperature (thermocouple), pressure, pH, and D-CH₄ indicators/sensors in sequence.

In a typical experiment, 12 L of either tap water or anaerobic effluent was first filled into the stainless-steel saturator tank. Afterward, simulated biogas (60/40 v/v% CH₄/CO₂, Air Liquide) was continuously fed from the bottom of the tank at a rate of 20 standard cubic centimeters per minute (SCCM) continuously to saturate the “effluent” with CH₄ fully. Then, the solution was pumped to the lumen side of the membrane module, while nitrogen gas (N₂, Air Liquide) was applied to the shell side of the module as the sweep gas at a rate of 20 SCCM. The temperature, pressure, pH, and D-CH₄ concentration (CH₄ sensor, Mini-Pro, Pro-Oceanus) were continuously monitored in the saturator tank. The gas flow rates (biogas and N₂) were regulated through two mass flow controllers (MFC, Cole-Parmer,

USA, 50 SCCM). The recovered biogas volume and the concentration was quantified with a digital bubble flowmeter (Bios Defender™ 530L), and gas chromatography (490 Micro GC Biogas Analyzer, Agilent Technologies), respectively. Counter-current operation mode was employed for all the experiments. **Table 2.2** and **Table 2.3** given below provide further details regarding the operation conditions of saturator tank and membranes modules.

Table 2.2 Operation conditions of saturator tank († Atmospheric conditions)

Headspace	Temperature (°C)	~24-25[†]
	Pressure (atm)	1 [†]
	Biogas composition (v/v%)	60/40
Liquid phase	Volume (L)	12
	Temperature (°C)	~24-25 [†]
	CH ₄ concentration (mg L ⁻¹)	15–12
	CO ₂ concentration (mg L ⁻¹)	550–576
General details	Biogas saturation ratio (%)	60–65
	Biogas feeding rate (mL min ⁻¹)	20
	Agitator speed (rpm)	100

Table 2.3 Operation conditions of membrane modules († Atmospheric conditions)

Membrane modules	Commercial membranes	In-house membranes
Liquid velocity range tested, min-max (m s⁻¹)	0.02-0.30	0.02-0.35
Reynold's number (Re)	~4-67	~ 9- 227
Packing density (φ)	~0.029-0.11	~0.03-0.10
%CO₂ in the sweep gas stream	~0.20-1.00	~0.20-0.50
%CH₄ gas in the sweep gas stream	~1.4-17.0	~1.2-7.0
Average CO₂/CH₄ flux ratio	~18	~9-11
Sweep gas flow rate (m s⁻¹)	20 (0.0005)	20 (0.0005)
Sweep gas pressure (atm)	1 [†]	1 [†]
Sweep gas temperature (°C)	~25 [†]	~25 [†]

2.3.2 Membrane module preparation

Figure 2.2 Photographs of a representative hollow fiber membrane module used in the project: (a) Whole module, and (b) side view of a module. (The matrix material that the hollow fibers are embedded in epoxy resin.)

Membrane modules were prepared by enclosing 6-100 pieces of fibers in PP-made tubes connected with stainless steel joints potted with epoxy glue at each end (as displayed in **Figure 2.2**).

2.3.3 Experimental analysis

2.3.3.1 CH₄ recovery flux and efficiency determination

The experimental recovery flux ($\text{mol m}^{-2} \text{s}^{-1}$) was calculated using the **Equation.2.1**:

$$\text{Flux (J)} = \frac{G(C_{i,G(\text{out})} - C_{i,G(\text{in})})}{A_M} \dots\dots\dots (2-1)$$

Where, G , $C_{i,G(\text{out})}$, $C_{i,G(\text{in})}$ and A_M are the gas flow rate ($\text{m}^3 \text{s}^{-1}$), species outlet concentration in the gas (mol m^{-3}), species inlet concentration in the gas (mol m^{-3}), and the membrane mass transfer area (m^2), respectively. The membrane mass transfer area was calculated considering the inner diameters of the fibers as lumen side operation was employed in all experiments. The percentage recovery of the gases (RE) is given by **Equation 2.2**, as seen below.

$$RE = \left(\frac{C_{i,L(in)} - C_{i,L(out)}}{C_{i,L(in)}} \right) \dots\dots\dots (2-2)$$

Where $C_{i,L(out)}$ and $C_{i,L(in)}$ species outlet concentration in the liquid (mol m^{-3}), and species inlet concentration in the liquid (mol m^{-3}).

2.3.3.2 Overall mass transfer coefficient determination

The experimental Overall Mass Transfer Coefficient (K_{OL} , m s^{-1}) can be calculated using the experimental gas flux and their concentrations [59], in which the following expression gives the **Equation. 2-3**,

$$K_{OL} = \frac{L (C_{i,L(in)} - C_{i,L(out)})}{A_M \cdot \Delta C_{lm}} \dots\dots\dots (2-3)$$

Where ΔC_{lm} is, the log-mean concentration difference (mol m^{-3}). The **Equation 2-4** gives the log mean concentration difference.

$$\Delta C_{lm} = \frac{(C_{i,L(in)} - H_i C_{i,G(out)}) - (C_{i,L(out)} - H_i C_{i,G(in)})}{\ln \left[\frac{C_{i,L(in)} - H_i C_{i,G(out)}}{C_{i,L(out)} - H_i C_{i,G(in)}} \right]} \dots\dots\dots (2-4)$$

where H represents Henry's law constant (dimensionless).

2.3.3.3 Wilson plot analysis for membrane mass transfer coefficient determination

Wilson's Plot Analysis is a useful method for determining the membrane mass transfer coefficient in membrane systems [64, 65, 138]. This method has been developed based on the resistance-in-series model, overall mass transfer resistance corresponding to the liquid side can be expressed in terms of individual liquid phase mass transfer coefficient, gas phase mass transfer coefficient and membrane mass transfer coefficient. The resistance-in-series model is depicted in the following equation (**Equation 2-5**):

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{d_i}{H.k_M.d_{lm}} + \frac{d_i}{H.k_G.d_o} \dots\dots\dots (2-5)$$

Where, K_{OL} , k_L , k_G , k_M , d_i , d_o , d_{lm} , and H represent the overall mass transfer coefficient based on the liquid side ($m\ s^{-1}$), individual liquid phases mass transfer coefficient ($m\ s^{-1}$), individual gas phases mass transfer coefficient ($m\ s^{-1}$), membrane mass transfer coefficient ($m\ s^{-1}$), membrane inner diameter (m), membrane outer diameter (m), log mean diameter (m), and the Henry's law constant (dimensionless), respectively.

The shell side and the tube side mass transfer coefficients depend on the hydrodynamics and the system geometry. Typically, for the gas-liquid MCs, the gas phase mass transfer resistance is often neglected as the resistance to flow gas species in a gaseous medium is too low compared to the liquid and membrane phase. Moreover, considering the liquid phase correlations in the literature, it is found that k_L is proportional to some power (α) of liquid velocity. Then the resistance-in-series model can be rearranged as in **Equation 2-6**, where a and b are numerical constants that can be derived from the graph between K_{OL}^{-1} and $v^{-\alpha}$, where the α is the value that gives the best fit to the graph.

$$\frac{1}{K_{OL}} = a v_L^{-\alpha} + b \dots\dots\dots (2-6)$$

2.4 Membrane fabrication and modifications

2.4.1 PVDF support membrane fabrication

Figure 2.3 Graphical representation of the hollow fiber spinning process by NIPS

Hollow fiber PVDF membranes were prepared using dry jet-wet spinning (non-solvent induced phase separation, NIPS) process with a custom-designed setup. **Figure 2.3** represents the typical hollow fiber spinning set-up with the NIPS process. Kynar 740 PVDF pellets were dried at 50°C under a vacuum for at least 12 hours to remove moisture before dope preparation. Based on Loh and Wang [178], the dope, containing 18% PVDF, 3% Pluronic F-127, and 3% LiCl dissolved in 76% NMP, was prepared in a jacketed flask with mechanical stirring at 60°C for 2 to 3 days to obtain a homogeneous solution. The dope solution was then cooled to room temperature before degassing and kept still for at least 1 day before spinning. The spinning parameters used for the fabrication of hollow-fiber membranes are summarized in **Table 2.4**. Finally, the nascent fibers from the spinning were immersed in Milli-Q water for 3 to 4 days with continuous changing of water to remove non-solvent trapped in the membrane.

Table 2.4 Spinning parameters

Spinning parameters	Value
Spinneret ID/OD (mm)	1/2
Bore fluid composition	70% (wt) NMP
External coagulant	Tap water
Dope flow rate (g min ⁻¹)	6
Bore fluid flow rate (ml min ⁻¹)	6
Air gap (cm)	1
Take-up speed	Freefall

2.4.2 Chapter 3: Surface hydrophobic modification and Taguchi method of analyzing modification parameters

2.4.2.1 Surface hydrophobic modification

The surface modification involved three major steps: activation of PVDF surface, reaction with Fluorolink S10/TEOS solution, and curing of membranes by application of heat. NaOH solutions with different pH values (8, 10, 12) were used to activate the surface of the PVDF. This process is termed dehydrofluorination as fluorine in the PVDF backbone is removed and substituted by hydroxide ion [179]. At mild conditions (low pH and short reaction times), hydroxyl groups on the PVDF surface serve as the active sites for TEOS to react with, allowing Fluorolink S10 to graft onto the membrane surface [180]. However, severe dehydrofluorination conditions will further oxidize the hydroxyl group on the PVDF surface which will result in the formation of carbonyl groups that cannot react with TEOS. The dehydrofluorination mechanism is mentioned elsewhere [181].

0.01M NaOH solution was prepared by dissolving NaOH pellets in Milli-Q water to obtain a NaOH solution of pH 12. This solution was then diluted to obtain NaOH solutions with pH 10 and 8. The membranes were immersed in NaOH solution for a certain

period (30, 60, or 90 min), and the reaction was quenched by rinsing the fibers with Milli-Q water for 2 to 3 min. The membranes were then immersed in a chemical solution containing TEOS and Fluorolink S10, which was prepared based on Wongchitphimon *et al.* [182], for a specific time (30, 60, or 90 min). Finally, the fibers were kept in the oven at 60°C for 1 hour to cure the membrane.

2.4.2.2 Taguchi method for parameters optimization

The Taguchi approach uses a highly fractionated orthogonal array (OA) to minimize the number of experiments required for evaluation of the effects of controlled parameters on system performance. For example, whereas 3^3 (27) experiments would be required to study three levels of three controlled parameters in the traditional one-factorial design method, the Taguchi approach greatly reduces this number to only 9. The Taguchi design method is widely used in many engineering design contexts [183, 184]. The L9 OA, which contains 9 runs with all possible combinations of each level of the parameters according to the Taguchi method, was selected for the parameter optimization of the hydrophobic surface modification of the PVDF membrane in **Chapter 3**.

Control parameters, levels, and orthogonal array formation

Through our preliminary experiments and the previous study conducted by Wongchitphimon *et al.* [182], the major parameters affecting the surface modification were identified in this study as the pH of the alkaline solution, the alkaline treatment time, and the TEOS/Fluorolink S10 grafting time. The L9 OA of the studied parameters with three levels is shown in **Table 2.5**. For each run, three replicate experiments were conducted, and the contact angle of five randomly selected fibers was measured, and average contact angles were reported.

Signal to noise ratio

The signal to noise (S/N) ratio indicates the scattering of the responses around a target value under different noise conditions [185]. The calculation of this ratio can be selected according to the requirement of the quality objective of the process. The Taguchi method prescribes three quality objectives: the-larger-the-better, the-smaller-the-better, and the-nominal-the-better [186]. Each of these quality objectives has a different S/N ratio. The major objective of this study is to maximize the contact angle. Thus, the most appropriate Taguchi quality objective is the-larger-the-better. The S/N ratio for this quality objective is given by the **Equation 2-7**.

$$\frac{S}{N} = -10 \log_{10} \left\{ \frac{1}{n} \sum_{i=1}^n \left(\frac{1}{CA_i} \right)^2 \right\} \dots\dots\dots (2-7)$$

Where n is the number of measurements under the same experimental conditions, and CA_i represents the contact angle of the ith experimental condition.

The mean values of the S/N ratios were taken for each experimental condition. The effect of S/N ratio on each control parameter was obtained according to the OA design in the Taguchi method. The deviation of the S/N ratio of each parameter from the grand mean value can be used to predict the S/N ratios for other operating conditions (**Equation 2-8**) [187].

$$\left(\frac{S}{N} \right)_{\text{Predicted}} = \mu + \sum_{i=1}^n (\bar{y}_i - \mu) \dots\dots\dots (2-8)$$

Where μ is the grand mean and $\bar{y}_i$ is the mean S/N ratio of the desired levels of the process parameters. The predicted S/N ratio can be used to calculate the average contact angle using

the formula of the S/N ratio for the-larger-the-better, as presented above, for a generic modification condition.

Table 2.5 Taguchi L9 orthogonal array

Exp. no	Modification parameters		
	pH	NaOH treatment time (min)	Fluorolink S10/TEOS grafting time (min)
1	8	30	30
2	8	60	60
3	8	90	90
4	10	30	60
5	10	60	90
6	10	90	30
7	12	30	90
8	12	60	30
9	12	90	60

Analysis of variance

Analysis of variance was performed on the S/N ratios. The purpose of analysis of variance is to establish whether the modification parameters have a statistically significant effect on the contact angle. The F-test (ratio of variances) and the percentage of contribution can be used to determine which modification parameter/s affect the contact angle the most. Generally, the greater the F value, the higher the effect of the control parameter. The F value can be calculated using **Equation 2-9**;

$$F = \frac{MS_A}{MS_e} \dots\dots\dots (2-9)$$

Where, MS_A and MS_e are the mean sum of squares of the parameter A and the error, respectively. MS_A and MS_e can be calculated by dividing the sum of the squares (SS_A or SS_e) by the degree of freedom (DOE) of each parameter. The following formulas give the sums of squares.

$$SS_A = \sum_{i=1}^{k_A} \left(\frac{A_i^2}{n_{Ai}} \right) - \frac{T^2}{N} \dots\dots\dots (2-10)$$

$$SS_T = \sum_{i=1}^N y_i^2 - \frac{T^2}{N} \dots\dots\dots (2-11)$$

$$SS_e = SS_T - SS_A \dots\dots\dots (2-12)$$

$$DOE_A = k_A - 1 \dots\dots\dots (2-13)$$

Where k_A is the number of levels in factor A, A_i is the sum of all observations of level i of factor A, n_{Ai} is the number of all observations at level i of factor A, T is the sum of all observations, and N is the total number of observations.

The percentage contribution for comparing the effect of each parameter on the process,

$$\% \text{ contribution} = \left(\frac{SS_A - DOE_A \times MS_e}{SS_T} \right) \times 100\% \dots\dots\dots (2-14)$$

2.4.3 Chapter 4: Theoretical considerations of mass transfer analysis and PDMS coating

2.4.3.1 Theoretical considerations of mass transfer analysis

Figure 2.4 Schematic of the MC module and mass balance for a small element along the length of one fiber

Figure 2.4 illustrates the basic MC configuration where the feed solution is circulated through the lumen side and the stripping gas through the shell side in counter-current mode. The basic equations to estimate the CH₄ flux and recovery can be derived assuming the steady-state operation as per the following equations.

Basic Equations

The elemental mass balance in the gas phase along a differential length (ΔZ) of the contactor at a steady state can be described as follows.

$$G(C_{i,G} + \Delta C_{i,G}) - GC_{i,G} = J(\pi d_i N_f \Delta Z) \dots\dots\dots (2-15)$$

Where G is the sweep gas flow rate ($\text{m}^3 \text{s}^{-1}$), $C_{i,G}$ is the molar concentration of gas i in the gas phase (mol m^{-3}), $\Delta C_{i,G}$ is the difference in the molar concentration of gas i (mol m^{-3}), J is the CH₄ desorption (or recovery) flux ($\text{mol m}^{-2} \text{s}^{-1}$), d_i is the inner diameter of membranes (m), and N_f is the number of fibers.

By integrating **Equation 2-15**, the outlet concentration of the gas can be obtained as:

$$C_{i,G(out)} = \frac{JA_M}{G} \dots\dots\dots (2-16)$$

Where A_M is the mass transfer area calculated from the inner radius of the membrane (m^2) and $C_{i,G(out)}$ is the molar concentrations of gas i in the gas outlet of the membrane module ($mol\ m^{-3}$). Applying the overall mass balance to the entire MC module, we can get the following equation.

$$LC_{i,L(in)} + GC_{i,G(in)} = LC_{i,L(out)} + GC_{i,G(out)} \dots\dots\dots (2-17)$$

Where L is the liquid flow rate ($m^3\ s^{-1}$); and $C_{i,L(in)}$, $C_{i,G(in)}$, and $C_{i,L(out)}$ are the molar concentrations of gas i in the liquid inlet, gas inlet, and liquid outlet of the membrane module ($mol\ m^{-3}$), respectively. As $C_{i,G(in)} = 0$, **Equation 2-17** can be simplified as follows.

$$C_{i,G(out)} = \frac{L(C_{i,L(in)} - C_{i,L(out)})}{G} \dots\dots\dots (2-18)$$

Combining **Equation 2-16** and 2-18, the equation for CH_4 flux can be obtained as shown below and can also be rewritten with the overall mass transfer coefficient (K_{OL} ; $m\ s^{-1}$).

$$J = \frac{L(C_{i,L(in)} - C_{i,L(out)})}{A_M} = K_{OL}\Delta C_{lm} \dots\dots\dots (2-19)$$

Using Eqs. (2), (4), and (19), the CH_4 flux can be calculated as in **Equation 2-20**.

$$J = \frac{LC_{i,L(in)}}{A_M} \left[1 + \frac{\left(1 - \frac{H_i L}{G}\right)}{\left(\frac{H_i L}{G}\right) - \exp\left(\frac{K_{OL} A_M}{L} \left(1 - \frac{H_i L}{G}\right)\right)} \right] \dots\dots\dots (2-20)$$

Note that for the case of liquid in shell side operation A_M should be calculated based on the outside fiber diameter, and all other parameters and equations will remain unchanged.

Theoretical calculation of K_{OL} and k_L

The resistance in-series model is given by **Equation 2-5**. The individual mass transfer coefficient in the liquid phase can be determined by Leveque's equation (**Equation 2-21**), given that the liquid used in the experiment flows through the lumen side of the MC module [188].

$$k_L = 1.62 \frac{D_{i,L}}{d_i} \left[\frac{d_i^2 u}{Z D_{i,L}} \right]^{\frac{1}{3}} = 1.62 \frac{D_{i,L}}{d_i} \left[\frac{4 L d_i}{A_M D_{i,L}} \right]^{\frac{1}{3}} \dots\dots\dots (2-21)$$

Where $D_{i,L}$ is the diffusion coefficient of gas i in the liquid phase ($m^2 s^{-1}$), u is the liquid velocity inside membrane fiber ($m s^{-1}$), and Z is the effective module length (m). **Equation 2-21** is valid for Gratz numbers greater than 4 where the Gratz number can be calculated from the previous literature [47]. In this study, all of the values calculated by **Equation 2-21** were used only when the Gratz numbers were greater than 4.

The k_M^P of porous membranes can be described as follows.

$$k_M^P = \frac{D_{i,M} \varepsilon}{\tau \delta} \dots\dots\dots (2-22)$$

Where $D_{i,M}$ is the diffusion coefficient gas i inside the membrane, ε is the membrane porosity, τ is the membrane tortuosity based on the Bruggeman relation [189], and δ is the

membrane thickness. As for the case that the ε is not detectable (i.e., non-porous membrane), the k_M^d was derived as follows [58].

$$k_M^d = \frac{\text{Permiability} \times \text{Partial Pressure}}{\delta} \dots\dots\dots (2-23)$$

Where the permeability coefficient and partial pressure are measured in $\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}$ and Pa respectively (The total pressure 1 bar; the partial pressure of CH_4 is 0.6 bar; and the liquid is saturated with biogas). For a composite membrane [190],

$$\frac{1}{k_M} = \frac{1}{k_M^d} + \frac{1}{k_M^p} \dots\dots\dots (2-24)$$

Where k_M^d is the membrane mass transfer coefficient of the dense coating layer (m s^{-1}), and k_M^p is the membrane mass transfer coefficient of the porous support layer (m s^{-1}). Lastly, the experimental k_M^{-1} required for the diagnosis of mass transfer dominance (i.e., $k_M^{-1} : K_{OL}^{-1}$) was roughly estimated by subtracting theoretical liquid-phase resistance (k_L^{-1}) from the experimental overall mass transfer resistance (K_{OL}^{-1}) obtained at different liquid velocities.

Given that the minimum gas to liquid flow rate (G/L) ratio to achieve a 98% recovery of dissolved CH_4 is found to be 0.034 [54], theoretical calculations were carried out over the range of higher G ($0.1\text{-}0.6 \text{ m}^3 \text{ day}^{-1}$, which translates into the variation in the G/L ratio from 0.05 to 0.3) at a fixed L of $2 \text{ m}^3 \text{ day}^{-1}$. For all the experimental and theoretical calculations, the influence of the gas phase was not considered as the gas-phase mass transfer resistance in the MC operation is negligible.

2.4.3.2 Membrane modifications

The hydrophobic membrane produced with optimum conditions in **Chapter 3** was used here as the PVDF porous membrane which was denoted as the PHM-PVDF membrane.

The preparation of the DHC-PVDF membrane was started by filling the pores of the PVDF membranes with glycerol to prevent the coating solution from penetrating the inner pores during the coating step. First, the PVDF membranes were submerged in 50 wt% glycerol for 2 days and then kept hanging for 1 day. Next, 20 pieces of dried hollow fiber membranes were placed inside a cylindrical shell with free ends and then potted with standard epoxy glue (Araldite®). Afterward, the PDMS coating solution was prepared by following the recommended mixing ratio for the PDMS kit of 10:1 (the elastomer base (Part A): cross-linker (Part B)). For the PDMS/PEG400 coating, PDMS and PEG-400 were dissolved in chloroform with the ratio of 3:1 to prepare a 20 wt% coating solution. Subsequently, the lumen of the hollow fiber membrane was rinsed with chloroform for 1 min prior to coating the hollow fiber lumen. The coating was conducted by feeding the coating solution alternatively to both ends of the hollow fibers for 2 min using a peristaltic pump at a flow rate of 180 ml min^{-1} . After that, the hollow fibers were cured at 80°C for 24 hrs and cooled down to room temperature. The modules packed with the cured fibers were immersed in water for 3 days to remove residual glycerol and kept at room temperature for drying.

2.4.4 Chapter 5: Composite membranes fabrication

Two types of PDMS-PVDF membranes were prepared by coating PVDF supports with PDMS: i) bulk-modified (BM), and ii) lumen-modified (LM) membranes. For the

surface modification of PVDF with a PDMS solution, we have first prepared the membrane modules. In a typical experiment, 20 pieces of dried hollow fiber membranes were placed inside a cylindrical shell with free ends and then potted with standard epoxy glue (Araldite®). Once the coating module gets cured, each end of the membranes was fed with n-hexane from their lumen side at the flow velocity of 0.3 m s^{-1} using a peristaltic pump. After ~1 min of rinsing with n-hexane, PDMS precursor mix solutions (of different concentrations: 0.5 or 5 wt%) were fed at the same flow rate for 2 min. (Those membranes were labeled as BM-00.5 and BM-05.0.) Then, N_2 gas at a pressure of 3 psi was purged through the lumen of the module for 1 min to remove excess coating solution and ensure the prepolymer penetrates through the membrane pores before setting. After that, the membrane modules were kept in the oven at 80°C for at least 24 hours for curing. Finally, the bulk-modified fibers were removed from the module and kept under room temperature.

Before coating the lumen side of the membranes with PDMS, the as-produced PVDF membranes were soaked in 50 vol% glycerol solution (prepared using Milli-Q water). Then, glycerol-exposed membranes were kept hanging for 24 hours to remove the excess solution trapped inside the membrane. Similar to the bulk modification case, these glycerol-treated fibers with the free ends were potted into a cylindrical shell with epoxy glue to prepare a module for feeding the PDMS precursor solution mix. The membrane lumen was then rinsed with n-hexane at the flow velocity of 0.3 m s^{-1} using a peristaltic pump for 1 min, followed by feeding of PDMS solutions of different concentrations (0.5, 5, or 10 wt%) in n-hexane at a velocity of 0.15 m s^{-1} for 2 min. Next, N_2 gas (at a pressure of 3 psi) was purged through the lumen of the module for 1 min to remove excess coating solution. After that, the modules (together with membranes inside) were kept in the oven at 80°C for at least 24 hours for further curing. Then, the modules were cooled down to

room temperature naturally. Finally, the modules were dismantled, and the surface-modified membranes were immersed in DI-water for 2 days to remove the trapped glycerol, followed by drying in the open air at room temperature. Obtained membranes were labeled as LM-00.5, LM-05.0, and LM-10.0, according to the PDMS concentrations used in their preparation.

Note that this method was adopted from Dr. Loh Chun Heng, who was a research fellow at Singapore Membrane Technology Center under Prof. Wang Rong in 2017.

2.4.5 Chapter 6: Anti-fouling membrane fabrication and energy analysis

2.4.5.1 Membrane modification

Before the surface modification, the washed and dried PVDF membranes were immersed to 50/50 (by volume) glycerol-water mixture for at least 48 hours to occupy the membrane pores with glycerol. Right after, these glycerol-impregnated membranes were dried at room temperature for 24 hours. To modify the PVDF supports with PDMS coatings, the coating setups were prepared as the first step by using membrane modules. Briefly, 20 pieces of glycerol-impregnated hollow fiber membranes were placed into a PP tube and stabilized from both ends with epoxy glue. After the glue sets, both ends of the module were trimmed and cleaned (to allow liquid passage). Then, a freshly prepared PDMS precursor mix, which is composed of an elastomer base (Part A) and cross-linker (Part B) at a ratio of 10:1 (by volume, as instructed by the manufacturer), was prepared in chloroform as a 10 wt% solution. At the same time, the membranes were initially wetted by pumping chloroform through the lumen sides at a liquid velocity of 0.3 m s^{-1} for 1 minute. (Note that glycerol and chloroform are practically immiscible.) Right after its preparation, the PDMS precursor solution was fed into each end of the membrane module

at a velocity of 0.15 m s^{-1} for 2 minutes. To remove the excess solution trapped inside, the coated membranes were later purged with nitrogen (N_2) gas at 3 psi (for 1 minute) and cured at 80°C (for 24 hours). The membranes were cooled down at room temperature for hours while inside the modules. Finally, the membranes were taken out from the module and soaked in DI water for 24-48 hours to remove entrapped glycerol and dried under room temperature. These PDMS-coated membranes were denoted as “PDMS-only,” which exhibit anti-wetting behavior against wastewater effluents.

For the preparation of the antifouling coatings, PDMS copolymers (PDMS-co-P1, PDMS-co-P2) were dissolved in chloroform as 20 wt% solutions and were kept under stirring for 30 minutes. Then, the just-prepared PDMS-PVDF membranes were exposed to PDMS copolymers while the curing state of the PDMS-coating was incomplete. To do so, one end of the coating module was sealed using a Viton™ tubing, and the PDMS copolymer solutions were fed from the other end. After allowing PDMS copolymer solutions to interact with just-prepared PDMS-coatings for around 3 minutes, the solutions were purged by N_2 flow at 3 psi for 1 minute. Then, the modules containing post-treated (hydrophilized) membranes were cured in the oven at 80°C (for 24 hours). After cooling down to the room temperature, the resulting membranes were taken out from the coating modules and immersed in DI water for 24-48 hours to remove the glycerol trapped in the membrane pores. Later, the membranes were dried naturally at room temperature. The membranes coated with polydimethylsiloxane-co-3-(2-(2-hydroxyethoxy)ethoxy)propylmethylsiloxane and poly[dimethylsiloxane-co-methyl(3-hydroxypropyl)siloxane]-graft-poly(ethylene glycol) methyl ether copolymers are termed as PDMS-co-P1 (short-side-chained), and PDMS-co-P2 (long-side-chained), respectively.

2.4.5.2 Theoretical considerations of energy analysis

The k_G can be described as below [191].

$$k_G = 8 \frac{D_{CH_4,G}}{d_e} \left(\frac{d_e^2 u_G \rho_G}{Z \mu_G} \right) \left(\frac{\mu_G}{\rho_G D_{CH_4,G}} \right)^{0.33} \dots\dots\dots (2-25)$$

where $D_{CH_4,G}$ is the diffusion coefficient of CH_4 in the gas phase ($m^2 s^{-1}$), d_e is the equivalent or hydraulic diameter (m), u_G is the sweep gas velocity ($m s^{-1}$), ρ_G is the density of the sweep gas ($kg m^{-3}$), and μ_G is the dynamic viscosity of sweep gas ($Pa s$). The d_e can be estimated from the following relationship.

$$d_e = \frac{d_s^2 - N_f d_o^2}{N_f d_o} = d_o \left(\frac{1 - \phi}{\phi} \right) \dots\dots\dots (2-26)$$

Where d_s is the module shell diameter (m), N_f is the number of fibers, and ϕ is the packing density. The ϕ can be obtained from **Equation 2-27** as below.

$$\phi = N_f \left(\frac{d_o}{d_s} \right)^2 \dots\dots\dots (2-27)$$

Meanwhile, the u_G can be described as follows.

$$u_G = \frac{4\phi d_i ZG}{A_M d_o^2 (1 - \phi)} \dots\dots\dots (2-28)$$

The net energy recovery per m^3 liquid treated (E_{NET} , $MJ m^{-3}$) of the MC operation can be determined using the following equation,

$$E_{\text{NET}} = E_{\text{MT}} - E_{\text{LP}} - E_{\text{GP}} \dots\dots\dots (2-29)$$

Where E_{MT} , E_{LP} , and E_{GP} is the energy required for the microturbine, liquid pump and the air blower in MJ m^{-3}

As mentioned in Wichitpan *et al.*, the productive energy by burning CH_4 using the microturbine can be calculated using the following equation [61],

$$E_{\text{MT}} = \frac{\eta_{\text{MT}} (\text{RE}_{\text{CH}_4} \omega_{\text{CH}_4} C_{\text{CH}_4, \text{L(in)}})}{L} \dots\dots\dots (2-30)$$

Where, η_{MT} , RE_{CH_4} , ω_{CH_4} , $C_{\text{CH}_4, \text{L(in)}}$ and L are, the efficiency of microturbine (0.3), CH_4 recovery, heating value of CH_4 (891 kJ mol^{-1}), effluent inlet CH_4 concentration (mol m^{-3}) and effluent flow rate ($\text{m}^3 \text{ s}^{-1}$).

Energy consumed by the liquid pump is given by,

$$E_{\text{LP}} = \frac{\Delta P_{\text{L}}}{\eta_{\text{motor}} \eta_{\text{ts}} \eta_{\text{pump}}} \dots\dots\dots (2-31)$$

Where ΔP_{L} and η represent the pressure drop (Pa) and the efficiency of the motor, transmission system (ts), and the pump, which are considered as 0.7.

The **Equation 2-32** expresses the pressure drop along the fibers,

$$\Delta P_{\text{L}} = 32 \frac{\mu_{\text{Water}} u Z}{d_i^2} \dots\dots\dots (2-32)$$

μ_{Water} , u , Z , and d_i are the dynamic viscosity of water (Pa s), liquid velocity (m s^{-1}), effective module length (m), and the fiber inner diameter (m).

All the constant values used in the literature is summarized in **Table 2.6** below.

Table 2.6 Constants used for calculations

Parameter	Value	Units	Reference
Diffusion coefficient of CH ₄ in water	1.88×10^{-9}	$\text{m}^2 \text{s}^{-1}$	[192]
Diffusion coefficient of CH ₄ in air	2.17×10^{-5}	$\text{m}^2 \text{s}^{-1}$	[193]
Diffusion coefficient of CH ₄ in N ₂	2.19×10^{-5}	$\text{m}^2 \text{s}^{-1}$	[143]
Henry constant for CH ₄	3.40×10^{-2}	Adiametional	[194]
Viscosity of water	8.90×10^{-4}	Pa s	[195]
Viscosity of air	1.85×10^{-5}	Pa s	[196]
Viscosity of N ₂	1.77×10^{-5}	Pa s	[196]
Density of water	997.08	kg m^{-3}	[195]
Density of air	1.20	kg m^{-3}	[197]
Density of N ₂	1.25	kg m^{-3}	
Universal gas constant	8.314	$\text{J mol}^{-1} \text{K}^{-1}$	[198]
Temperature	298	K	
Initial CH ₄ concentration	8.40×10^{-1}	mol m^{-3}	
Molecular weight of methane	1.60×10^{-2}	kg mol^{-1}	
Specific heat capacity of methane	55.65	MJ kg^{-1}	[199]
η_{MT}	0.3		
η_{motor}	0.7		
η_{ts}	0.7		
η_{pump}	0.7		
η_{blower}	0.7		
P_{in}	1.01×10^5	Pa	
P_{out}	1.52×10^5	Pa	

3 Hydrophobic Modification of PVDF with Fluorinated Agents¹

3.1 Introduction

D-CH₄ recovery from anaerobic wastewater effluents is still at the very early stage even though G-L MC technology grows older. However, to date, most of the studies used commercially available microporous PP or dense PDMS for recovering D-CH₄ from anaerobic effluents that both showed the similar mass transfer behavior but higher CH₄ recovery for the former than the latter highlighting the prominence of the micro-porosity. Besides having higher CH₄ recovery, it is equally important to improve the efficiency of the process for the optimum utilization of energy and other resources. Reducing the self-mass transfer hindrance of the membrane would be a promising approach for enhancing the efficiency of the process.

Howbeit, one of the most ordinary but critical problems those devices suffer from is membrane wetting, yet no perfect solution attained. For example, Wang et al. [200] reported that an overall mass transfer flux reduction of 20% could be expected from just 5% of pore wetting. Further, there is no hard and fast tool to claim the extent of hydrophobicity that needed to avoid membrane wetting since wetting is highly depending on the membrane type and the application. Still, hydrophobicity is the basic but pivotal requirement for a membrane to utilize in G-L MC applications.

Our previous study [59] successfully demonstrated the application of in-house-made Matrimid[®] membranes, hydrophobically modified with fluorinated silica particles, for CH₄ recovery from AnMBR effluent. However, major drawbacks with this membrane are the difficulty and complexity of the modification process, the high brittleness of the membrane

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due to the silica particles, and the non-homogeneity of the modification process. For these reasons, in this study, our goal was to fabricate a microporous hydrophobic membrane with a simple hydrophobic modification procedure and better physical characteristics and CH₄ recovery performance. In this context, the objective of this study is to fabricate a highly porous and durable membrane with a simple fabrication process for applying in D-CH₄ recovery from anaerobic reactor effluents.

Polyvinylidene fluoride (PVDF) was selected as the membrane material in this study. PVDF is the most studied membrane for HFMC applications due to its excellent chemical and thermal resistance and ease of processability [201, 202]. Although PVDF is hydrophobic in nature, membranes fabricated with this material may become hydrophilic due to the non-solvent additives used in the polymer dope solution. Therefore, here, the PVDF membrane support was hydrophobically modified by grafting Fluorolink S10, which is a perfluoropolyether while using TEOS as the silica precursor. Such modification was previously demonstrated by Wongchitphimon et al. [182] for a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membrane, for which the contact angle of the PVDF-HFP membrane was found to increase from 95.5° to 127.8°. Because this method of chemical modification involves several steps, including dehydrofluorination (removing fluorine from the polymer backbone) and chemical grafting, it is necessary to optimize the modification parameters to obtain a highly hydrophobic membrane.

The Taguchi method for process parameter optimization considers multiple parameters at multiple levels and can predict the optimal operating point of a process in a robust and precise manner. This method allows all factors to be varied simultaneously and can predict which have the greatest influence on the process. Several studies have tried to apply this method for membrane fabrication, but the application of this approach for the

surface modification of membranes is still very rare. For example, Idris et al. [203] used the Taguchi method to optimize the production of reverse osmosis (RO) membrane made of cellulose acetate hollow fiber. The most influential spinning parameters for the RO flux were found to be the bore fluid and the dope extrusion rate. Mohammadi et al. [204] studied the parameters affecting vacuum membrane distillation and found that increasing temperature and decreasing vacuum pressure improved the permeate flux.

Herein we have demonstrated membrane hydrophobicity optimization *via* the Taguchi approach to applying in a G-L MC application to remove CH₄ from anaerobic effluent. The respective optimized membrane operated with both synthetic and real AnMBR effluent and benchmarked with a commercial PP membrane used for the degasification of water. Further, the stability of the membrane was confirmed by long-term experiments.

3.2 Results and discussion

3.2.1 Characteristics of unmodified porous PVDF membrane

The membrane fabricated using the spinning conditions given in **Table 2.4** was highly porous, having a PWP of $4364.8 \pm 162 \text{ L m}^{-2} \text{ MPa}^{-1}$ and average bulk porosity of about 82%. Although the PVDF material itself is intrinsically hydrophobic, the dynamic contact angle of the membrane was measured as $84.48 \pm 2.21^\circ$. This hydrophilic behavior is due to the non-solvent additive, Pluronic F 127, which can cause hydrophilicity even with trace amounts entrapped inside a membrane [178].

Figure 3.1 shows the FESEM images obtained for the cross section, outer surface, and inner surface of the unmodified PVDF membrane. The asymmetric structure of the

membrane is a consequence of the non-solvent-induced phase separation technique used for its fabrication. Finger-like macro voids could be observed underneath the outer surface, suggesting a rapid liquid-liquid de-mixing during the phase inversion due to the strong external coagulant (water). The sponge-like structure underneath the inner surface is a product of the delayed de-mixing, as a soft bore fluid (70% NMP) was used in the phase inversion process

Figure 3.1 Unmodified PVDF membrane morphology (a) cross-section (b) outer surface (c) inner surface.

3.2.2 Chemical surface modification of PVDF membrane

The success of chemical surface modification was confirmed by FTIR–attenuated total reflectance (FTIR-ATR) analysis for both the original and modified PVDF membranes, as shown in **Figure 3.2**. The amorphous phase bands of the original PVDF membrane can be seen at 839 and 880 cm^{-1} . The bands at 1072 cm^{-1} can be attributed to the crystalline phase of PVDF. Characteristic asymmetrical and symmetrical stretching bands of CF_2 appear at 1169 and 1279 cm^{-1} , respectively. The peak at a frequency of 1404 cm^{-1} can be assigned to the deformed vibration of CH_2 [205]. In contrast with the original membrane, the surface functional groups in the modified PVDF membrane were altered due to the dehydrofluorination and surface modification with silane.

The newly appearing vibrational bands in the FTIR spectrum are marked in **Figure 3.2** with colored boxes. The silicon-carbon stretching can be observed at 683 cm^{-1} . The broad peak between 1072 and 1194 cm^{-1} corresponds to the silicon-oxygen-silicon bond.

The characteristic bands at 959, 1072, and 1194 cm^{-1} arise from silicon-carbon-ethyl vibrations in Fluorolink. The vibrations of amide groups can be observed at 1541, 1711, and 3325 cm^{-1} [182].

Figure 3.2 FTIR-ATR spectra for modified and original membranes.

3.2.3 Signal to noise ratio analysis

The Taguchi approach was used to determine the significance and optimal values of three controlled surface modification parameters, including the NaOH concentration, NaOH treatment time, and Fluorolink S10/TEOS grafting time, to yield the optimal contact angle of the fabricated PVDF membrane. **Table 3.1** shows the mean contact angle, the standard deviation of the contact angle, and the S/N ratio for each of the experimental conditions detailed in **Table 2.5**.

Table 3.1 Mean contact angle (CA), standard deviation (STD), and S/N ratio

Exp. No	1	2	3	4	5	6	7	8	9
Mean CA	107.	107	106.6	111.0	110.0	106.4	105.0	104.6	96.9
	4		6	7	6	8	7	9	5
STD	0.72	1.33	0.58	1.05	0.45	1.47	1.52	0.96	1.52
S/N	40.6	40.5	40.56	40.91	40.83	40.54	40.43	40.4	39.7
	2	9							2

Based on these experimental data, the level-mean S/N ratio for each parameter was estimated as summarized in **Table 3.2**. The highest S/N ratio represents the optimal level of each parameter for this modification because it indicates that the response (the contact angle) is the highest irrespective of the noise level [187]. According to the results in **Table 3.2**, the optimal modification conditions, yielding the highest contact angle of the modified PVDF membrane, were as follows: pH 10, NaOH treatment time of 30 min, and Fluorolink S10/TEOS grafting time of 90 min. Which later in our work, the membrane fabricated from this condition is named as the optimized PVDF membrane. As discussed in the following section, the analysis of variance was performed to further understand the effect and significance of each modification parameter with respect to the contact angle.

3.2.4 Analysis of variance

The statistical results of the analysis of variance are shown in **Table 3.3**. The percentages of the contribution of each factor to the surface modification show that the pH of the NaOH solution is the most influential factor. NaOH treatment time also has a significant effect. However, the Fluorolink S10/TEOS grafting time has a very slight effect on the surface modification.

Table 3.2 Mean contact angle and mean S/N ratio for each level of each factor from Taguchi method

Control parameter	Level	Mean contact angle (°)	Level-mean S/N ratio
pH	8	107.03	40.59
	10	109.14	40.76
	12	102.13	40.18
NaOH treatment time (min)	30	107.80	40.65
	60	107.22	40.61
	90	103.22	40.28
Fluorolink S10/TEOS grafting time (min)	30	106.17	40.52
	60	104.80	40.41
	90	107.23	40.61

Table 3.3 Analysis of variance (ANOVA) table

Control factor	Sum of squares	DOE	Variance	F	Percentage contribution
pH	1.59	2	0.795	59.59	61.82%
TT	0.76	2	0.380	28.44	28.95%
GT	0.18	2	0.090	6.75	6.07%
Error	0.24	18	0.013		
Total	2.77	24			

F*critical (F2,18,0.01): for 99% confidence level

It can be seen that when the pH of the NaOH solution increased from 8 to 10, the contact angle increased; however, the contact angle then fell when the pH further increased to 12. This behavior can be explained as follows. Increasing the pH of the NaOH solution from 8 to 10 allows more hydroxyl groups to be attached on the membrane surface and then react with the TEOS in the grafting solution, hence allowing more Fluorolink S10

molecules to be attached. However, the further increment of pH from 10 to 12 damages the integrity of the membrane by enabling further reactions in which the attached hydroxyl groups in the PVDF backbone are converted into carbonyl groups. This lowers the availability of hydroxyl groups to react with TEOS and thus reduces the contact angle of the modified membrane. The NaOH treatment time also affects the surface modification of the PVDF membrane. When the NaOH treatment time increased from 30 min to 60 min, the contact angle showed only a slight reduction; however, it fell drastically when the treatment time was increased to 90 min. Possibly, a dehydrofluorination time of 90 min allows further reaction with NaOH to convert the hydroxyl groups of the PVDF membrane surface to carbonyl groups and thus hinder the attachment of TEOS. In the present case, the formation of carbonyl groups was not detectable by FTIR; however, the mechanism of degradation of PVDF by NaOH has been demonstrated by previous studies [181]. According to the ANOVA in **Table 3.3**, shows that the Fluorolink S10/TEOS grafting time had only a very slight effect on the contact angle. This may indicate that even the shortest grafting time allowed most of the active sites to react with TEOS or Fluorolink S10, making them unavailable for further reaction, thus preventing further addition of Fluorolink S10 onto the PVDF surface. To perform method validation, the data generated by the Taguchi analysis were used to predict the contact angle for a different set of operating conditions. The predicted contact angles had a confidence interval of ± 1.07 with the experimental results, which confirmed the validity of this method for the surface modification.

In addition, the experimental data were subject to a degree of error, as shown in **Table 3.3**. This error corresponds to the uncontrollable parameters, such as temperature and humidity variations, that affect the membrane modification. Generally, the percentage contribution of errors should not exceed 50% [183]. The error in this study was calculated

as only around 3%. This confirms that the variation of the contact angle was mostly due to the controlled surface modification parameters.

A new batch of PVDF membrane was modified by using the optimum conditions obtained from the Taguchi method (pH:10, NaOH treatment time: 30 min TEOS/Fluorolink grafting time: 90 min) to be tested in the HFMC unit. The contact angle obtained for the new batch of optimized PVDF membrane was reported as $111.65 \pm 1.79^\circ$, while the Taguchi's predicted contact angle for this condition was 112.11° .

3.2.5 Characterization of the optimized membrane

Figure 3.3 Membrane morphology of the optimized PVDF membrane. a: cross-section, b: outer surface.

The cross-section and outer surface morphology of the optimized PVDF membrane are shown in **Figure 3.3**. A significant difference can be observed in the modified membrane outer surface, relative to the unmodified membrane. The surface roughness data in **Table 3.4** also support the fact that the membrane outer surface was changed (smoothened) by hydrophobic modification. Fluorolink S10 is a member of the perfluoropolyether (PFPE) family, which have low surface energies and binding energies, leading to reduced adhesion and greater water/oil repellency. This allows them to create smooth hydrophobic surfaces [164].

Table 3.4 summarizes several other characteristics of both the original and optimized membrane, including the dynamic contact angle, mean pore size, porosity, LEP_w , and root-mean-square (RMS) surface roughness. The contact angle of the original membrane was increased from 84.48° to 111.65° due to the modification. The mean pore size was also increased compared with the original membrane, probably due to the dehydrofluorination by NaOH. The bulk porosity was decreased from 84% to 79% because the high-molecular-weight Fluorolink S10 molecules covered a certain fraction of the voids on the membrane surface. The effect of surface modification on the mechanical strength of the membrane was observed to be marginal.

Table 3.4 Properties of the original membrane and modified PVDF membrane

Parameter	Original membrane	Modified membrane
Dynamic contact angle	$84.48 \pm 2.21^\circ$	$111.65 \pm 1.79^\circ$
LEP_w (bar)	0.14	1.00
Mean pore diameter (nm)	118.13 ± 7.52	135.35 ± 8.84
Bulk porosity (%)	82	79
RMS roughness (nm)	0.520 ± 0.057	0.026 ± 0.001
Mechanical strength (MPa)	1.41 ± 0.09	1.38 ± 0.02
Stress at break (MPa)	1.37 ± 0.09	1.35 ± 0.01

3.2.6 Methane recovery performance

A PP hollow-fiber membrane, commercially used for membrane degassing applications, was used to benchmark the performance of the modified PVDF membrane for CH_4 recovery. The details of the module and membrane are summarized in **Table 3.5**. The CH_4 and CO_2 concentrations at the liquid inlet were at 14.03 mg L^{-1} and 559.08 mg L^{-1} , respectively, during the biogas recovery experiment.

Table 3.5 Details of membranes and modules employed in membrane contactor system

Parameter	PVDF	PP
Module details		
Inner diameter (mm)	9.525	9.525
Length (cm)	18.5	18.5
Membrane details		
Number of fibers	8	100
Inner diameter (μm)	636.07 ± 3.54	189.39 ± 1.41
Outer diameter (μm)	911.53 ± 1.35	313.41 ± 5.04
Mass transfer area (cm^2)	25.58	94.43
Contact angle ($^\circ$)	111.65 ± 1.79	106.46 ± 2.42
Bulk porosity (%)	79	49

Figure 3.4 CH₄ recovery from synthetic effluent. a: CH₄ stripping flux b: CO₂ stripping flux of optimized PVDF membrane and commercial PP membrane

Figure 3.4 shows the CH₄ flux and CO₂ flux of both optimized and commercial PP membranes as a function of the liquid velocity, respectively. The gas stripping fluxes of both membranes follow the same trend with respect to the liquid velocity, in which the gas flux increases with the increasing liquid velocity. This trend is intuitive to be expected because a higher liquid velocity reduces the mass transfer resistance and thereby increases the gas flux [206]. The reduction of mass transfer resistance implies an increase in the

overall mass transfer coefficient, which is clearly shown in **Figure 3.5a**. It can also be noted that the overall mass transfer coefficient of CH₄ is much greater than CO₂ because it has a lower Henry's constant (Henry's constant: CH₄ = 1.4×10^{-5} mol m⁻³ Pa⁻¹, CO₂ = 3.4×10^{-4} mol m⁻³ Pa⁻¹ [194]). The lower Henry's constant, the lower gas solubility; thus, the gas can easily diffuse into the gas phase. **Figure 3.5b** shows that the percentage of gas recovery of both gases decreases with the increase in liquid velocity. This may indicate that increasing the liquid velocity reduces the time available for the desorption of the gases from the liquid effluent. The same observation was reported by Cookney et al. [54] for the recovery of dissolved methane from anaerobic effluent using a porous PP membrane. At the same time, the percentage recovery of CH₄ is greater than that of CO₂. The variation of CO₂/CH₄ ratio in the gas outlet of the HFMC is also depicted in **Figure 3.5b**. The CO₂/CH₄ ratio increased with the liquid velocity which implying that more CO₂ is stripped out at higher liquid velocities.

Figure 3.5 CH₄ mass transfer performance a) Overall mass transfer coefficient of the optimized membrane. b) Percentage recovery of CH₄ and CO₂ and CO₂: CH₄ concentration ratio in the HFMC outlet (data related to the optimized membrane)

Interestingly, the optimized PVDF membrane in this study achieved a higher CH₄ flux than the commercial PP membrane. In addition, the CH₄ flux of the PVDF membrane (within the liquid velocity range studied here) is higher than that of the Matrimid membrane tested in our previous work [59]. Evidently, the lower bulk porosity of the commercial PP

membrane (~49%) and the Matrimid membrane (62.9%) limited their stripping gas fluxes compared with the PVDF membrane. These results demonstrate that greater microporosity can enhance the recovery flux across the membrane.

Figure 3.6 shows the permeability-selectivity variation of the optimized PVDF membrane with respect to Robeson 2008 upper bound. Interestingly, when the liquid velocity increases, both CO₂:CH₄ selectivity and permeability increase shifting the optimized PVDF membrane toward the upper bound. The permeability improvement of both the CO₂ and CH₄ gases is anticipated due to the improved liquid side hydrodynamics (as a result of the increment of the feed velocity); however, the CO₂ selectivity enhancement indicated that the amount of CO₂ permeability increment surpasses that of CH₄ at higher liquid velocities.

Figure 3.6 Comparison of optimized PVDF membrane with Robeson upper bound

The Wilson plot method was used to determine the membrane mass transfer resistance. As described in our previous work [59], CO₂ gas was used as the transporting component. The value of alpha (α) was selected as 0.6, which gave the best-fitted line for the reciprocal of the overall mass transfer coefficient ($1/K_{OL}$) vs. liquid velocity^{- α} ($v^{-\alpha}$). The

Wilson plot in **Figure 3.7** shows that the equation for the linear correlation obtained for the experimental data had an R^2 of 0.98. The intercept of the equation indicates the membrane mass transfer resistance, given the assumption that the gas-phase mass transfer has a negligible effect on the mass transfer between gas and liquid phases. The membrane mass transfer coefficient for the PVDF membrane studied here was calculated as $1.53 \times 10^{-4} \text{ m s}^{-1}$, which was higher than our Matrimid membrane ($1.41 \times 10^{-4} \text{ m s}^{-1}$). The higher microporosity of the PVDF membrane resulted in a higher membrane mass transfer coefficient and thereby, a lesser mass transfer resistance. Although the contact angle of the optimized PVDF membrane is well below that of the modified Matrimid membrane (123° to 125°), it seems that the hydrophobicity of the PVDF membrane induced by the surface modification with Fluorolink S10 and TEOS is high enough to prevent partial wetting of the membrane, while offering a better flux, under the experimental conditions used in this study.

Figure 3.7 Wilson plot of CO_2 permeation data of surface modified PVDF membrane.

3.2.7 Long-term operation

The long-term methane recovery flux of the optimized PVDF membrane was measured to investigate the wetting resistance of the pores and the extent of fouling during the MC operation. Synthetic effluent, made by dissolving biogas in tap water, was fed into the lumen of the membrane module continuously for 10 days to investigate the resistance to pore wetting. Meanwhile, real AnMBR effluent (total organic carbon (TOC) = 8.777 ppm, soluble chemical oxygen demand (sCOD) = 21 ppm, turbidity = 2.94 NTU) from an AnMBR pilot located in a water reclamation plant in Singapore was used for monitoring the fouling issue.

Figure 3.8 Long-term performance of the optimized PVDF membrane. (Feed: tap water saturated with 60:40 CH₄/CO₂ mixture.)

Figure 3.8 shows the long-term performance of the modified membrane, operated at liquid and sweeping gas velocities of 0.062 m s⁻¹ and 0.0005 m s⁻¹, respectively, using the synthetic effluent as the feed solution. The CH₄ flux was observed to be very stable during the 10 days of the experiment. The slight fluctuations of the flux were mostly due to the variation of dissolved gas concentration in the feed stream arising from changes in

temperature and pressure inside the saturator tank. This result strongly confirmed the applicability of our membrane in MC processes without susceptibility to pore wetting.

As illustrated in **Figure 3.9**, the methane recovery flux decreased only marginally after 8 days of continuous operation. The fluctuation of the methane flux was less than 10% in our membrane and 12% for the commercial PP membrane during the operation. The liquid and sweep gas velocities were maintained at 0.04 m s^{-1} and 0.0005 m s^{-1} , respectively. This is a good indication that our membrane can be operated at a higher flux than the commercial PP membrane while performing similarly in terms of the flux decline behavior, when using real AnMBR effluent.

Figure 3.9 Long-term performance of (a) optimized PVDF and (b) PP membrane. (Feed: AnMBR effluent: TOC = 8.777 ppm, sCOD = 21 ppm, turbidity = 2.94 NTU.)

3.2.8 Membrane performance with respect to conventional technologies

The performance of the hollow fiber membrane contactors was compared with the existing D-CH₄ methods and summarized in **Table 3.6**. Clearly, to achieve a higher CH₄ recovery efficiency, the conventional devices need either higher G/L ratios or higher contact times or both with respect to membrane contactors. Even though the maximum removal efficiency obtained for the tested membranes in this study is around 75%, it should be noted that this can go beyond 99% with optimum G/L ratios (lower gas-liquid flowrates, note that at lower liquid velocities the resultant CH₄ gas concentration in the sweep gas is very low thus causing limitations in taking measurement with the micro GC). Additionally, Wessel *et al.* [207] in their work of CH₄ removal from drinking water systems showed that all the three systems, which are the packed column, tray aerator, and membrane contactor, are capable of removing D-CH₄ with an efficiency over 99%. To obtain the desired removal efficiency, they deployed a packed tower with a bed height of 4.5 m, a plate aerator with 1.62 m flow length, and a 2.5×8” Liqui-Cell membrane contactor. Even though they recommended to keep 3 – 4 modules in series for achieving higher efficiencies, clearly the footprint and the contamination between gas and liquid phase is minimum for membrane contactors as compared to conventional devices.

Table 3.6 Comparison of optimized PVDF and commercial PP HFMCs with other existing techniques

Technique/Source of feed water	Specific surface area (m² m⁻³)	Contact time (s)	G/L ratio	Removal efficiency (%)	Ref
Spray aerator /groundwater	N/A	N/A	5 – 30	45 – 55	[34]
Packed Column/ ground water	175	N/A	153	99.6	[207]
Tray aerator/ ground water	6.7	90 – 156	80	98.9	[207]
Packed Column/ UASB effluent	N/A	7200	0.064– 0.043	70	[27]
Spray aerator/ UASB effluent	N/A	N/A	0.77 – 19.2	72	[28, 29]
Membrane Contactor/ Synthetic effluent (optimized PVDF)	225	3 – 10	0.16 – 6.7	8 – 75	This work
Membrane Contactor/ Synthetic effluent (Commercial PP)	927	3 – 10	2.5 – 5	22 – 75	This work

3.3 Conclusions

The hydrophobic modification of a microporous PVDF membrane was optimized using the Taguchi method. The NaOH concentration, dehydrofluorination time, and the grafting time of the fluorinated silane solution (Fluorolink S10/TEOS) were identified as the major control factors for the analysis. By analysis of variance, the most critical of those factors for this modification was identified as the NaOH concentration. Dehydrofluorination time also had a significant effect on the modification, whereas

fluorinated silane grafting time had a slight or negligible effect. These predictions were confirmed through experiments conducted under the respective modification conditions.

The membrane optimized through the Taguchi approach exhibits a very high stripping flux and high membrane mass transfer coefficient compared with a commercial PP degassing membrane, as well as with the Matrimid membrane tested in our previous study. Furthermore, long term-operation with both synthetic and real AnMBR effluent confirmed that our membrane has excellent methane recovery ability, with higher flux than the commercial PP hollow-fiber membrane, and strong resistance to pore wetting and fouling, indicating its potential application in methane recovery from AnMBR effluent.

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4 The Influence of membrane characteristics and operating parameters¹

4.1 Introduction

In the MC process, a membrane, commonly a hollow fiber membrane, is employed as a mass transfer barrier between two phases [47, 208]. Both dense (nonporous) and porous membranes are currently available in the market as multipurpose MC membranes. For liquid-gas MC applications, (micro)porous MC membrane designs are more suitable due to their enhanced gas transport behaviors that help reduce the device footprints and energy consumption accordingly [15, 54, 209]. Nevertheless, introducing microporosity makes MC membranes relatively more prone to liquid wetting [68, 210]. And, the liquid water penetrated in membrane pores act as a stagnant fluid layer, which exerts additional limitation for mass transfer [211-213]. The selection of a membrane with high hydrophobicity and a small pore size profile might prevent wetting [68, 100, 214]. However, increasing the surface hydrophobicity of membranes may speed up the biofouling as well as organic fouling [215-217]. Reducing the porosity of membranes (particularly at the membrane surface) might even help to delay membrane fouling [218]. But, the utilization of low-porosity membranes is also not always beneficial for improving the overall performance in (gas-liquid) MC applications, because low porosity often leads to low recovery flux [20, 210].

Another challenge identified for microporous membranes is the “capillary condensation,” which is a concern even for wetting-proof membranes with high hydrophobicity [133, 138, 219]. The driving force behind the phenomenon of capillary

condensation is that the vapor pressure difference between the two sides of membranes induces the evaporation of water, creating a water vapor flux across the porous membrane [220-222]. Eventually, water vapor condenses across the membrane pores, causing an increase in membrane resistance (as observed in the case of the “membrane wetting” problem). Crucially, smaller the membrane pore size, higher the propensity of capillary condensation because the local vapor pressure may overcome the critical vapor pressure of water much easier in that case [137, 222]. For hollow fiber membranes, the selection of optimally hydrophobic membrane materials, utilization of suitable pore-forming agents, and fine-tuning of spinning parameters may help suppress capillary condensation [124, 157, 223, 224]. However, the fabrication of MC membranes with optimal hydrophobicity and pore size distribution is a challenging task, making the surface modification of the membranes necessary [95, 225, 226].

In this context, dense membranes could be an excellent platform [68, 100, 214]. However, dense membranes can cause a huge mass transfer resistance as the bulk diffusion of gas molecules is restricted, while the permeation through the membrane matrix becomes predominant [210]. Therefore, the pros and cons need to be rigorously studied. It is also the case for the hydrophobic membranes in that there are no detailed criteria for hydrophobic modification to the extent that they can guarantee not to confer significant resistance but to prevent the pore wetting.

Meanwhile, as another alternative, a composite membrane consisting of both a porous support layer and a dense skin layer is likely to meet the two requirements (*i.e.*, the capability of preventing the pore wetting and high permeability) as a compromise between porous and non-porous membranes. However, it does not necessarily mean that a composite membrane should be the best option for CH₄ recovery with no questions because CH₄

recovery is affected simultaneously by a large number of variables such as operation-related parameters as well as membrane-related parameters. Thus, it is required to scrutinize the synergistic effects of membrane-related parameters on CH₄ recovery under various operating conditions before concluding key factors in preparing high-performance membranes for CH₄ recovery

As discussed in previous chapters, D-CH₄ recovery membranes also have critical challenges due to pore wetting [3], that hinder their industrial application. Because pore wetting can deteriorate overall performance by increasing mass transfer resistance [8], the membrane should have pores capable of preventing liquid water from seeping. In this context, dense (e.g., PDMS [9, 10]) or highly hydrophobic membranes may provide an excellent platform [11-13]. However, dense membranes can also lead to huge mass transfer resistance because the bulk diffusion of gas molecules is restricted, while permeation through the membrane matrix becomes predominant [14]. These trade-offs need to be rigorously evaluated. This is also the case for hydrophobic membranes: there are no detailed criteria for the hydrophobic modification that can absolutely avoid significant mass transfer resistance while simultaneously preventing pore wetting (e.g., how much we should increase the hydrophobicity of a porous membrane with a certain size of pores to prevent pore wetting).

As another alternative, a composite (e.g., PDMS-coated porous PVDF [15]) membrane consisting of both a porous support layer and a thin dense skin layer is likely to meet the two requirements (i.e., waterproof property and high permeability). However, it is not necessarily mean that a thin-film composite membrane is the best option for CH₄ recovery, given that CH₄ recovery is also affected by a large number of variables, including operation- and membrane-related parameters. As such, it is necessary to scrutinize the

influence of membrane-related parameters on CH₄ recovery under various operating conditions before concluding which factors must be considered in membrane design. For this reason, many researchers have devoted considerable efforts to the optimization of membrane- or operation-related parameters to attain both waterproof properties and high permeability of different kinds of membranes including non-porous, microporous (e.g., PP [16, 17]), and composite membranes [3, 18].

However, to the best of our knowledge, no studies have comprehensively investigated the synergistic effect of membranes' physicochemical characteristics and various operating parameters on biogas recovery encompassing a wide range of variables such as hydrophobicity, pore size, porosity, several physical characteristics (e.g., inner diameter, membrane area, and module length) of hollow fibers, and operating parameters (e.g., liquid flow rate). Also evident is the lack of theoretical guidance for the enhancement of D-CH₄ recovery in this area. In this regard, we were motivated to analyze the D-CH₄ recovery performance of the three types of membranes, as mentioned above (i.e., porous, non-porous, and composite membranes) under various operating conditions along with theoretical studies to provide criteria for achieving the optimal CH₄ recovery efficiency. A commercial PP membrane was used as a surrogate of a less hydrophobic, porous, and symmetric membrane while a commercial PDMS membrane was chosen to estimate the performance of a more hydrophobic, dense, and symmetric membrane, given that the two materials (i.e., PP and PDMS) are one of the most widely used ones to prepare membranes for biogas recovery [3, 9, 10, 16-20]. Also, we prepared two different kinds of modified membranes *via* a selective surface coating of PDMS and chemical grafting of Fluorolink S10 (Optimized membrane in **Chapter 3**) with TEOS to confer hydrophobic properties, but different structures.

4.2 Results and discussion

4.2.1 Characterization of four kinds of membranes in terms of morphological and chemical properties

Figure 4.1 SEM images of the lumen surface of (a) commercial PP (b) commercial PDMS, and (c) unmodified PVDF membranes. (d) SEM image of the lumen surface and (e) cross-sectional SEM image of a DHC-PVDF membrane. (f) SEM image of the lumen surface of a PHM-PVDF membrane.

Figure 4.1a and **Figure 4.1b** reveal the porous and dense lumen surfaces of the commercial PP and PDMS membranes, respectively. **Figure 4.1c** shows the lumen surface of the unmodified PVDF membrane, which features a mean pore size of $0.12 \pm 0.01 \mu\text{m}$, an overall porosity of 83%, and a contact angle of 84.5° . We confirmed that the unmodified PVDF membrane had quite a porous surface, probably as a result of the weak bore fluid used in the spinning process, as reported previously [227]. Meanwhile, the DHC-PVDF membrane, which was prepared by covering the lumen surface with a mixture of PDMS and PEG-400, had a dense layer **Figure 4.1d** with a thickness of about $6 \mu\text{m}$ (**Figure 4.1e**) while the PHM membrane, modified by chemical grafting with a TEOS/Fluorolink S10

mixture, exhibited a similar surface appearance to that of the unmodified PVDF membrane (**Figure 4.1c** and **Figure 4.1f**).

Figure 4.2 Cross-sectional SEM images of (a) unmodified PVDF, (b) DHC-PVDF, and (c) PHM-PVDF membranes. O elemental mapping of (d) unmodified PVDF, (e) DHC-PVDF, and (f) PHM-PVDF membranes; Si elemental mapping of (g) unmodified PVDF, (h) DHC-PVDF, and (i) PHM-PVDF membranes. Color scheme: O, green; Si, yellow. Scale bars indicate 30 μm for all of the images.

Next, we identified silicon (Si)-related elements using EDS and FTIR analyzes to investigate the distribution of surface modification reagents and changes to the surface chemistry after each modification. While there was almost no signal in the O and Si elemental mappings of the unmodified PVDF membrane (**Figure 4.2d** and **Figure 4.2g**), we confirmed that the lumen surface of the DHC-PVDF membrane was dotted with a number of Si atoms (**Figure 4.2h**), implying that a selective surface coating was effective owing to the pre-filling of pores with glycerol prior to coating. Unlike the DHC-PVDF

membrane, the PHM-PVDF membrane displayed evenly distributed O (**Figure 4.2f**) and Si (**Figure 4.2i**) elemental mappings throughout the entire thickness. Thanks to the Si-related segments, which are studded over the cross-section, the PHM-PVDF membrane was expected to prevent pore wetting despite its porous surface effectively.

The successful surface modifications of the hollow PVDF fiber membranes were also verified by FTIR-ATR analysis. **Figure 4.3a** shows four IR bands assigned to the functional groups generated by the modifications in different colors, which are distinct from the unmarked amorphous phase bands of the PVDF (at 839 and 880 cm^{-1} [227]) and the deformed vibration of CH_2 (1404 cm^{-1} [227]). In detail, three bands at 685, 1072, and 1185 cm^{-1} are ascribed to the wagging vibration of $-\text{CF}_2\text{-CHF-CF}_3$ [228], ethoxy silane (or crystalline phase of PVDF) [227, 229], and CF_3 vibration [230], respectively. The three functional groups are highly likely to pertain to the materials such as Fluorolink S10 ($-\text{CF}_2\text{-CHF-CF}_3$, ethoxy silane, and CF_3 vibration) and TEOS (ethoxy silane) used to modify the PHM-PVDF membrane. The bands at 798 and 1076 cm^{-1} are associated with the CH_3 rocking in Si-CH_3 and Si-O-Si , respectively [231], suggesting that the DHC-PVDF membrane has the terminal group and siloxane backbone of PDMS on its lumen surface. As a result of the successful hydrophobic modification, the contact angle of the PVDF membrane, which was 84.5° before the hydrophobic treatment, became comparable to (DHC-PVDF membrane) or even higher (PHM-PVDF membrane) than that of the commercial PDMS membrane, as shown in **Figure 4.3b**. **Table 4.1** summarizes the all the details about membranes, module preparation and operational parameters we utilized in this study.

Figure 4.3 (a) FTIR spectra of the lab-made PVDF membranes before and after the modifications. The bands observed at 685, 798, 1072, 1076, and 1185 cm^{-1} are assigned to the wagging vibration of $-\text{CF}_2\text{-CHF-CF}_3$, CH_3 rocking in Si-CH_3 , ethoxy silane (or crystalline phase of PVDF), Si-O-Si , and CF_3 vibration, respectively. (b) Contact angles of the commercial PP, commercial PDMS, DHC-PVDF, PHM-PVDF membranes. Error bars indicate the standard deviations obtained from five different samples.

Table 4.1 Membrane, module, and operation details used in MC experiments.[†]

Details	Parameter	Commercial PP	Commercial PDMS	DHC- PVDF	PHM- PVDF
Membrane details	d_i (μm)	189 (± 1)	190	588 (± 3)	636 (± 4)
	d_o (μm)	313 (± 5)	300	885 (± 5)	912 (± 1)
	Porosity (%)	49	N.A.	N.A.	79
	Pore size (μm)	0.02	N.A.	N.A.	0.14 (± 0.04)
Module details	Module diameter (cm)	0.95	0.95	0.95	0.95
	Number of fibers	100	30	10	10
	Effective module length (m)	0.19	0.11	0.19	0.19
	Mass transfer area (m^2)	11.3×10^{-3}	1.0×10^{-3}	3.51×10^{-3}	3.80×10^{-3}
Operation details	Liquid flow rate ($\text{m}^3 \text{ day}^{-1}$, $\times 10^{-3}$)	4.3 to 72	1.4 to 23	5.8 to 81	5.4 to 82
	Liquid velocity (m s^{-1})	1.79×10^{-2} - 30.0×10^{-2}	1.91×10^{-2} - 31.3×10^{-2}	2.47×10^{-2} - 34.5×10^{-2}	1.97×10^{-2} - 29.9×10^{-2}
	Gas flow rate ($\text{m}^3 \text{ day}^{-1}$)	0.03			
	G/L ratio	7.0 to 0.42	21 to 1.3	5.2 to 0.37	5.6 to 0.37

[†] The information for the membrane and module details of the commercial PDMS membrane was taken from the datasheet provided by the manufacturer.

4.2.2 Theoretical analysis of CH₄ flux and recovery

We conducted a theoretical analysis to identify the factors affecting the membrane contactor performance and their impact. According to **Equation 2-20**, the main parameters affecting the CH₄ flux are i) membrane-related parameters (*e.g.*, the d_i and the A_M), ii) operation-related parameters (*e.g.*, G and L), and iii) the K_{OL} . Assuming that the K_{OL}^{-1} is governed primarily by the k_L^{-1} and that the membrane is kept dry throughout the operation, the K_{OL} can be simplified to the single k_L , which is identical to that described in Leveque's equation, as shown in **Equation 2-21**. Provided that K_{OL} is replaced with k_L , the membrane- and operation-related parameters remain influential determinants of the CH₄ flux. We, therefore, review how each parameter affects the CH₄ flux, supposing that all other parameters are kept constant, to distinguish the effects of specific parameters more clearly. Note that the physical properties of CH₄ were extracted from the literature and are listed in **Table 4.2**.

Table 4.2 Diffusion coefficients and Henry constant of CH₄ (25 °C and 1 atm)

Parameter	Value	Reference
Diffusion coefficient of CH ₄ in N ₂ (m ² s ⁻¹)	2.19×10 ⁻⁵	[143]
Diffusion coefficient of CH ₄ in air (m ² s ⁻¹)	2.17×10 ⁻⁵	[193]
Diffusion coefficient of CH ₄ in water (m ² s ⁻¹)	1.88×10 ⁻⁹	[192]
Henry constant of CH ₄ (mol m ⁻³ Pa ⁻¹)	1.40×10 ⁻⁵	[194]

4.2.2.1 The effect of membrane-related parameters on CH₄ flux and recovery

First, when it comes to the effect of the d_i on the CH₄ flux among the two membrane-related parameters, k_L is inversely proportional to the cubic root of the d_i , as

shown in **Equation 2-21**. This relationship implies that a smaller d_i can lead to a higher k_L at the fixed liquid velocity, resulting in higher CH_4 flux across the membranes (**Figure 4.4a**) given that the K_{OL} in Eq (2-19) can be replaced with the k_L based on the previous hypothesis (*i.e.*, $J = K_{OL}\Delta C_{lm} = k_L\Delta C_{lm}$). Rajabzadeh et al. [188] observed a similar phenomenon in CO_2 absorption using PVDF hollow fiber membrane contactor. This was also the case for CH_4 recovery. In detail, the CH_4 recovery increases from about 73% to 98% as the d_i is reduced from 1 to 0.1 mm (**Figure 4.4a**). As such, d_i is a critical parameter for obtaining higher CH_4 flux and recovery.

Figure 4.4 Parameters affecting CH_4 flux and recovery. (a) Effect of membrane inner diameter (A_M : 8 m², L : 2 m³ day⁻¹, G : 0.1 m³ day⁻¹). (b) Effect of mass transfer area (L : 2 m³ day⁻¹, G : 0.1 m³ day⁻¹, d_i : 5×10⁻⁴ m)

Next, we investigated the A_M as the other membrane-related parameter affecting CH_4 flux and recovery. Increasing A_M is expected to enhance the CH_4 recovery by improving the chance that CH_4 is transported through the membrane while noticeably reducing the CH_4 flux, as shown in **Figure 4.4b**. This decreasing flux can be explained by the larger A_M decreasing k_L , as shown in Equation 2-21.

4.2.2.2 The effect of operation-related parameters on CH_4 flux and recovery

Figure 4.5 Parameters affecting CH_4 flux and recovery. (a) Effect of liquid flow rate (A_M : 8 m^2 , G : $0.1 \text{ m}^3 \text{day}^{-1}$, d_i : $5 \times 10^{-4} \text{ m}$). (b) Effect of gas flow rate (A_M : 8 m^2 , L : $2 \text{ m}^3 \text{day}^{-1}$, d_i : $5 \times 10^{-4} \text{ m}$)

Operation-related parameters, such as L and G , also need to be carefully controlled to facilitate optimization. The CH_4 flux increases in tandem with L , as shown in **Figure 4.5a**. This is understandable given the sequence of phenomena (*i.e.*, a higher L results in higher u , making the k_L larger), which leads to improved mass transfer. In contrast, increasing L is detrimental to CH_4 recovery, which is consistent with experimental studies on CH_4 recovery from anaerobic effluents [20, 59, 232]. The inverse correlation between L and CH_4 recovery is likely to stem from the liquid's lower residence time in the module when L is higher. Meanwhile, increasing G results in marginal increases to both CH_4 flux and recovery, as shown in **Figure 4.5b**. Specifically, beyond a G value of $0.3 \text{ m}^3 \text{ day}^{-1}$, changes to both the CH_4 flux and recovery are negligible. Such results imply that the G has very little effect on the K_{OL} , as it is governed almost single-handedly by the k_L^{-1} .

4.2.3 The influence of real-world factors on the experimental K_{OL}^{-1}

Figure 4.6 shows the theoretical k_L^{-1} and experimental K_{OL}^{-1} for the four membranes tested in this study. Based on **Equation 2-21** k_L increases (and k_L^{-1} decreases) as d_i and the effective module length become smaller and shorter, respectively, provided that the liquid velocity is constant. Accordingly, the commercial PP and PDMS membranes, which had much smaller d_i than the lab-made membranes, were expected to display a smaller k_L^{-1} (based on the theoretical k_L^{-1}) (**Figure 4.6a**). However, the experimental K_{OL}^{-1} exhibited a different tendency. For instance, the theoretical k_L^{-1} (**Figure 4.6a**) was high in the order of $\text{DHC-PVDF} \approx \text{PHM-PVDF} > \text{commercial PP} > \text{commercial PDMS}$ membranes throughout the whole liquid velocity range (the difference in the theoretical k_L^{-1} for the two commercial membranes derives from the different effective module length). On the other hand, the order in the experimental K_{OL}^{-1} was found to have changed at different liquid velocities (**Figure 4.6b**). More importantly, most experimental K_{OL}^{-1} was much larger than

the corresponding theoretical k_L^{-1} (Figure 4.6c to Figure 4.6f). Those discrepancies are likely due to other variables that can influence mass transfer in real-world applications, such as the capillary pressure, the wetting problem, or membrane resistance (k_M^{-1}). Therefore, the experimental K_{OL}^{-1} for the four membranes was examined with a focus on such real-world factors.

Figure 4.6 (a) Theoretical k_L^{-1} and (b) experimental K_{OL}^{-1} of four different membranes plotted against the liquid velocity. The theoretical k_L^{-1} was obtained based on Leveque's equation. Theoretical k_L^{-1} (solid lines) and experimental K_{OL}^{-1} (scattered data) of (c) commercial PP, (d) commercial PDMS, (e) lab-made DHC PVDF, and (f) lab-made PHM-PVDF membranes were also individually plotted against the liquid velocity to make it easy to compare theoretical k_L^{-1} and experimental K_{OL}^{-1} of each membrane. Error bars indicate the standard deviations obtained from two different samples

4.2.4 The influence of capillary pressure on the experimental K_{OL}^{-1}

First, we were particularly attuned to both the commercial PP and PDMS membranes showing significantly higher experimental K_{OL}^{-1} than the two lab-made membranes, especially at the low liquid velocity of 0.02 m s^{-1} (**Figure 4.6b**). Among possible causes (k_M^{-1} , k_L^{-1} , pore wetting, or capillary pressure), neither the k_M^{-1} nor the pore wetting can explain the high K_{OL}^{-1} of commercial membranes because the PP membrane possesses a negligible k_M^{-1} (51.5 sm^{-1}) while the PDMS membrane is considered too dense to experience the pore-wetting problem. Meanwhile, the k_L^{-1} was also excluded from consideration based on the fact that the k_L^{-1} of the commercial membranes should be lower than those of the two lab-made membranes due to their smaller d_i (**Table 4.1**), as discussed based on **Equation 2-21**.

Unlike the factors mentioned above, capillary pressure accounts for the high experimental K_{OL}^{-1} value for both commercial membranes at 0.02 m s^{-1} . Specifically, the capillary pressures ($= \frac{2\gamma \cos\theta}{r}$; γ : the surface tension of water, θ : the contact angle of water, r : the inner diameter of hollow fibers) for the PP (about 35 kPa) and PDMS (about 13 kPa) membrane modules were much higher than the other modules (around 2 kPa). Such a large difference in capillary pressure suggests the possibility that the feed solution was unable to get into some of the fibers in the commercial membrane modules at 0.02 m s^{-1} ; this, in turn, could make their observed K_{OL}^{-1} soar. Later, as the liquid velocity increased to up to 0.05 m s^{-1} , the experimental K_{OL}^{-1} for the commercial PP and PDMS membranes dramatically dropped by c.a. 90% and 30%, respectively (**Figure 4.6b**). The lowered K_{OL}^{-1} was probably caused by the higher liquid velocity, which could help the feed solution overcome capillary pressure. From the results, therefore, we can conclude that although reducing d_i is beneficial

for lowering k_L^{-1} , it can be undesirable at a low liquid velocity because the capillary pressure may be too high to overcome. Hence, before determining the optimal d_i , the operating liquid velocity and capillary pressure must be considered.

4.2.5 The influence of pore wetting on the experimental K_{OL}^{-1}

The experimental K_{OL}^{-1} of the commercial PP membrane was observed to gradually dwindle (by about 50%) as the liquid velocity increased from 0.05 to 0.30 m s⁻¹ (**Figure 4.6c**). This decrease demonstrates that increasing the liquid velocity reduced the value for k_L^{-1} , which eventually led to a lower K_{OL}^{-1} . Nevertheless, the experimental K_{OL}^{-1} was about 50-60% higher than the theoretical k_L^{-1} over the liquid velocity range from 0.05 to 0.30 m s⁻¹ (**Figure 4.6c**). Of the above-mentioned potential factors (i.e., k_M^{-1} , k_L^{-1} , pore wetting, or capillary pressure), this difference was most likely to have been caused by pore wetting. The commercial PP membrane was more likely to suffer from pore wetting because its surface was much less dense than commercial PDMS or the DHC-PVDF membrane and less hydrophobic than the PHM-PVDF membrane.

To understand how pore wetting negatively affects the experimental K_{OL}^{-1} , one must also consider the influence of pore wetting on k_M^{-1} . To be specific, the percolated liquid filling the subsurface voids is so stagnant that it is extremely unlikely to transport the dissolved CH₄; this presents a stark contrast to the liquid flowing through the lumen, where the convective flow of the dissolved CH₄ occurs. The liquid in the pores, therefore, necessarily comes to have the higher k_L^{-1} than that of the bulk liquid, which in turn significantly increases k_M^{-1} . Such increases to k_M^{-1} by pore wetting are believed to increase the experimental K_{OL}^{-1} for the commercial PP membrane. This hypothesis is supported by

Figure 4.7 demonstrating that the k_M^{-1} of the commercial PP membrane with large pores accounts for almost 40% of its experimental K_{OL}^{-1} .

Figure 4.7 Contribution rate of k_M^{-1} to the experimental K_{OL}^{-1} of four different membranes plotted against the liquid velocity. For the commercial PP and PDMS membranes, the values obtained at 0.02 m s⁻¹ were ruled out because their Gratz numbers at 0.02 m s⁻¹ were smaller than 4

4.2.6 The influence of k_M^{-1} on the experimental K_{OL}^{-1}

Unlike the commercial PP membrane, the commercial PDMS membrane was so dense that it was highly unlikely to allow pore wetting independently of the liquid velocity. Nevertheless, the commercial PDMS membrane also showed about 2.5-3.7 times higher experimental K_{OL}^{-1} than the theoretical k_L^{-1} throughout the entire liquid velocity range, with the exception of 0.02 m s⁻¹ (**Figure 4.6d**). This result indicates that k_M^{-1} is not negligible in dense membranes. Indeed, the k_M^{-1} of the commercial PDMS membrane was found to contribute to about 70% of its experimental K_{OL}^{-1} (**Figure 4.7**). It is also the case for the experimental K_{OL}^{-1} for the DHC-PVDF membrane, which was 1.34-1.98 times higher than the theoretical k_L^{-1} (**Figure 4.6e**). Such poor performance is likely to result from the dense coating layer, taking into account that its pore size is too small to be detected (**Table 4.1**). It is also evident from the fact that the k_M^{-1} of the DHC-PVDF membrane

almost reached about 50% of its experimental K_{OL}^{-1} (**Figure 4.7**). Our results strongly suggest that it is desirable for membranes used in CH_4 recovery to possess both the anti-pore wetting property and high porosity to diminish K_{OL}^{-1} .

In this regard, the PHM-PVDF membrane meets the requirements, as it is not only hydrophobic enough to avoid wetting as severe as the commercial PP membrane but also much more porous than the dense commercial PDMS and the lab-made DHC-PVDF membranes. This fact is evidenced by its contact angle (**Figure 4.3b**), pore size (**Table 4.1**), and negligible contribution of the PHM-PVDF membrane's k_M^{-1} to its experimental K_{OL}^{-1} (**Figure 4.7**), respectively. Indeed, the PHM-PVDF membrane exhibited an experimental K_{OL}^{-1} that was about 30-40% lower than the commercial PDMS membrane and comparable to the commercial PP membrane for liquid velocity ranging from 0.15 to 0.30 m s⁻¹ (**Figure 4.6b**) despite its larger d_i . It is also worth noting that the experimental K_{OL}^{-1} of the PHM-PVDF membrane was the closest (0.87-1.07 times) to the theoretical k_L^{-1} for the entire liquid velocity range (**Figure 4.6f**). The similarity between the PHM-PVDF membrane's experimental K_{OL}^{-1} and theoretical k_L^{-1} implies that it is crucial for a membrane contactor to have both hydrophobicity and a porous structure to reduce the experimental K_{OL}^{-1} to the extent of the theoretical k_L^{-1} .

4.2.7 The influence of the A_M on CH_4 flux

In this section, we examine the influence of membrane- and operation-related parameters on CH_4 flux, focusing on the A_M and K_{OL} -related parameters (e.g., pore wetting, k_L , and k_M) but exclude capillary pressure (i.e., CH_4 flux obtained at 0.02 m s⁻¹ was excluded from consideration). First, upon considering that there was no significant difference (within $\pm 2\%$; **Figure 4.8a**) between the experimental K_{OL} for the commercial

PP and the PHM-PVDF membranes beyond 0.10 m s^{-1} , we compared the two porous membranes' CH_4 fluxes to evaluate A_M 's influence. Note that pore wetting and k_L (Figure 4.8b) were already captured in the experimental K_{OL} and, as such, are not responsible for the difference in the CH_4 fluxes for the two membranes.

Figure 4.8 (a) Experimental K_{OL} (b) theoretical k_L of four different membranes plotted against the liquid velocity. The theoretical k_L was obtained based on Leveque's equation. Error bars indicate the standard deviations obtained from two different samples

Figure 4.9 shows that the PHM-PVDF membrane's CH_4 flux was about 2.4 and 2 times higher than the commercial PP membrane at 0.05 and 0.10 m s^{-1} , respectively, and maintained at about 1.8 times higher when the liquid velocity exceeded 0.10 m s^{-1} . Looking back to Eq (2-20) to investigate differences in the CH_4 fluxes, only A_M remains as a valid explanation of the higher CH_4 flux for the PHM-PVDF membrane, as the experimental K_{OL}

was negated and the other variables are kept constant. We thus conclude that the PHM-PVDF membrane had a higher CH_4 flux than that of the commercial PP membrane due to its smaller A_M (**Table 4.1**). This finding thus supports the conclusion from the theoretical analysis that A_M needs to be optimized for the best performance.

4.2.8 The influence of k_M on the CH_4 flux

Figure 4.9 CH_4 flux of four different membranes plotted against the liquid velocity. Error bars indicate the standard deviations obtained from two different samples.

We further examined the effect of k_M on CH_4 flux by contrasting the DHC- and PHM-PVDF membranes. We were able to distinguish the k_M of the two lab-made membranes from the other K_{OL} -related parameters because they not only have almost the same theoretical k_L (within $\pm 5\%$; **Figure 4.8b**) and A_M (about 10% difference; **Table 4.1**) but also effectively prevent pore wetting while having significantly different k_M values (6.16×10^{-5} and $1.79 \times 10^{-2} \text{ m s}^{-1}$ for the DHC- and PHM-PVDF membranes, respectively). Thus, the higher K_{OL} of the PHM-PVDF membrane (**Figure 4.7a**) probably resulted from the much larger k_M . Furthermore, given that the PHM-PVDF membrane's CH_4 flux was nearly double, as shown in **Figure 4.9**, it is extremely likely that the higher k_M drove the

difference. As such, k_M also matters to CH_4 flux at times, although it is generally known that the k_L primarily governs the K_{OL} .

4.2.9 The influence of d_i and u on CH_4 recovery

Lastly, we investigated the influence of membrane characteristics and operating parameters on CH_4 recovery. As discussed in section 4.2.3, d_i , A_M , and u are important enough to sway CH_4 recovery. Theoretically, d_i and u have a negative correlation with CH_4 recovery, whereas A_M has a positive impact. However, it was difficult to experimentally detect any obvious correlations between A_M and CH_4 recovery, as the impact of A_M was relatively smaller than d_i and u . In contrast, it is evident from **Figure 4.10** that u strongly influenced the CH_4 recovery, regardless of the membrane type. The CH_4 recovery rates for each membrane used in this study decreased as u increased, suggesting that it is necessary to control u to achieve optimal CH_4 flux and recovery simultaneously. The d_i was also confirmed to have a distinct influence on the CH_4 recovery given that a similar trend was observed between membranes with similar d_i , even though each pair (i.e., commercial PP and commercial PDMS membranes; DHC- and PHM-PVDF membranes) had different pore sizes and hydrophobic properties. Therefore, adjusting d_i may also be necessary to balance CH_4 flux and recovery while maximizing the use of the membrane-contact system.

Figure 4.10 CH₄ recovery of four different membranes plotted against the liquid velocity. Error bars indicate the standard deviations obtained from two different samples.

4.2.10 The influence of concurrent CO₂ removal on the membrane selectivity

During the removal of D-CH₄ from anaerobic effluent, the simultaneous removal of all other dissolved gases, including CO₂, is unavoidable. However, since CH₄ and CO₂ are the two main gases in biogas, it is equally important to discuss the effect of CO₂ removal on D-CH₄ recovery. With this respect, the influence of CO₂ in D-CH₄ recovery is discussed in the following section.

As compared to the CH₄ flux (**Figure 4.9**), the experimental CO₂ flux across the membranes (**Figure 4.11a**) is almost 10 times greater in magnitude. This is expected, due to the higher concentration of D-CO₂ (~ 13-15 mol m⁻³) than that of the D-CH₄ (~ 0.71-0.86 mol m⁻³) in the anaerobic reactor effluent. Note that CO₂ is ~25 times soluble in water as compared to CH₄. Thus, inevitable CO₂ removal is anticipated as a result of the larger concentration gradient across the membrane. In this sense, all the membranes are favorable for stripping out more CO₂ than CH₄ which will contaminate the stripped-out gas reducing the purity.

Figure 4.11 (a) Experimental CO₂ recovery flux (b) experimental K_{OL}^{-1} for CO₂ (c) CO₂:CH₄ selectivity (d) CO₂: CH₄ recovery efficiency ratio

Despite the potential larger CO₂ recovery flux, the gas transport across the membrane is determined by the K_{OL} of the membrane, as discussed in the previous sections of this chapter. **Figure 4.11 b** shows the experimental K_{OL}^{-1} obtained based on CO₂ for all the four membranes used in this study. As compared to **Figure 4.6b** the variation of the K_{OL,CO_2}^{-1} is similar to that of K_{OL,CH_4}^{-1} aligning with the previously discussed gas transport behavior of the four tested membranes. Interestingly, for all the membranes the order of the K_{OL,CO_2}^{-1} and K_{OL,CH_4}^{-1} are comparatively the same but with a larger magnitude for K_{OL,CO_2}^{-1} , probably due to the effect of the lower CO₂ volatility as compared to CH₄ that will lead to increase the membrane mass transfer resistance. Note that based on the mass transfer resistance analysis, the membrane resistance for CH₄ transport of commercial PDMS and

DHC-PVDF membranes was reported to be ~70% and ~50%, respectively. Higher values of membrane resistance for CO₂ transport were reported for those non-porous membranes (~76% and ~65% for commercial PDMS and DHC-PVDF, respectively).

Since K_{OL} consists of the fluid hydrodynamics of all three phases (the liquid, membrane, and gas phases), the best way to interpret the selectivity of the membrane is the ratio of the K_{OL} of CO₂ over CH₄ [233]. Assuming that the mass transport across the membrane is purely restricted by the liquid phase resistance (ideal situation), the membrane selectivity can be obtained from taking the two-third of the ratio of liquid phase diffusion coefficients between CO₂ and CH₄ (~1.08, according to the Leveque's Equation). **Figure 4.11c** shows the CO₂ selectivity (*i.e.*, the ratio of CO₂ and CH₄ overall mass transfer resistance) of the membranes. Both commercial PP and PHM-PVDF membranes were reported closer to the reference state, perhaps the liquid phase dominant mass transfer *or* lesser membrane contribution on mass transfer resistance due to the microporosity. However, the CO₂: CH₄ selectivity of those microporous membranes increased with the elevating liquid velocity up to 0.1 m s⁻¹ then stabilized. This observation might be due to the gas phase-controlled mass transfer at higher G/L ratios (lower liquid flowrates since gas flowrate is constant in this study), as also noted by McLeod *et al.*[234]. The complete gas phase controllers mass transfer situation results in CO₂:CH₄ selectivity around 0.75 whereas the starting point of both microporous membranes is around the same number. However, with the increment of the liquid flow rate, the effect of gas-phase mass transfer has been diminished which is convinced by the increment of the CO₂ selectivity up to 0.1 m s⁻¹. Both non-porous membranes showed higher and consistent CH₄ selectivity over the tested liquid velocity range compared to the microporous membranes. The dominance of membrane resistance might be the underlying reason for obtaining the CH₄ selective

membrane. This was further reflected from the lower K_{OL, CO_2} compared to K_{OL, CH_4} . Based on the experimental observations, non-porous membranes (dense *or* composite membranes) are better than the microporous membrane in terms of CH_4 selectivity despite the lower CH_4 flux due to the higher membrane mass transfer resistance. Thus, the trade-off prevails between the CH_4 recovery flux and CH_4 selectivity of the membranes, which should be carefully controlled. The experimental CO_2 recovery efficiencies further manifested the CH_4 selectivity of the membranes to that of CH_4 recovery efficiency which is shown in **Figure 4.11d**.

4.3 Conclusion

In this study, we systematically investigated membrane characteristics and the operating parameters that affect mass transfer and recovery of dissolved CH_4 from anaerobic effluents, both theoretically and empirically. According to our theoretical study, the d_i , A_M , and u were verified to influence two performance parameters, as follows.

- 1) Both CH_4 flux and recovery could be improved by reducing d_i and thereby increasing k_L .
- 2) Increasing A_M was found to enhance CH_4 recovery while decreasing k_L , thereby leading to a lower CH_4 flux.
- 3) Increasing L was found to be accompanied by an increase in both u and k_L , thereby inducing a higher CH_4 flux while reducing CH_4 recovery due to the decreased residence time in the module.

Our experimental results for four membranes with distinct structural and chemical properties reflect the parameters necessary to control real-world applications.

- 1) The capillary pressure imposed by the inlet of hollow fibers can dramatically increase K_{OL}^{-1} at low liquid velocities by preventing the liquid from flowing in some inlets.
- 2) Pore wetting can whittle down the k_M because the liquid filling the subsurface voids become too stagnant to promote mass transfer.
- 3) k_M^{-1} may be significant enough to affect K_{OL}^{-1} in dense membranes.
- 4) A_M may have an influence on CH_4 flux (the smaller the area, the higher the CH_4 flux) if other parameters are kept constant.
- 5) d_i and u were found to govern CH_4 recovery, which decreased as d_i and u increased.

Furthermore, we can conclude from the above observations to enhance both CH_4 flux and recovery.

- 1) d_i should be reduced as long as the capillary pressure imposed by the module inlet does not become significant.
- 2) A_M must be optimized to balance CH_4 flux and recovery.
- 3) L (or u) should be increased but only to the extent that it helps overcome capillary pressure but does not compromise CH_4 recovery.
- 4) Porous surfaces are favorable for enhancing CH_4 flux.
- 5) The membranes' hydrophobic properties should be maximized to prevent pore wetting. It was experimentally confirmed to be effective in mitigating the wetting of porous membranes with $0.12\ \mu m$ pores when the contact angle was increased from 84.5° to higher than approximately 110° .

Lastly, we encourage more researches to investigate how mass transfer coefficients, CH_4 flux, and recovery vary, provided that the feed solution is fed to the shell side. The

attempt could show the other side of the effects of the parameters addressed in this study, considering that many differences have been found when the feed solution is fed to the shell side (*e.g.*, the bypass and channeling phenomena [235], lower mass transfer coefficient and pressure drop [235], less wetting [235], and influence of packing density [47]). We also think it is worth trying to overcome the trade-off between the anti-wettability and gas permeability of a composite membrane based on the density of a coating layer or whether to coat the lumen or shell side for future work. Such a comprehensive discussion on membrane- or operation-related parameters would be beneficial to determine how the findings of this study could be realized in a variety of practice settings.

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5 Coating of PVDF Membranes with PDMS for Antiwetting Functionality¹

5.1 Introduction

In this study, PDMS-coated PVDF hollow fiber membranes for the efficient recovery of D-CH₄ from anaerobic effluents is reported. The rationale behind developing such a composite membrane was twofold. First, PDMS is appealing for MC applications due to its high gas permeability, hydrophobic nature, and good processability [236, 237]. PVDF-based hollow fiber membranes utilized, on the other hand, provide a robust platform for designing high-performance MC membranes since a high porosity of as high as 85% and a dense shell surface structure can be readily prepared by controlling the spinning conditions [227]. To modify the PVDF hollow fiber substrates with PDMS, we have employed two approaches: i) bulk (surface) modification, and ii) lumen (surface) modification. The bulk modification approach is a technically facile method since it involves no precaution to preserve the innate porosity profile of the support membranes. From a fundamental perspective, the lumen modification process we apply is a “top-layer surface modification” approach that aims at preserving the porosity profile of the support as much as possible [238]. Being this said, the rationale behind the selection of the “lumen” surface rather than the “shell” side is that the lumen side operation provides superior recovery performance compared to shell side operation [59, 143, 227].

Since the surface chemistry and morphology of the support membranes have been altered during membrane modification, the resulting MC membranes were characterized with field emission scanning electron microscopy (FESEM), energy-dispersive X-ray

¹This chapter is produced with the permission of Sethunga, G. S. M. D. P., Karahan, H. E., Wang, R., & Bae, T-H., PDMS-coated porous PVDF hollow fiber membranes for efficient recovery of dissolved biomethane from anaerobic effluents. *Journal of Membrane Science*. 584(2019) 333-342. Copyright © 2019 Elsevier

spectroscopy (EDS), atomic force microscopy (AFM), and water contact angle (WCA) measurements. The D-CH₄ recovery experiments were performed at room temperature and under atmospheric pressure by feeding with CH₄-saturated tap water, or actual industrial effluents obtained from an anaerobic membrane bioreactor (AnMBR) or up-flow anaerobic sludge blanket (UASB). For benchmarking purposes, we also compared D-CH₄ recovery, and fouling propensity of in-house made PDMS-coated PVDF, commercial polypropylene (PP), and commercial PDMS membranes. Our results show that a simple PDMS coating routine is sufficient for converting high-porosity PVDF supports into high-performance MC membranes for D-CH₄ recovery. Thus, the demonstrated approach is of industrial relevance for dissolved gas recovery applications.

5.2 Results and discussion

5.2.1 PDMS modification of PVDF membranes

The PVDF hollow fiber membrane support fabricated based on the procedure described in our previous work has a bulk porosity of ~85%. As shown in **Figure 5.1a**, the lumen side of this PVDF support has an open structure due to the soft bore fluid employed in the fabrication process. (For further details, please refer ref. [227].) Membrane wetting problem aside, having a skin-free inner surface is advantageous for MC membranes to be employed in lumen mode since surface pores reduce the mass transfer resistance at the liquid-gas interface [138]. **Figure 5.1b** and **Figure 5.1c** show the FESEM images of the bulk-modified membranes, both of which preserve the surface pore structures largely after the PDMS coating. The slight reduction in the open cellular structure of the lumen surface is likely because the membrane modification was carried out by flowing the PDMS precursor solution through the lumen side. Likewise, as seen in the cross-sectional views

of the membranes given as the inset image of **Figure 5.1b**, no significant change occurred in the pore structure of membrane bulk at low PDMS concentration (0.5 wt%). For the case of 5 wt% PDMS, a slight change was observable (compare inset images of **Figure 5.1a** and **Figure 5.1c**).

Figure 5.1 SEM images of unmodified, bulk-modified, and lumen-coated membranes: (a) unmodified, (b) BM-0.50, (c) BM-05.0, (d) LM-0.50, (e) LM-05.0, and (f) LM-10.0. Large images show inner surface morphologies of membranes, while inset figures show cross-sectional views of the same membranes. (All scale bars of the inset figures indicate 10 μm .)

The primary aim of the lumen modification was to obtain a composite PDMS-PVDF membrane involving a thin and dense PDMS coating on the lumen side of microporous PVDF support. The pores of the support were pre-occupied with glycerol to limit the dispersion of PDMS across the bulk of the membrane, which helps preserve the bulk porosity during modification [238]. The FESEM images of the lumen surfaces of PVDF membranes upon PDMS coating with different concentrations are shown in **Figure 5.1d**, **Figure 5.1e**, and **Figure 5.1f**. **Figure 5.1d** indicates that a PDMS prepolymer mix of 0.5 wt% is not enough for obtaining a skin-like conformal coating under our experimental conditions. But, both 5 wt% and 10 wt% PDMS prepolymer concentrations could provide dense and conformal coatings. Notably, the cross-sectional images of 5 wt% (**Figure 5.1e**, inset) and 10 wt% (**Figure 5.1f**, inset) conditions suggest that the PDMS coating slightly

perforated the denser part of PVDF supports. Notably, the penetration of the PDMS coating to the support membrane is desirable for preventing possible delamination problems during the operation.

Figure 5.2 The cross-sectional EDS maps of bulk- and lumen-modified membranes based on silicon (Si K α 1) signal as the representative element of PDMS modification: (a) BM-0.50, (b) BM-05.0, (c) LM-05.0, and (d) LM-10.0. Note that the inset charts indicate the relative intensity profiles of F and Si signals. (All scale bars indicate 50 μ m.)

To assess the homogeneity of PDMS-based surface modification, we have performed EDS analysis, as well. **Figure 5.2** shows the silicon (Si) distribution maps (as the representative element of the PDMS modification). As clearly seen in **Figure 5.2a** and **Figure 5.2b**, the bulk modification process provides a rather uniform coating across the membranes. Accordingly, the bulk porosities of BM-0.50 and BM-05.0 were determined as ~83% and ~74%, respectively, while the porosity of the unmodified membrane was ~85%. For the lumen modification, on the other hand, the PDMS coating was localized on the lumen surface of the membrane (**Figure 5.2c** and **Figure 5.2d**). Importantly, increasing the concentration of PDMS prepolymer solution from 5 wt% to 10 wt% provided a thicker and denser coating based on the comparison of **Figure 5.2c** and **Figure 5.2d**. Also, the quantitative representations of Si inclusion ratios with respect to fluorine (F) reveal that the BM-05.0 has the highest Si content (see the inset charts in **Figure 5.2**). The water contact

angle values are seen in **Table 5.1** also support these EDS observations. The WCA of the membranes exhibited a minimum of ~14% increase (BM-0.50) upon PDMS modification. The contact angle values of BM-05.0, LM-05.0, and LM-10.0 were in agreement with the reported contact angle value of PDMS materials (*i.e.*, 120°) [239].

Table 5.1 The details of the commercial and inhouse made membranes tested for D-CH₄ recovery experiments, and the modules prepared using those membranes. (Note that the commercial PDMS membrane, PDMSXA-10, come in a module containing 30 fibers with following specifications: Φ_{inner} , 190 μm ; Φ_{inner} , 300 μm ; length, ~9.3 cm.)

	UM- PVDF	BM-0.50	BM-05.0	LM-05.0	LM-10.0	PP-DGM
Φ_{inner} (μm)	700.1 $\pm$ 1.8	698.1 $\pm$ 2.6	710.3 $\pm$ 1.4	553.2 $\pm$ 4.2	540.8 $\pm$ 4.7	189.3 $\pm$ 1.4
Φ_{outer} (μm)	985.5 $\pm$ 2.3	976.1 $\pm$ 1.5	983.6 $\pm$ 2.0	826.8 $\pm$ 2.5	803.6 $\pm$ 4.1	313.4 $\pm$ 5.0
WCA [†] (°)	98.5 $\pm$ 1.4	112.4 $\pm$ 2.2	116.5 $\pm$ 2.4	120.4 $\pm$ 2.3	123.3 $\pm$ 1.8	not tested
Porosity (%)	~85	~83	~75	~79	~77	~49
Modules prepared						
Length (cm)	not tested	18.5	18.5	18.5	18.5	18.5
No. of fibers	not tested	6	6	6	6	100

[†] The WCA of the unmodified PVDF membrane was “98.5 $\pm$ 1.4” under the same measurement conditions. The contact angle values of unmodified membranes dropped around 30% in less than 3 minutes

We would also like to highlight that the lumen-modified membranes showed a reduction in both inner and outer diameters (as seen in **Table 5.1**). This outcome is due to the shrinkage of membrane support during the curing of PDMS 80 °C [240, 241]. Interestingly, the inner and outer diameters of bulk-PDMS-modified membranes remained almost unchanged during the PDMS curing. We attributed this observation to the even distribution of PDMS over the entire cross-section of PVDF support, which prevents the dwindling of resulting membranes.

5.2.2 Analysis of D-CH₄ recovery flux

The CH₄ recovery performance of the modified PVDF membranes was benchmarked against a commercial degassing membrane (DGM) made of PP (in short, PP-DGM). In these experiments, the lumen operation was selected since it is more effective in achieving higher gas fluxes [242]. To provide a standardized comparison, those experiments were performed using simulated anaerobic effluents (*i.e.*, tap water saturated with simulated/synthetic biogas). **Figure 5.3a** shows the CH₄ fluxes of modified membranes as a function of the liquid velocity. The increase in liquid velocity decreases the liquid boundary layer resistance and thus increases the CH₄ fluxes [20, 54]. It is clearly observed that the CH₄ flux obtained for all modified membranes in this study is higher compared to the commercial PP-DGM. This outcome is probably due to the higher bulk porosity of PVDF-based membranes. Note that the porosity values of all PVDF-based membranes were greater than 75%, while the respective value for PP-DGM was only 49%. The higher performance of BM-0.50 compared to BM-05.0 suggests that an extensive modification becomes detrimental, expectedly due to the reduction of bulk porosity. In a similar vein, the LM-05.0 exhibited the best CH₄ recovery performance among all membranes, exceeding LM10.0. The LM-05.0 membrane has a thin but seemingly

conformal PDMS coating, rendering a lower mass transfer resistance compared to the thicker coating layer.

For a clearer understanding of the CH₄ recovery flux of different membranes, the experimental overall mass transfer coefficients were analyzed and compared in **Figure 5.3b**. Among all membranes, the LM-05.0 has the lowest overall resistance. K_{OL} reflects the combination of all three individual mass transfer coefficients correspond to liquid, gas, and membrane phases related to the well-known resistance-in-series model depicted by **Equation 2-5** [243]. For the gas-liquid systems, the gas phase mass transfer resistance is negligible if the membrane operates at a fully dry condition [244]. Thus, K_{OL} is totally controlled by the liquid phase and membrane mass transfer coefficients, in which the corresponding theoretical estimations are adequately described in **Equation 2-19** to **2-21**, respectively. These correlations suggest that the critical parameters affecting K_{OL} are the membrane-related physical parameters (i.e., inner diameter, thickness, porosity, tortuosity) if the operational parameters (e.g., liquid velocity) and effective membrane module length are fixed. (Accordingly, the lower the membrane inner diameter, the higher the k_L and the lower the membrane porosity lower the k_M .)

For all membranes showed in **Figure 5.3b**, the K_{OL} values increase as the liquid velocity increases, which could be attributed to the reduction of the thickness of the boundary layer in the liquid phase [238]. Albeit small inner membrane diameters are favorable for lowering the liquid phase mass transfer resistance (in line with Leveque's equation), the overall mass transfer resistance (K_{OL}^{-1}) of the PP-DGM membrane (with the lowest inner membrane diameter) is the highest among the membranes we studied. To determine the membrane inner diameter effect to the overall mass transfer resistance, the theoretical k_L^{-1} determined from Leveque's equation was weighted with the experimentally

derived K_{OL} (showed in **Figure 5.3c**). The data was obtained for a representative liquid velocity of around 0.1 m s^{-1} . Surprisingly, LM-05.0 and BM-0.50 had closer k_L^{-1} contribution compared to the overall mass transfer resistance whereas the former has the highest among the tested membranes. The sequence of the percentage contribution of the k_L^{-1} to K_{OL}^{-1} follows the ascending order of PP-DGM<LM-10.0<BM-05.0<BM-00.5<LM-05.0, which is different from the inner membrane diameter variation of the membranes, highlighting the membrane phase resistance is non-negligible.

As anticipated, the effect of porosity on the membrane mass transfer resistance to the overall mass transfer resistance of the porous membranes followed the sequence of PP-DGM>BM-05.0>BM-0.50 as same as the ascending order of porosity. Further, the lumen-coated membranes exhibit an identical behavior: the higher porosity lowers the membrane phase resistance. However, still, the observation was divergent when comparing LM-05.0 and BM-0.50. It is also noteworthy to highlight that the bulk porosity reported in **Table 5.1** is an indication of the average porosity of the membrane. And, as long as the membrane modification does not cause a dense layer (in bulk or lumen), it is hard to differentiate the effect of modification modality. Thus, the membrane resistance exerted due to the thin PDMS layer on the lumen surface in LM-05.0 is negligible (**Figure 5.2c**) as the support layer porosity might still be near its original value of ~85%. On the other hand, the mass transfer had severely affected in LM-10.0 due to the formation of a much thicker and denser PDMS layer on the lumen. (In agreement with the **Equation 2-23**, the thicker and denser the coating layer the higher the membrane mass transfer resistance.) Additionally, as evident by the EDS results are given in **Figure 5.2c** and **Figure 5.2d**, the penetrated PDMS amount in LM-10.0 (**Figure 5.2d**) seems to be higher. Thus, the porosity of the support layer becomes lower, and thereby, it is reasonable to expect a higher membrane mass

transfer resistance. **Figure 5.3c** compares the overall mass transfer coefficients (K_{OL}) of membranes. Among all membranes, the LM-05.0 has the lowest overall resistance. As the liquid velocity increases, the thickness of the boundary layer in the liquid phase decreases resulting in a decrease in the liquid phase mass transfer resistance [53]. Thus, as the next step, we have performed Wilson plot analysis, which provides the mass transfer coefficients of membranes (k_M), ruling out the contribution of liquid phase mass transfer resistance. The lumen side liquid mass transfer coefficient can be determined by the Leveque solution in which the K_{OL} is a direct function of the minus one-third power of liquid velocity. Thus, by substitution of the Leveque solution in the resistance-in-series model and rearranging, the membrane mass transfer resistance can be found from the y-intercept of the plot of K_{OL}^{-1} versus $v_L^{-1/3}$ (**Figure 5.3d**). The membrane mass transfer coefficients of all in-house membranes (listed in **Table 5.2**) were higher than that of PP-DGM due to their higher bulk porosity compared to PP-DGM (**Table 5.1**). On another aspect, a thicker lumen coating layer can impose an undesirable increase in membrane mass transfer resistance. For instance, the membrane resistance of LM-10 is ~26% higher than that of LM-05.0 due to its thicker PDMS coating. Importantly, the LM-05.0 membrane provided the best membrane mass transfer coefficient among all membranes, which explains why it provided the highest D-CH₄ recovery from simulated anaerobic effluents.

Figure 5.3 The performance of bulk- and lumen-modified membranes in D-CH₄ recovery. (a) The D-CH₄ recovery flux trends, (b) Overall Mass Transfer Coefficients of different membranes, (c) Percent contribution of liquid phase mass transfer resistance to overall mass transfer resistance, and (d) Wilson Plot of bulk-modified (BM-00.5, BM-05.0) and lumen-modified (LM-05.0, LM-10.0) membranes compared to the reference membrane (PP-DGM) as a function of the changing liquid velocities.

The experimental overall mass transfer resistance (K_{OL}^{-1} , at a liquid velocity of 0.25 m s⁻¹) and the membrane resistance (from Wilson plot summary in **Table 5.2**) for LM 05.0 were 41653 s m⁻¹ and 6225 s m⁻¹ respectively. Thus, ~15% of the overall mass transfer resistance comes from the membrane resistance, which is lower than we could achieve before. Wongchitphimon *et al.* [59] performed the membrane mass transfer analysis for two different Matrimid® hollow fiber membrane supports modified with polymer fluorinated silica and reported around 17.7% contribution of the membrane mass transfer resistance to the total resistance for the best membrane (porosity: 62.9 ± 2.0 %, WCA:

122.6 ± 1.8 °). Comparatively, higher membrane support porosity of LM-05.0 makes it more attractive in terms of D-CH₄ recovery. Accordingly, the LM-05.0 membrane was selected and employed in gas recovery tests using actual anaerobic effluents obtained from industrial AnMBR and UASB, as discussed in the following section.

Table 5.2 Details of the Wilson Plot analysis and the mass transfer coefficients of membranes obtained based on CO₂ gas flow.

Membrane	Equation	R ²	k _M (m s ⁻¹)
BM-0.50	$1/K_{OL,CO_2} = 23710v^{-\frac{1}{3}} + 7177.6$	0.9970	8.39×10^{-5}
BM-05.0	$1/K_{OL,CO_2} = 26021v^{-\frac{1}{3}} + 8656.6$	0.9896	7.02×10^{-5}
LM-05.0	$1/K_{OL,CO_2} = 22299v^{-\frac{1}{3}} + 6225.0$	0.9960	1.11×10^{-4}
LM-10.0	$1/K_{OL,CO_2} = 25494v^{-\frac{1}{3}} + 7823.8$	0.9945	7.03×10^{-5}
PP-DGM	$1/K_{OL,CO_2} = 14866v^{-\frac{1}{3}} + 9512.6$	0.9702	6.91×10^{-5}

5.2.3 Performance of selected membranes at realistic conditions

To evaluate the performance of the LM-05.0 membrane under more realistic conditions, we have also made tests using actual anaerobic effluents obtained from treatment plants (note that **Table 2.1** shows the wastewater characteristics). **Figure 5.4a** shows the performance comparison of LM-05.0 and (commercial) PP-DGM with an AnMBR effluent. The fluxes of both membranes were almost steady during 8 days of operation, with a flux fluctuation of below 5%. Such a low drop in flux indicates that not only the membrane wetting but also the severe fouling does not take place when AnMBR effluent which contains low concentrations of foulants is used as the feed. However, both LM-05.0 and PP-DGM showed a noticeable flux decline with UASB effluent, albeit PP-DGM performed worse (**Figure 5.4b**). To gain an insight regarding the possible influence

of surface roughness, we have attempted to make AFM studies on cut-open LM-05.0 and PP-DGM fibers. Despite the challenges of making AFM measurements in the lumen side of the fibers, we could obtain 2-3 images per fiber. Based on these images, the root mean square (RMS) roughness values of LM-05.0 and PP-DGM are 30.7 ± 3.6 nm and 41.8 ± 0.7 nm, respectively. These results altogether imply that a smooth and dense membrane surface is less susceptible to membrane fouling, which is in agreement with the observations of other researchers [244]. Meanwhile, the flux behavior of LM-05.0 and PDMSXA-10 membranes were comparable as both membranes have a dense PDMS surface that contacts with the feed solution. On another aspect, the flux decline of both membranes reached 20% at day 6 and then leveled. This observation gives a hint that cleaning the membranes after 5 days of operation would be suitable. However, further analysis is needed to suggest a detailed membrane cleaning procedure.

To gain further insight regarding the fouling behavior of membranes, we did membrane autopsy with FESEM, as well. **Figure 5.5** shows the inner surface morphologies of PP-DGM and LM-05.0 membranes before and after 10 days of exposure to UASB effluent. Apparently, both PP-DGM (compare **Figure 5.5a** and **Figure 5.5b**) and LM-05.0 (compare **Figure 5.5c** and **Figure 5.5d**) membranes could not resist fouling. However, the biocake layer formed on PP-DGM (**Figure 5.5b**) was dense and could cover the large protrusions existing on the bare membrane surface (see inset of **Figure 5.5a**). While the surface features of LM-05.0 were still observable after the operation, and the foulants adhered to the surface were patchy. Importantly, these visual observations also correlate with the severe flux decline profile shown in **Figure 5.4b** for PP-DGM and relatively lower performance loss of LM-05.0.

Figure 5.4 Inner surface of (a,b) commercial PP-DGM, and (c,d) LM-05.0 membranes (a,c) before, and (b-d) after being exposed to UASB effluent. The inset figures in Figure 5.4a and Figure 5.4c are the AFM images of the same membranes captured on arbitrary locations.

Figure 5.5 Long-term CH_4 fluxes of LM-05.0 in comparison to the commercial membrane(s) using (a) AnMBR, and (b) UASB effluents. (Note that the UASB effluent was prefiltered with a loose cotton swap, which helps to clarify the large aggregates and hence reduces the risk of fiber blocking during operation.)

5.3 Conclusions

A PDMS-modified PVDF hollow fiber MC membranes for recovery of D-CH₄ from anaerobic effluents were designed in this study. The experiments conducted on the bulk- and lumen-modified membranes clearly demonstrated the benefit of preserving the bulk porosity of the membranes upon surface modification. Our results suggested that the bulk modification causes a significant level of reduction in bulk porosity (even at a low PDMS concentration). For lumen modification, on the other hand, PDMS concentration should be optimized, considering both surface coverage and bulk porosity. Along these lines, we have fabricated an optimized PDMS-PVDF membrane by lumen modification. In the experiments performed using a simulated effluent, this optimized membrane demonstrated over two times higher CH₄ flux compared to commercial PP-DGM over a large liquid velocity window. In equal importance, the demonstrated composite membrane was capable of operating with AnMBR effluent without a considerable performance loss for more than a week. However, the same membrane has experienced a ~20% flux drop in a 10-days operation with UASB effluent. Meanwhile, the commercial PP-DGM showed a more drastic membrane fouling under the same conditions, resulting in a ~70% flux decline. This result suggests that having a dense skin layer is beneficial in reducing membrane fouling in actual operations. Nevertheless, further studies should be undertaken for mitigating the fouling issue with high-strength effluents as well as developing a cleaning procedure.

6 Antifouling Coating of PDMS-PVDF Membranes with Amphiphilic Additives

6.1 Introduction

In **Chapter 5**, it was reported PVDF membranes (supports) coating with polydimethylsiloxane (PDMS) for tackling the wetting problem [142]. The PDMS-modified PVDF membranes (in short, PDMS-PVDF) demonstrated high D-CH₄ recovery performance with simulated anaerobic effluents. More importantly, they could afford low-strength anaerobic effluents obtained from a membrane bioreactor (AnMBR), as well. However, even the best PDMS-PVDF membranes failed at operating with a high-strength anaerobic effluent obtained from an up-flow sludge blanket reactor (UASB) [142].

For providing a fair assessment of the application potential of the MC process for D-CH₄ recovery from the anaerobic effluents, this study aims to design an anti wetting membrane with low fouling propensity. To this end, as it is potentially scalable and readily anti-wetting, it was decided to upgrade the PDMS-PVDF membrane proposed in **chapter 5** [142] by adding on fouling resistance functionality, considering its wide adoption for preparing antifouling surfaces and membranes. Here, the PDMS-coatings were post-treated with PDMS-based amphiphilic copolymers tethered with PEG like segments. Studies have reported that PEG and polyethylene oxide (PEO) containing materials can improve fouling resistance capability for organic as well as bio foulants [160, 245, 246]. These substances can easily form a hydration layer with water via hydrogen bonds restraining the protein adsorption due to the energy barrier between the membrane surface and the protein molecule [165]. Using simulated anaerobic effluents, the D-CH₄ recovery fluxes of PDMS-

PVDF and hydrophilized the PDMS-PVDF membranes against the commercially available PP degassing membranes were experimented. Later, all membranes were benchmarked for short- and long-term operations under actual anaerobic effluents (both AnMBR and UASB). Lastly, an energy analysis was performed for the membranes and demonstrated the viability of the MC process for actual practice.

6.2 Results and discussion

6.2.1 Characterization of wetting- and fouling-resistant membranes

To recover D-CH₄ from anaerobic effluents (*via* G-L MC process) effectively, a membrane should ideally exhibit the following three characteristics: (1) high porosity (to favor mass transfer), (2) hydrophobicity (to limit wetting-related resistance to mass transfer), and (3) fouling resistance (to ensure long-term performance). The PVDF-based microporous hollow fiber membranes meet the first criterion very well with its porosity level of around 82- 85% [142, 227]. By increasing the WCA over 20% (from ~98.5° to ~120.4°), the PDMS-coating helps to suppress the wetting problem and meets the second criterion [142]. Besides, despite sealing the surface pores considerably (compare **Figure 6.1a** and **Figure 6.1b**), the PDMS-coating does not cause a significant hindrance against mass transfer since being highly permeable to the gas molecules [142]. Therefore, to meet all three criteria at once, the PDMS-PVDF composite membrane needs to be improved with an antifouling coating without altering the properties of bulk support (PVDF) and anti-wetting layer (PDMS) significantly. As shown in **Figure 6.1c** and **Figure 6.1d**, the coating process we adopted for modifying the PDMS-PVDF membranes with PDMS-based amphiphilic coatings preserves the bulk porosity (compare the inset figures). And, the

surface morphology of the membranes also does not change drastically, which suggests that this process could modify the membranes in a surface-localized manner.

Figure 6.1 FESEM images of unmodified and surface-coated PVDF membranes: (a) PVDF (support) membrane, (b) PDMS-coated membrane (PDMS-only, PDMS-PVDF), (c) PDMS-co-P1-coated membrane (PDMS-co-P1), and (d) PDMS-co-P2-coated membrane (PDMS-co-P2). (The main and inset images show inner surface and cross-section morphology of the membranes, respectively. All the scale bars indicate 5 μm .)

To evaluate the impact of membrane surface modifications, FTIR, WCA, and SSP characterizations offer useful insights. By FTIR measurements (**Figure 6.2**), it is confirmed the PVDF surface can be modified with a PDMS-coating (forming PDMS-PVDF composite membrane). The PVDF membrane displayed its characteristic peaks at 876, 1171, 1277, and 1400 cm^{-1} , which are corresponding to the crystalline phases along with the peak at 840 cm^{-1} relating to the asymmetric stretching of CF_2 [247-249]. Further, the peaks around 2916 and 2976 cm^{-1} represented the CH_2 symmetric and asymmetric stretching vibrations of PVDF [247]. All the modified membranes showed the characteristic FTIR peaks of PVDF along with their own representative peaks. Since the modified membranes contained PDMS as the base coating, the peaks at 793, 1013–1059, 1259, and 2962 cm^{-1} were clearly visible that are corresponding to CH_3 rocking in Si-CH_3 , Si-O-Si stretching, CH_3 symmetric bending in Si-CH_3 and asymmetric CH_3 stretching of Si-CH_3 [250]. The broad peak around 3483 cm^{-1} confirmed the $-\text{OH}$ stretching of PDMS-

co-P1 [251]. The peaks around $2900\text{--}2960\text{ cm}^{-1}$ represent the --CH_2 stretching of PDMS copolymers used in this study [250]. For both PDMS-co-P1 and PDMS-co-P2, another peak for C–O stretching of ether groups (C–O–C) around $1070\text{--}1150\text{ cm}^{-1}$ was also expected. However, possibly due to the strong crystalline peaks of PVDF [251] and the inclusion of the copolymer-based antifouling coating as a very fine layer, those features could not clear. FTIR measurements also evidenced that the post-treatment procedure applied was successful in modifying the PDMS-coated PVDF membranes with block copolymers.

Figure 6.2 FTIR spectra of the (i) unmodified PVDF, (ii) PDMS-coated PVDF (PDMS-only or PDMS-PVDF), (iii) PDMS-co-P1-coated PDMS-PVDF, and (iv) PDMS-co-P2-coated PDMS-PVDF membranes. (Note that the shaded regions are to highlight the clear variations among the spectral features of membranes. Also, note the numbers indicated inside the figure indicate the wavenumber values at peak maxima.)

Figure 6.3 Wettability evaluation of surface-modified PVDF membranes based on the observation of WCA values as a function of time.

The WCA measurements summarized in **Figure 6.3** provide further evidence on the success of the facile coating procedure introduced in here. Being hydrophobic, the PDMS-only coating (PDMS-PVDF membrane) provided a pretty stable contact angle of around 112.5° over 60 seconds. Both PDMS-co-P1 and PDMS-co-P2 membranes, on the other hand, showed a hydrophilic behavior with WCA values at $\sim 14^\circ$ and $\sim 29^\circ$ when the water droplets age for 60 seconds on the membranes. One important implication of WCA measurement is that it provides a useful insight for anticipating the biofouling propensity of the surfaces [252]. When the surfaces are polar, the hydration effects reduce the adsorption of polar foulants (*e.g.*, certain macromolecules/particles and microorganisms). In this sense, it is reasonable to expect PDMS-co-P1 membranes to exhibit a higher level of resistance to fouling. Besides, the evaluation of the electrokinetic potential provides a useful indicator for anticipating the interactions of membrane surfaces with charged/noncharged foulants [253]. The PDMS-only surface exhibited the highest surface charge (with an SSP value of around -18.3 mV) due to its hydrophobic nature (**Table 6.1**). The PDMS-co-P1 and PDMS-co-P2 membranes had much lower SSP values at around

−4.1 mV and −8.4 mV, respectively. Thus, it is expected PDMS-co-P1 to have a less favorable interaction with nonpolar foulants, which often represents the major players responsible for organic fouling, as the same observation confirmed by Fu *et al.* [253].

Table 6.1 Streaming potential values of unmodified (PVDF-bare), anti-wetting-coated (PDMS-only), and antifouling-coated (PDMS-co-P1 and PDMS-co-P2) membranes.

Membranes Used for MC process	Streaming Potential (mV)
PVDF-bare (as-produced hollow fiber support)	-12.8 ± 1.7
PDMS-only (PDMS-coated PVDF, PDMS-PVDF)	-18.3 ± 0.3
PDMS-co-P1 (PDMS-co-P1-coated PDMS-PVDF)	-4.1 ± 0.3
PDMS-co-P2 (PDMS-co-P2-coated PDMS-PVDF)	-8.4 ± 0.9

6.2.2 Methane recovery performance and mass transfer analysis

The surface modification porous PVDF membranes affect the intrinsic gas recovery performance of the MC process significantly. For the case of PDMS-coated PVDF membranes, the PDMS-coating seals the surface pores very effectively, limiting the wetting phenomenon. However, at the same time, the PDMS-coating (as well as the post-treatment by PDMS-based copolymers) hinders the diffusion of gas molecules during the gas-liquid MC process. To be able to interpret the impact of those effects in actual operation, the CH₄ recovery performance of in-house and commercial membranes using simulated anaerobic effluents (*i.e.*, tap water supplemented with synthetic biogas) was initially tested. The physical characteristics of the membranes and the modules are listed in **Table 6.2**.

Table 6.2 Details on the physical description of the membranes and modules.

Parameter	PDMS-only	PDMS-co-P1	PDMS-co-P2	PP-DGM
Inner diameter (μm)	438.6 ± 2.3	429.3 ± 1.5	449.3 ± 1.2	189.3 ± 1.4
Outer diameter (μm)	671.7 ± 3.1	675.2 ± 2.1	677.4 ± 1.6	313.4 ± 5.0
Module diameter (cm)	0.95	0.95	0.95	0.95
Number of fibers	10	10	10	100
Effective length (m)	0.185	0.185	0.185	0.185

Figure 6.4 CH_4 recovery performance of membranes. (a) CH_4 recovery flux as function liquid velocity (b) percentage contribution of liquid phase resistance to overall mass transfer resistance.

Figure 6.4a shows the CH_4 recovery flux of all studied membranes with respect to the velocity of liquid feed. The CH_4 recovery flux of all the in-house membranes surpassed the performance of commercial PP degassing membranes (PP-DGM) mainly due to the higher PVDF support porosity ($\sim 82\text{--}85\%$) compared to that of PP-DGM ($\sim 49\%$). Among the in-house membranes, PDMS-only showed the best performance, which was approximate $\sim 14\text{--}20\%$ higher than the following membrane (when the liquid velocity was above 0.08 m s^{-1}), PDMS-co-P1. This small but meaningful reduction in performance is attributed to the extra fouling-resistant coating layer that hindered mass transfer through the membrane.

Since the overall mass transfer coefficient (K_{OL}) serves as a key indicator for evaluating the CH_4 recovery flux performances, analysis of the K_{OL} of each membrane is necessary. The K_{OL} comprises of the individual mass transfer coefficients of liquid, membrane, and gas phases, which can be combined with the in-series model to reach K_{OL} [254]. For the gas-liquid MC process, the mass transfer resistance of gas phases has no significant impact on K_{OL} compared to the resistances exerted by liquid and membrane phases [226]. Still, the gas phase mass transfer resistances were determined using the shell side mass transfer correlation established for hydrophobic membranes with low Reynolds numbers ($0 < Re < 500$) and low packing densities (0.04–0.40) by Prasad *et al.* [255]. The calculated results showed no significant variation with the liquid velocity, and the average resistance values were around 350.50, 360.70, 359.93, and 370.84 $s\ m^{-1}$ for PDMS-only, PDMS-co-P1, PDMS-co-P2, and PP-DGM, respectively. However, as the calculated gas-phase resistances were lower than 2% of the total experimental resistance ($R_{OL,exp}$), their contribution was omitted for further analysis. The liquid resistance, on the other hand, was quite significant for all membranes including the PDMS-only membrane, as summarized in **Figure 6.4b**. However, the PDMS-only membrane had the best performance over the entire tested liquid velocity range showing less than 20% contribution of the R_M to the R_{OL} . Subsequently, PDMS-co-P1 and PDMS-co-P2 showed their liquid phase contributions as ~43% and 25%, respectively. Moreover, the highest membrane contribution to the R_{OL} was reported for commercial PP membrane (~62%). Those variations of R_{OL} can be attributed to the hindrance of the mass transfer due to the secondary coating layer of the PDMS-co-P1 and PDMS-co-P2 membranes, and lower porosity of commercial PP membrane which is around 49%. The R_{OL} contrast between PDMS-co-P1 and PDMS-co-P2 is captivating since modification conditions and procedures for both membranes are the same.

Nevertheless, the chemistry and the size of the hydrophilic segments tethered to the PDMS backbone are different in the two copolymers (**Figure 6.5**). Given the side-chain length of the PDMS-co-P2 was much greater than PDMS-co-P1, it is plausible to expect the formation of a thicker hydration layer on the PDMS-co-P2 surface. Accordingly, the liquid passing through the PDMS-co-P2 membrane is presumably to exhibit a stagnant-like behavior, which might negatively affect the overall mass transport of the membrane [256-258].

Figure 6.5 Chemical formula of PDMS-based amphiphilic copolymers with (a) short (PDMS-co-P1) and (b) long (PDMS-co-P2) side chains.

6.2.3 Analysis of long-term operation with actual wastewater effluents

Avoiding the membrane wetting during long-term operations is one of the major motivations behind coating the PVDF supports with PDMS. With this respect, first, the long-term performance of PDMS-only membrane against simulated effluent and an actual AnMBR effluent for 7 days were tested by monitoring the CH_4 flux. As summarized in **Figure 6.6** (the normalized CH_4 flux for tap water was almost stable for a week, which shows the anti-wetting nature of PDMS-only membrane in long-term operation.

Importantly, the CH₄ flux decline was also insignificant for the test with AnMBR effluent until day 6. On the other hand, the AnMBR effluent brings an additional resistance (of ~5-12%), which is due to the membrane fouling effect (see **Figure 6.6b**). This observation shows that the PDMS-coating is useful for suppressing wetting but prone to fouling even for low-strength wastewater effluents. Thus, it is vital to improving the PDMS-PVDF composite membrane with an antifouling coating for exploiting gas-liquid MC process CH₄ recovery from anaerobic effluents.

Figure 6.6 Long-term performance of PDMS-coated membranes against simulated effluent and a low-strength actual effluent obtained from an AnMBR unit: (a) normalized CH₄ flux of the membrane (as normalized to the CH₄ flux value obtained for simulated effluent at day-1); (b) the time-dependent overall resistance ($R_{t=t}$) with respect to the initial overall resistance ($R_{t=0}$) for the long-run with both tap water and real AnMBR effluent.

In accordance with the preliminary fouling test with synthetic and realistic AnMBR anaerobic wastewater effluent, the fouling formation is too little to make comparison with the fouling-resistant membranes fabricated since the UASB technology still dominates the industrial-scale wastewater treatment applications. Hence, further studies with a UASB-based anaerobic effluent are needed. **Figure 6.7a** illustrates the normalized CH₄ flux of all tested membranes for a one-week continuous operation. Both PDMS-only and PP-DGM cases experienced ~20% performance decline by 3 days. The performance of the PDMS-

co-P2 membrane declined ~8% by 5 days, while an additional loss of ~13% took place in 2 more days only. PDMS-co-P1 membrane also demonstrated a similar trend with PDMS-co-P2, but only around 11% performance loss took place in 7 days. The performance decline of the PDMS-only and PP-DGM cases, on the other hand, was ~29% and >52%, respectively. Therefore, the copolymer-based post-treatment strategy shows a dramatic improvement in performance, which attributes to the fouling resistance enabled by surface hydrophilization.

Figure 6.7 Long-term membrane performance. (a) Normalized CH₄ flux variation of membranes (UASB effluents) (d) Overall mass transfer resistance profile for UASB effluent. (Note that the abbreviation “OMT” stands for “Overall Mass Transfer” in the figure labels.)

The evaluation of the overall mass transfer resistance provides further quantitative insights regarding the role of membrane fouling in D-CH₄ recovery performances. As illustrated in **Figure 6.7b**, the mass transfer resistances of PDMS-co-P1 and PDMS-co-P2 increase only by ~13% and 31%, respectively. The mass transfer resistance of PP-DGM, on the other hand, increases by over 150%, which shows that the fouling layer acts as the main barrier against CH₄ recovery. The behavior of the PDMS-only membrane was rather peculiar, with almost 90% increase in 4 days followed by a gradual decrease of ~20% in

the next 3 days. Membrane fouling layers are often dynamic in nature, typically involving further deposition, dispersal, and compaction. Thus, for the case of the PDMS-only membrane, the dispersal rate likely overcomes the contribution of further deposition. (Note that the MC process does not involve high-pressure; thus, the compaction effect is normally low or negligible.)

At this point, it can be concluded that the surface hydrophilicity and surface charge of the polymer played a critical role in mitigating organic fouling. Comparatively, PDMS-co-P2 which still possess surface hydrophilicity is not as effective as the former, but capable enough to maintain a low degree of membrane fouling. Evidently, the shorter tethered chained PDMS copolymer grafted membrane showed better CH₄ recovery flux as well as the antifouling capability against high strength wastewater. The better antifouling capability of short-chain PEG self-assembly macromolecules was previously observed by Soteropulos *et al.* [259]. Perhaps, the steric effect for longer chained PDMS copolymer is considerably higher than that of the other polymer leading to low adsorption density [260].

6.2.4 UASB effluent analysis

Unlike membrane distillation and filtration process, there is no concentration polarization or high-pressure effect on the CH₄ recovery MCs inducing membrane fouling. Yet, membrane fouling is critical in CH₄ recovery MCs, especially operation with high strength wastewater like UASB effluent, as demonstrated in the above section.

Figure 6.8 Characterization of the industrial anaerobic wastewater treatment effluents used: (a,b) Normalized EEM spectra, and (c,d) LC-OCD results of (a,c) AnMBR, and (b,d) UASB effluents.

As per the characteristics of wastewater effluent summarized in **Table 2.1**, although inorganic substance present in the effluent, the effect of inorganic fouling is insignificant as no concentration polarization effect during membrane operation. To acquire better insight into the dissolved organic matter (DOM) present in the liquid effluent, the Excitation-emission matrix fluorescent spectroscopy (EEM-FS) was obtained and depicted in **Figure 6.8**. The resultant spectroscopy images were compared with the regions, as suggested by Chen *et al.*, to identify the major foulants present in the feed effluents use for MC application [261]. Notwithstanding, the AnMBR effluent (**Figure 6.8a**) shows a broad range of DOM (**Figure 6.8c**) with a higher intensity for the Excitation-Emission area covering 260 – 500 nm assign for proteins and fulvic acid regions as suggested by Chen *et al.* [261]. Further, the effluent contains a significant amount of humic acids (area covered by excitation range 300 – 350 nm and emission range 400 – 450 nm) and slightly soluble

microbial by-product (SMP) like substances (area covered by excitation range 250 – 300 nm and emission range 325 – 375 nm). Comparatively, the UASB effluent (**Figure 6.8b**) has the DOM (**Figure 6. 8d**) covering the whole five reigns as explained in the reference chart that are proteins, humic acids, fulvic acids and SMP whereas, the protein presents in a larger which can be identified as the major culprit of membrane fouling in this application.

6.2.5 Morphological and chemical evaluation of fouling layers

Through a rigorous review of the respective foulants in the liquid effluents, it is clear that the major culprit foulants responsible for CH₄ recovery membranes are organic substances and bio-foulants.

Figure 6.9 FESEM observation of fouled membranes. (a) PDMS-only membrane subjected to tap water-based simulated effluent, (b) PDMS-only membrane fouled with AnMBR effluent, (c) PDMS-only membrane fouled with UASB effluent, (d) PDMS-co-P1 membrane fouled with UASB effluent, (e) PDMS-co-P2 membrane fouled with UASB effluent, and (f) commercial PP-DGM membrane fouled with UASB effluent. (The main and inset images show the inner surface and cross-section views, respectively. All the scale bars indicate 10 µm.)

To gain further insights regarding the fouling layers, membrane autopsies were obtained using FESEM (**Figure 6.9**). As shown in **Figure 6.9a**, the synthetic anaerobic effluents have caused no fouling to the PDMS-only membrane in a 7-day operation, which

can be considered as a negative control for our purposes. However, since the PDMS-only membrane is prone to fouling, the AnMBR effluent could form a fouling layer, as shown in **Figure 6.9b**. (Note that the cracks form upon the drying of the cake layers.) To prevent the clogging of hollow fibers during operation, the UASB effluent was pre-filtered with a cotton swab. But still, being high-strength compared to AnMBR effluent (**Table 2.1**), the UASB effluent caused severe fouling on the PDMS-only membrane (**Figure 6.9c**). Interestingly, fouling layers were also observed on PDMS-co-P1 (**Figure 6.9d**) and PDMS-co-P2 (**Figure 6.9e**) membranes. At this point, the thickness of the fouling layers becomes critical, which becomes more evident for the case of PP-DGM (as shown in **Figure 6.9f**).

Figure 6.10 EEM-FS-based characterization of (a) UASB effluent, and UASB-based fouling layers formed on the in-house made membranes (b) PDMS-only, (c) PDMS-co-P1, and (d) PDMS-co-P2 membranes, and (e) the commercial PP-DGM. The EEM-FS profile of (f) tap water is blank and general legend for assignments (based on the ref. [261]).

To be able to postulate a proper membrane cleaning procedure for extended membrane lifetime, EEM-FS measurements on UASB effluent (**Figure 6.10a**) and re-dispersed fouling layers formed on the membranes exposed to UASB effluent (**Figure 6.10b** to **Figure 6.10e**) were conducted. According to the assignments made by Chen *et al.* [261] (see **Figure 6.10f** for the regions), UASB effluent contains aromatic proteins (dominant), humic acid-like substances, soluble microbial byproduct-like substances, and fulvic acid-like substances, in the same order of relative abundance. The foulants deposited on the PDMS-only membranes were rich in aromatic proteins and soluble microbial byproduct-like substances (**Figure 6.10b**). In agreement with the FESEM observations (**Figure 6.9c** to **Figure 6.9e**), the signal intensity of the fouling layer on the PDMS-only membrane was much higher than that of on fouling-resistant membranes (**Figure 6.10c** and **Figure 6.10d**), with a clear dominance of aromatic proteins. Expectedly, the EEM-FS profiles of PDMS-co-P1 (**Figure 6.10b**) and PDMS-co-P2 (**Figure 6.10c**) were similar, again, with a very clear dominance of aromatic proteins. Thus, with the support of the CH₄ flux results (**Figure 6.7**), it is clear that cleaning of the fouling-resistant membranes on day-6 is appropriate with the help of an enzymatic cleaning solution to hydrolyze the proteins.

6.2.6 Energy considerations

In previous studies, it was alleged that the possibility of producing positive net electrical energy with the recovered D-CH₄ from anaerobic effluents [20, 58, 61]. However, the long-term effects such as membrane fouling and frequent cleaning cause energy penalties curtailing the total extractable energy. At this point, performing an energy analysis would provide better insight into long-term effects on energy recovery with the membranes used in this study.

6.2.6.1 Effect of the downstream gas quality

The quality of the stripped-out gas strongly determines the combustibility of the gas mixture in the turbine for power generation. The gas mixture must not be too lean or too rich to combust, thus should be in the combustible zone. **Figure 6.11** shows the CH_4 , CO_2 , and air flammability diagram which was re-drawn using the data from Schroeder *et al.* [262]. Clearly, to obtain a combustible mixture, the limiting gas composition (LGC) should be 65% air, 6% CH_4 , and 29% CO_2 in the gas mixture. Note that according to the flammability diagram the lower and upper flammability limit of CH_4 in the air (absence of excess CO_2) is 4.3 and 16.5 % mol, respectively. Therefore, the CH_4 purity in the downstream gas plays a critical role in *in-situ* power generation.

Figure 6.11 Flammability diagram for CH_4 , air, and CO_2 gas mixtures (redrawn from the data obtained from Schroeder *et al.* [262]).

Figure 6.12a and **6.12b** show the CH_4 recovery efficiency and the downstream gas purity as a function of the liquid velocity of the membranes tested in this study. Clearly, for all the liquid velocities tested, the resultant downstream CH_4 purity is far from the minimum requirement for obtaining a combustible gas mixture. Moreover, although high CH_4 purity is obtainable at increasing liquid velocities, the recovery efficiency drastically dropped which is not acceptable. Thus, to overlook the challenge between

the downstream gas purity and the overall CH₄ recovery efficiency plus *in-situ* power generation, the only possible way to concentrate the stripped-out gas mixture.

Figure 6.12 (a) CH₄ recovery (b) Downstream CH₄ purity as a function of liquid velocity

Substantial reduction of the sweep gas flowrate while confirming the non-limited gas phase-controlled mass transfer might be a better solution of concentrating CH₄ in the downstream gas mixture. **Figure 6.13a** and **6.13b** show the theoretical analysis of the gas phase contribution and the purity of the CH₄ in the outlet gas stream with respect to the G/L ratio. The G/L ratio was adjusted, changing the G at a fixed L in this section. Upon consideration of the correlation between the r_G and k_G ($r_G = \frac{H \cdot d_i}{k_G \cdot d_o}$), looking into the k_G is a good place to start to get a line on the influence of the r_G on the R_{OL} . As shown in **Equations 2-25** and **2-28**, the k_G is determined by the two variables, G and ϕ . Among the two variables, the packing density was set at 0.5, given that the packing density of commercial modules is typically above 45% [263]. Hence, the contribution degree of the r_G to the R_{OL} varies with the G (or G/L ratio at a fixed L) was examined. **Figure 6.13a inset** shows the r_G contribution to the R_{OL} is considerably significant at a low G/L ratio range (0.005 to 0.05). This is also the case even for the

G/L ratio of 0.034, which causes the r_G contribution above 12% at the A_M of 1 m². In contrast, since the r_G contribution drops to 10% at the G/L ratio of 0.0425, it is found to be dramatically whittled down as the G/L ratio becomes larger. Indeed, **Figure 6.13a** displays that the r_G contribution falls below 1% as the G/L ratio goes beyond 0.5. However, too high a G/L ratio can substantially decrease the CH₄ purity in a final sweep gas. Moreover, given that 10% of the R_{OL} is considered negligible [264], 0.0425 would be best as a G/L ratio at the A_M of 1 m². Moreover, **Figure 6.13b** shows the CH₄ purity as well as the recovery ratio with respect to the same G/L ratio range studied. As clearly can be seen for the lower G/L ratios of less than 0.2, over 6.5% CH₄ purity can be expected. Therefore, using the best suitable G/L ratio for the operation avoid challenges due to the forming of non-combustible downstream gas mixtures.

Applying mild vacuum conditions instead of utilizing sweep gas is another option to enhance the downstream gas purity. Several studies showed [20, 54, 58, 143] that the vacuum is a better driving force than the stripped gas mode, which offered enhanced mass transfer across the membrane along with high CH₄ purity. However, the anticipated membrane wetting during operation for microporous membranes is inevitable [143]. Moreover, Wichitpan *et al.* [61] showed that vacuum mode operation negatively affects the net energy recovery due to the comparatively high electrical demand for operating the vacuum pump, thus recommended to combine both vacuum- and the stripping- mode operations together to harness maximum energy. Further, they showed that mild vacuum pressures closer to the atmospheric pressure is preferable to achieve the maximum net energy. Albeit, vacuum mode of operation is beneficial for producing high purity gas mixtures, still needs to dilute with air to carryout *in-situ* electrical generation by CH₄ ignition [58]. Hence, stripping mode operation with

optimal operating parameters would be an attractive way to overcome the downstream CH₄ purity problem, thus the generation of *in-situ* electrical power.

Figure 6.13 (a) Gas phase mass transfer resistance to R_{OL}^{-1} (b) CH₄ Purity and recovery efficiency as a function of G/L ratio

Additionally, the recovered biogas from the liquid effluent can be combined with the headspace gas of the anaerobic reactor which has more purity to feed the microturbine for power generation.

6.2.6.2 The net energy potential of the tested membranes

Figure 6.14 shows the proposed MC operation for the utilization of retrieved D-CH₄ in electrical production. In this configuration, the air stripes-out D-CH₄ and directly feeds the micro-turbine for energy generation. Assuming that the electrical conversion efficiency of micro-turbine is ~30% ,the efficiency of the liquid pump is ~0.34 (70% efficiency of all the devices motor, transmission system and pump) and the negligible (<1%) contribution of air blower, the daily net energy potential (E_{NET}) of each membrane used in this study was calculated and summarized in **Table 6.3** (the all relevant equations are mentioned in section 2.4.5.2) [61].

Figure 6.14 The air stripping operation for D-CH₄ recovery and energy production

Table 6.3 Energy analysis of different membranes

Membrane	% CH ₄ Recovery	Pressure drop (Pa)	E _{LP} (MJ m ⁻³)	E _{NET} (MJ m ⁻³)
PDMS-only	59	1260	0.004	0.135
PDMS-co-P1	52	1294	0.004	0.115
PDMS-co-P2	41	2494	0.007	0.089
PP-DGM	54	9069	0.026	0.102

In fact, both CH₄ recovery and E_{LP} significantly affected the differences in the E_{NET} for each the membranes on day 1. For instance, the PDMS-only membrane had the highest E_{NET} among the tested membranes as a result of its larger methane recovery and the lowest E_{LP} at the tested liquid velocity. Moreover, even though the CH₄ recovery of PP-DGM is comparatively higher, the resultant E_{NET} is ~ 13% lower than that of PDMS-co-P1 because the elevated pressure drops as a consequence of smaller membrane inner diameter

consumes more E_{LP} (see **Table 6.2** and **Table 6.3**). Most importantly, the additional coating layer in PDMS-co-P1 imparts a $\sim 12\%$ reduction in CH_4 recovery leading to $\sim 15\%$ net energy loss than that of PDMS-only membrane stressing the negative side of having two coating layers. However, as exemplified in **Figure 6.15**, the antifouling layer is of great significance to maintaining a continuous energy flux over a long period without membrane cleaning (Note that the exact same long-term behavior of membranes was assumed for air as N_2). Membrane fouling caused 30 and 64% drop of energy recovery potential in PDMS-only and PP-DGM membranes, respectively, after a week operation. With the antifouling coating, the respective loss was suppressed lower than 10%, highlighting the importance of high performing membrane for energy recovery.

Figure 6.15 Long-term net electrical energy production potential of membranes (all the membranes were operated at a liquid velocity of 0.06 m s^{-1})

The dotted line shows the E_{NET} potential of PDMS-co-P1 that provides a baseline to compare with PDMS-only membrane. Clearly, in the first 3 days, the latter showed better energy recovery than the former but eventually dropped due to severe membrane fouling. At the end of the operation, the PDMS-co-P1 membrane could extract 3% more energy

than the PDMS-only membrane. The amount of energy recovery is scalable by optimizing the operating conditions in the membrane module (*i.e.*, lower the liquid velocity, the higher the CH₄ recovery). Thus, improving the fouling resistance property diminishes the additional downtime plus the operational cost for cleaning while enhancing the energy recovery.

6.3 Conclusions

It was demonstrated that a wetting- and fouling-resistant hollow fiber membrane could successfully recover D-CH₄ from high-strength anaerobic effluents by the MC process, with an energy gain. PVDF-based porous membranes served as a suitable support for the preparation of wetting-resistant membranes by a simple PDMS-coating step. And, the post-treatment of PDMS-coated PVDF membranes (PDMS-PVDF) with PDMS-based copolymers provided fouling resistance in a facile manner. The modification of the PDMS-PVDF membrane with PDMS-based copolymers reduced the D-CH₄ recovery performance when simulated effluents are employed. However, when a high-strength effluent from a UASB unit used, fouling-resistant membranes provided better performance compared to (wetting-resistant) PDMS-PVDF (PDMS-only) membrane and PP-based commercial degassing membranes (PP-DGM). Among the copolymer-modified membranes, short-side-chained PDMS-based copolymers provided superior performance, which can be attributed to its higher hydrophilicity. Although a dedicated membrane cleaning study was not performed, membrane autopsies suggested that an enzymatic solution might be appropriate for cleaning. As a result, the energy analysis results evidenced that the MC process is promising for D-CH₄ recovery from industrial anaerobic effluents when wetting-fouling-resistant membranes are employed.

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7 General Conclusions and Future Prospects

7.1 Overall conclusion

The thesis presents performance enhancement of the D-CH₄ recovery process using gas-liquid membrane contactors by realizing governing factors for gas stripping and net energy recovering. Currently, the researchers extensively utilized commercial microporous PP and dense PDMS for D-CH₄ recovery from anaerobic effluents since those membranes are readily available in the market. However, there is no clear indication of the membrane-related factors affecting D-CH₄ recovery improvement.

Moreover, the understanding of membrane fouling during prolonged operation is inadequate. Besides, all the membranes could produce positive net electrical energy potential, yet the key parameters affect to maximize energy gain are lacking. In this regard, a detailed study was conducted to understand the factors affecting maximizing the energy recovery efficiency of D-CH₄ from anaerobic effluents using membrane contactors using a lab-scale membrane contactor rig.

The significant contributions of this whole work are divided into two sections based on the experimental and theoretical analysis and concluded in the following sections.

- Theoretical study of the influence of membrane and operational-related parameters on CH₄ removal

It is challenging to optimize both the membrane- and operation-related parameters simultaneously, as some parameters are closely linked with each other or involve trade-offs (e.g., the relationship between d_i and A_M). However, it is desirable to reduce the

membrane inner diameter (d_i) as long as it does not compromise the processability of the membrane module. Or does not cause high resistance to the module (Note that this conclusion is based on the liquid in lumen operation). Further, the membrane mass transfer area (A_M) and effective module length (Z) need to be optimized together to obtain the desired performance (which can be defined as a balanced CH_4 flux and recovery). Moreover, increasing liquid flowrate (L) was found to be accompanied by an increase in both liquid velocity (u) and liquid side mass transfer coefficient (k_L), thereby inducing a higher CH_4 flux while reducing CH_4 recovery due to the decreased residence time in the module.

The results from four membranes (Chapter 4) with distinct structural and chemical properties reflect the parameters necessary to control real-world applications. The capillary pressure imposed by the inlet of hollow fibers can dramatically increase K_{OL}^{-1} at low liquid velocities by preventing the liquid from flowing in some inlets. Pore wetting can whittle down the membrane mass transfer coefficient (k_M) because the liquid filling the subsurface voids become too stagnant to promote mass transfer. k_M^{-1} may be significant enough to affect K_{OL}^{-1} in dense membranes. A_M may have an influence on CH_4 flux (the smaller the area, the higher the CH_4 flux) if other parameters are kept constant.

- Membrane modifications for performance improvement of HFMCs in CH_4 recovery

Table 7.1 summarizes the performance of each membrane tested in this study. The optimized PVDF membrane was the best performing membrane in terms of the membrane resistance, which indicated the lowest among the other tested membranes due to the highest

porosity. However, this membrane was able to operate with low strength AnMBR reactor effluents only, whereas the membrane was not able to tolerate high strength UASB reactor effluents due to severe membrane fouling. Thus, this membrane is suitable for handling low strength anaerobic reactor effluents without sacrificing CH_4 recovery flux in the long run.

Table 7.1 Comparison of the membranes tested in this study

Membrane	R_M^a (s m^{-1})	E_{NET}^b (MJ m^{-3})	Long-term operation		Chapter
			AnMBR	UASB	
Optimized PVDF (PHM-PVDF)	4518.0	0.112	Stable flux 08 days	Wetting after 3 days	3 (4)
BM-0.50	7177.6	0.138	Not tested	7 days 50% flux drop	5
BM-5.0	8656.6	0.138	Not tested	Not tested	5
LM-5.0 (PDMS-only)	6225.0	0.135	Stable 08 days	10 days ~25% flux drop	5 (6)
LM-10.0	7823.8	0.090	Not tested	Not tested	5
PDMS-co-P1	6528.9	0.115	Not tested	5 days stable flux then dropped <10%	6
PDMS-co-P2	8706.2	0.089	Not tested	5 days stable flux then dropped <20%	6
Commercial PP (PP-DGM)	9512.6	0.102	<10% flux drop within 8 days	40% flux drop within 3 days	3,5 (4,6)
Commercial PDMS	12668	0.077	Not tested	10 days >25% flux drop	4,6

^a the membrane resistance was obtained from Wilson plot method

^b the E_{NET} was calculated for liquid velocity 0.06 m s^{-1}

Albeit the lumen side, PVDF coated membrane (LM-5.0) showed ~38% elevated membrane resistance compared to the optimized PVDF membrane; it could be able to withstand both AnMBR and UASB effluent with a maximum flux reduction of 25% within 10 days of operation. Thus, coating the gas-liquid boundary with a thin dense film coating layer might be a useful improvement to avoid membrane wetting, as well as membrane

fouling, occurred inside pores. Moreover, in line with the theoretical study, the LM 05.0 membrane showed better CH₄ flux and recovery efficiency due to the lower membrane inner diameter. Thus, indicating that this membrane is the best candidate in this study to operate with low strength anaerobic effluents.

Nevertheless, PDMS is prone to severe membrane fouling when handling high strength anaerobic reactor effluents (~same flux drops for both commercial PDMS membrane and PDMS-only membrane). As such, the PDMS-co-p1 showed the best performance in this work with harsh UASB effluents showing 5 days stable flux and then gradually dropping 10% in total 7 days continuous run. It is noteworthy that ~5% membrane resistance was reported due to the further modification of LM -05.0.

Moreover, all the membranes produced in this study could produce positive net energy in the absence of membrane fouling. Although having a smaller inner membrane diameter is beneficial for obtaining higher CH₄ flux and recovery efficiency, it negatively affects extracting energy because of the massive pressure drop occurred along the membrane length, which caused significant energy consumption of the liquid pump. Thus, choosing proper membrane inner diameter would be crucial for obtaining more energy without compromising the CH₄ flux and the recovery efficiency. Further, since membrane fouling significantly decays the potential energy production, antifouling membrane modification is vital to apply those membranes in CH₄ recovery from anaerobic reactor effluents.

The cost analysis for the best membrane modifications is listed in **Table 7.2**. According to the estimated material cost, the cheapest membrane modification to handle low strength anaerobic reactor effluent is applying a thin dense PDMS coating. Further, the same membrane is showed the best performance (cost per mass transferred) over the other membranes due to the lower material cost as well as, the lower pumping cost. Note that for commercial PP membrane, the material cost includes the total module cost; however, the

pumping cost for this membrane is the highest among other membranes due to the smallest membrane diameter.

For the development of the antifouling membrane modification, it is needed to incur an additional \$191.485 m⁻², which is a ~71% increment cost compared to the anti-wetting modification. However, the extra expense for anti-fouling modification would be too high as compared to the performance index. Thus, leading to a conclusion for finding out more cost-effective antifouling modifications without compromising membrane performances.

Table 7.2 Cost analysis for the best membrane modifications of this study[†]

Membrane	Estimated total material cost (US\$ m ⁻²)	Estimated operating cost ^a (cost per 1m ³ effluent treated)	Performance index (cost per mass transferred) ^b
PVDF support	1.028	NA	NA
Optimized PVDF	369.112	0.0007	152.24
PDMS-PVDF	2.703	0.0012	0.86
PDMS-co-P1	194.188	0.0013	81.32
Commercial PP	5.97 ^c	0.0018	7.71

^{an} operating cost includes the total gas and liquid pumping cost only

^b the performance index was calculated based on the method described by Wickramasinghe *et al.* [265]

^c the commercial degassing module includes material plus module cost (commercial PP degassing membrane module cost \$370, total membrane mass transfer area 62 m², effective module length 1020 mm)

[†] The effect of membrane fouling has been neglected for the cost analysis

Note that all the membranes were subjected to ultrasonication for 10 minutes and observed the membrane morphology under FESEM-EDS to ensure the coating stability of the modified membranes in long-term operation. Further, there is no risk of delamination

of coating layers because the mild operating conditions in this MC application (low liquid flow rates, atmospheric pressure operation).

The membrane modifications were carried out in the lumen surface of the membrane (except for optimized PVDF membrane), which was very easy to carry out (pumping the coating solution and drying). Thus, scaling up of such modification is easy because of the simplicity of the modification process. Plus, over the maximum tested period (10 days), no membrane failure was reported due to the flexibility of PVDF support. Therefore, there is the potential to commercialize the membrane modification, especially the lumen PDMS coated membrane.

7.2 Recommendations for future research

CH_4 dissolution and lost in the liquid effluents cause massive energy shortfall plus anticipate environment and safety concerns in the anaerobic wastewater treatment process. Since G-L MCs have potential efficacy over conventional devices in recovering those dissolved gases, currently few studies investigated the feasibility of the process in laboratory-scale experiments. However, still, scale-up of G-L MC for D- CH_4 recovering is beyond the horizon due to some critical concerns that need substantial research.

1. Wetting and fouling resistant membrane development

The development of a high performing durable membrane is the key for meeting intended objectives because the membrane is the core of the process. Forthcoming membrane wetting and fouling during prolonged operation challenges the robust membrane operation causing notorious flux to drop, thereby the recovery decline. Therefore, the ideal membrane should be able to generate higher CH_4 fluxes enduring those challenges. In this sense, the composite membrane mentioned in this dissertation

that comprising both anti-wetting and -fouling showed better performance during the long run. Yet, the CH₄ flux dropped compared to the original membrane due to the additional resistance exerted by the coating and the drop-in film permeance as a consequence of anti-fouling modification. Thus, extensive study is needed to fabricate highly permeable thin-film composite layers containing both wetting and fouling proof properties.

Further, it is recommended to incorporate novel anti-wetting and anti-fouling approaches such as omniphobic modifications to investigate the long-term effects of CH₄ recovery. Moreover, membrane modification should be simpler to scale-up for large scale production with low investments and fewer environmental impacts, which is of great importance in the journey of commercialization of CH₄ recovery from anaerobic effluents.

2. Membrane cleaning procedure

Not relying on membrane modifications only, it is advisable to adhere to fouling mitigation techniques during the MC operation. However, currently effluent pretreatment by simple filtration techniques has been reported, still not enough to mitigate membrane fouling. Thus, further studies must be carried out to pretreat the effluents, especially for bacteria removal, before applying in the MC system. The bacteria secrete extra cellulose polymeric substances that can stick on the membrane surface, which is very difficult to clean. Moreover, a proper membrane cleaning schedule with appropriate cleaning agents should be studied since cleaning downtime cause significant energy loss.

3. The module designs and configurations

Determining the best module configuration for extracting higher energy through CH₄ stripping is also equally important rather than using the typical counter-current configuration. For instance, even in the counter-current operation, liquid in the shell side generates lower CH₄ recovery (because of liquid bypassing) and severe membrane fouling (due to handling a more considerable amount of effluent at once). Not limited to that, the liquid in lumen mode cause blockage at the inlet as a consequence of larger particles inside the effluent but can produce enhanced CH₄ recovery and less prone to fouling. However, large pressure drops can be expected for this mode of operation that can lead to membrane wetting. Thus, to efficiently utilize the operational mode, the module modifications might be required. Hence, more research is needed to find the best design to operate MC.

In fact, on the large scale, one module is not enough for achieving the separation, thus needs to test multiple modules at a time. Therefore, studying the CH₄ recovery and energy potential under different membrane configurations and multiple modules might be insightful research for upgrading to the industrial level.

4. Mathematical modeling and simulations based on operational parameters and membrane performance

During theoretical estimations on CH₄ recovery and net energy gain, it was revealed that operational parameters and membrane physical parameters are inevitably interlinked. At this point, mathematical modeling of those related parameters would be beneficial for determining the best combination of operating parameters, and that is well fitted to the membrane and the module configuration. Hence, it is recommended to develop

mathematical models to simulate the process for optimization in terms of operational parameters as well as the cost (*i.e.*, number of pumps, modules needed, etc.).

5. Pilot-scale testing

Pilot-scale testing of MC is essential for the identification of possible risks of scaling up the technology for practical use. The performance of all the membranes fabricated was tested in the absence of a real anaerobic reactor. Thus, the possible uncertainties due to effluent fluctuations, feed quality changes were not experienced. Therefore, the experiments are needed for actual pilot-scale plant coupled membrane contactors to confirm the feasibility of scaling up this technology on the large scale.

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