

Ph.D. THESIS

**Study on polydimethylsiloxane membrane
contactors to recover dissolved gases (CH₄, CO₂)
from anaerobic effluents**

**Prepared
at University of Pannonia in the framework of the
Doctoral School of Chemical Engineering and Materials Sciences**

**Written by:
Merve Visnyei
Chemical Engineer, MSc.**

**Supervisor:
Péter Bakonyi, Ph.D.
Senior Research Fellow**

**University of Pannonia
Faculty of Engineering
Research Centre for Biochemical, Environmental
and Chemical Engineering
Research Group on Bioengineering,
Membrane Technology and Energetics**

**Veszprém
2025**

Introduction

As the global demand for clean water increases and freshwater sources continue to dwindle, wastewater is no longer viewed solely as a byproduct to discard, but increasingly as a valuable resource. Anaerobic wastewater treatment has emerged as a promising solution, offering multiple advantages over conventional aerobic systems. Biogas, primarily composed of methane (CH₄) and carbon dioxide (CO₂), can serve as a renewable alternative. However, a significant fraction of these gases—especially methane—remains dissolved in the treated effluent and is subsequently lost, not only reducing energy yield but also contributing to greenhouse gas emissions. This challenge has underscored the need for efficient post-treatment technologies that can capture these dissolved gases before they escape into the environment. Gas-liquid membrane contactors (GLMCs) have emerged as a promising approach to recovering dissolved CH₄ and CO₂ from anaerobic effluents. Hollow fibre membrane modules are advantageous due to their high surface area and efficient mass transfer properties. When integrated into anaerobic membrane bioreactor (AnMBR) systems, they offer a low-energy, scalable solution for improving gas recovery and minimizing environmental impact.

Objectives

The aim of this research was to enhance the performance of AnMBR systems by investigating the application of non-porous PDMS hollow fibre membrane contactors for the recovery of CH₄ and CO₂. The study progressed in three phases. In the initial phase, model solutions were prepared by purging known CH₄/CO₂ mixtures into deionized water to simulate anaerobic effluents. These were used to explore the effects of gas and liquid flow rates on recovery efficiency. Building on these results, the second phase introduced binary gas mixtures to more accurately replicate real anaerobic effluents, allowing for a detailed study of simultaneous methane and carbon dioxide recovery, as well as the influence of their interactions under varying operating conditions. The final phase transitioned to real-world conditions by using actual anaerobic effluents, integrating in-line dissolved methane sensors for real-time monitoring of the recovery process and evaluating long-term performance. By comparing the behaviour of synthetic and real effluents under identical membrane configurations, this research highlights both the potential and the limitations of GLMCs in practical applications.

Results

Anaerobic digestion is a widely applied method for converting organic waste into stabilized sludge and renewable biogas. This study aimed to enhance the recovery of dissolved gases—methane (CH₄) and carbon dioxide (CO₂)—from the fermentation liquor using gas-liquid membrane contactors (GLMCs). Three experimental series were conducted, examining gas recovery from both synthetic and real anaerobic effluents.

In the first phase, model solutions with varying CH₄/CO₂ ratios were tested using a non-porous PDMS hollow fibre membrane. Results showed that CH₄ recovery dropped significantly in mixtures containing CO₂—falling from 35.9% with pure CH₄ to just 11.9% at a higher sweep gas flow rate in a 50:50 mixture—highlighting CO₂'s negative effect on methane recovery and the potential of GLMCs to mitigate such losses.

The second series explored simultaneous CH₄ and CO₂ removal from synthetic effluents. Increased liquid flow rates reduced CH₄ recovery across all gas ratios, while CO₂ recovery improved with higher gas flow. These findings suggest an inverse relationship in transport behavior, where CO₂ presence hinders CH₄ recovery—underlining the importance of flow optimization in real applications.

In the final series, long-term experiments were conducted using real anaerobic effluents in a fed-batch reactor. The system produced 120 L of biogas over 120 days with periodic glycerol feeding. Using in-line sensors and membrane contactors, the study revealed lower gas recovery efficiency in real effluents compared to synthetic ones due to operational challenges such as membrane fouling. Nonetheless, CH₄ concentration in the gas mixture had only a minor effect on recovery, while gas-to-liquid ratio adjustments showed small but consistent impacts.

Ultimately, the findings contribute to the development of more sustainable and efficient wastewater treatment technologies by bridging the gap between theoretical research and industrial feasibility.

Thesis statements

Thesis I: I have demonstrated that the recovery percentages of CH₄ from model solutions using a non-porous PDMS hollow fibre membrane contactor was influenced by significant presence of CO₂ in the mixture (50:50 CH₄/CO₂%) and the sweep gas flow rate. In the case of model solution consisting pure CH₄; CH₄ recovery remained stable (57-58.6%) in the range of the sweep gas flow rates of 5-20 mL/min, however, it was dropped to 35.9% at 60 mL/min. Conversely, when dealing with a mixed gas model solution (50:50 CH₄/CO₂%), the recovery percentages of CH₄ ranged from 61.3% to 53.1% with sweep gas flow rates of 5-20 mL/min and dropped to 11.9% at 60 mL/min. CH₄ recovery was negatively affected by CO₂ presence in the model solutions. CO₂ recovery increased from 9.2% to 61.6% as the sweep gas flow rate increased from 5 to 60 mL/min in model solution-2 (100 CO₂ vol.%) and model solution-3 (50:50 CH₄/CO₂%). Applying a sweep gas flow rate of 20 mL/min, the recovery rate of both gases from model solution-3 (50:50 CH₄/CO₂%) exceeded 50%.

Thesis II: I have proven that gas transport and recovery percentages of dissolved gases in synthetic effluents (CH₄/CO₂) using non-porous PDMS hollow fibre membrane contactors are influenced by the liquid (effluent) flow rate in the range of 10-20 mL/min favours the CH₄ transport, while a higher sweep gas flow rate is preferable for the CO₂ transport over CH₄. As it is aligning with the previous Thesis Statement I., a negative impact of CO₂ on the CH₄ recovery was observed once again. However, I have shown that this effect can be mitigated by increasing the CH₄ concentration in the gas mixture. Depending on the actual biogas composition and the CO₂ content of the effluent (associated with the actual composition of biogas), the CH₄ recovery could be improved up to 63 % under steady-state conditions. Experiments with 1.0 m² and 2500 cm² demonstrated an independency of the membrane size on the recovery percentages of CH₄ and CO₂, indicating that similar observations could be made regardless of the membrane module surface area.

Thesis III.: I have successfully established a fed-batch biogas fermenter with a 2L volume using sludge from anaerobic digester treating secondary sludge from a municipal wastewater treatment plant and operated for 120 days on glycerol as the sole substrate and evaluated the long-term biogas production performance. Digestion of glycerol significantly enhanced biomass activity, achieving stability with a pH of 7.1. Moreover, the averaged cumulative biogas composition was CH₄: 67.4 ± 10.3 %; CO₂: 32.5 ± 10.3 %; H₂: 0.1 ± 0.1 %. The glycerol load was optimized for enhanced methanogenic activity, and the bioreactor was routinely supplemented with 3.3 g/L of pure glycerol as a substrate loading in every 4–5 day intervals. After 120 days, 120 litres of biogas were produced, averaging 1 L/day.

Thesis IV.: I have demonstrated the recovery of dissolved CH₄ from prefiltered real anaerobic effluent using a PDMS hollow fibre membrane contactor with real-time monitoring via an in-line methane sensor. I have investigated the effects of gas and liquid flow rates on removal efficiency, comparing results with synthetic effluents. The effluent was processed in a stirred tank with a PDMS membrane contactor and methane sensor under varying biogas compositions (70/30, 50/50, 30/70 vol% CH₄/CO₂). The ratio of sweep gas (N₂) to effluent flow rates (G/L) impacted the degassing efficiency. The higher G/L ratio had a greater impact on CH₄ transport compared to the composition, while higher CH₄ composition in the biogas mixture corresponded to the slightly higher CH₄ recovery percentages. This effect was higher in synthetic effluent experiments carried out in similar operating conditions. The CH₄ recovery as 12.4 ± 4.4%, 13.6 ± 6.1%, 17.3 ± 8.0% was observed as the CH₄ concentration increased in the biogas (30, 50 and 70 vol%), while the dissolved CH₄ concentration of the prefiltered effluent fed to the membrane (5.7 ± 0.8 mg/L, 4.9±1.8 mg/L, 4.5±1.1 mg/L) was nearly stable along with the experimental settings. No significant changes in CH₄ recovery or dissolved CH₄ concentration in the feed were observed, regardless of CH₄ content of the biogas. The dissolved methane recoveries observed with the synthetic effluents (>50 %) considerably surpassed those with the real effluent (<20%). However, both cases indicated that the lower G/L ratio and the higher CH₄ content in the gas mixtures are favourable to enhance the CH₄ recovery.

List of publications

Publications on which this dissertation is based:

1. **Visnyei, M.**, Bakonyi, P., Bélafi-Bakó, K., Nemestóthy, N.: „Integration of gas-liquid membrane contactors into anaerobic digestion as a promising route to reduce uncontrolled greenhouse gas (CH₄/CO₂) emissions”, *Bioresource Technology*, 2022, 364, 128072 (**IF: 11.40**)
2. **Visnyei, M.**, Bakonyi, P., Rózsenszki, T., Koók, L., Komáromy, P., Bélafi-Bakó, K., Nemestóthy, N.: „Mitigated CH₄ release of anaerobic waste fermentation is enabled through effluent degassing system equipped with a polydimethylsiloxane membrane contactor” *Chemical Engineering Journal Advances*, 18, 100607. (**IF: 5.5**)
3. **Visnyei, M.**, Bakonyi, P., Nemestóthy, N., Bélafi-Bakó, K.: “Separation of Dissolved Gases from Aqueous Anaerobic Effluents Using Gas-Liquid Membrane Contactors”, *Hungarian Journal of Industry and Chemistry*, 2022, 50(2), 23–26. (**IF: 0.2**)

Publication in Hungarian journal: 1

4. **Visnyei, M.**, Bélafi-Bakó, K., Nemestóthy, N.: “Study on a demethanization process by membrane contactors”, *Membrántechnika és Ipari Biotechnológia*, 2022, 13(1), 2-5.

Oral presentation in foreign language:

1. **Visnyei, M.,** Bakonyi, P., Nemestóthy, N., Bélafi-Bakó, K.: "Separation of dissolved gases from aqueous anaerobic effluents using gas-liquid membrane contactors" 50th Chemical Engineering Days, 26-28.04. 2022., Veszprém, Hungary
2. **Visnyei, M.,** Bakonyi, P., Nemestóthy, N., Bélafi-Bakó, K.: "Recovery of dissolved gases from model anaerobic effluents by using gas-liquid membrane contactors" 48th International Conference of the Slovak Society of Chemical Engineering SSCHE 2022 and Membrane Conference PERMEA 2022, 23-26.05.2022., Tatranské Matliare, Slovakia
3. **Visnyei, M.,** Bakonyi, P., Bélafi-Bakó, K., Nemestóthy, N.: "Deployment of polydimethylsiloxane gas-liquid membrane contactors for recovery of dissolved CH₄/CO₂ by investigating with different synthetic anaerobic effluents", Water and Wastewater Treatment in the Industry 2022 Conference, 13.10.2022., Zalakaros, Hungary
4. **Visnyei, M.,** Bakonyi, P., Bélafi-Bakó, K., Nemestóthy, N.: "Progress and challenges in recovering dissolved CH₄/CO₂ through the use of PDMS gas-liquid membrane contactors: „A study of synthetic and real effluents”, 07.03.2023, Online Presentation.