Ph.D. THESIS

Study on polydimethylsiloxane membrane contactors to recover dissolved gases (CH_4, CO_2) from anaerobic effluents

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ABSTRACT

The methane lost during the biogas production may represent one of the main sources of greenhouse gasses (GHGs). This is a major issue since it is essential to minimize fugitive emissions and optimize the energy output of the facilities by recovering the dissolved methane in the anaerobic digester effluent. Therefore, using appropriate post-treatment technologies for addressing this issue is essential to move forward with the larger-scale development of biogas reactors. In this study, three experimental series were conducted by using gas-liquid membrane contactors (GLMCs). Initially, a polydimethylsiloxane (PDMS) non-porous hollow fibre membrane module was used to evaluate the desorption process using synthetic effluents with CH_4/CO_2 mixtures (in the ratios of 0-100%). The results demonstrated that although the sweep gas flow rate had no effect on the CH_4 recovery rate, it had an impact on the CO_2 recovery rate, which reached over 50% recovery at a 20 mL/min sweep gas flow rate. The second series focused on using PDMS hollow-fibre GLMCs with varying gas-to-liquid (G/L) ratios. It was found that higher liquid flow rates favoured CH_4 transport, while higher sweep gas flow rates enhanced CO_2 transport, with methane recovery reaching up to 63% under optimal conditions. Real anaerobic effluents from a biogas fermenter were used in the third series of experiments. The study highlighted those synthetic effluents achieved higher methane recovery (>50%) compared to real effluents (<20%), emphasizing the influence of sweep gas and liquid flow rates on recovery efficiency. In anaerobic digestion, GLMCs have the potential to improve methane recovery, which would increase energy production and lower greenhouse gas emissions. Moreover, it is important to note that further optimization is needed to address challenges with real effluents.

ÖZET

Biogaz üretimi sırasında kaybolan metan gazı, sera gazlarının başlıca kaynaklarından birini temsil eder. Bu, emisyonların en aza indirilmesi ve anaerobik sindirim sonrasında çözünmüş metanın geri kazanılmasıyla tesislerde enerji optimize edilmesi gerektiğinden büyük bir sorundur. Bu nedenle, bu sorunun ele alınması için uygun teknolojilerin kullanılması, daha büyük ölçekli biogaz reaktörlerinin geliştirilmesi için önemlidir. Bu çalışmada, gaz-sıvı membran kontakları (GLMC'ler) kullanılarak üç deneysel seri gerçekleştirilmiştir. Başlangıçta, sentetik CH_4/CO_2 karışımları (0-100% oranlarında) ile desorpsiyon sürecini değerlendirmek için polidimetilsiloksan (PDMS) gözeneksiz boş lif membran modülü kullanıldı. Süpürme gazı akış hızının CH_4 geri kazanım oranını etkilememesine rağmen, CO_2 geri kazanım oranı üzerinde etkisi olduğunu ve 20 mL/dk süpürme gazı akış hızında %50'nin üzerinde geri kazanım sağlandığını gösterdi. İkinci seri, değişen gaz-sıvı (G/L) oranlarıyla PDMS boş lifli GLMC'lerin kullanımına odaklandı. Daha yüksek sıvı akış hızlarının CH_4 taşınmasını desteklediği, daha yüksek süpürme gazı akış hızlarının ise CO_2 taşınmasını artırdığı, optimal koşullarda metan geri kazanımının %63'e ulaştığı bulundu. Üçüncü seri, bir biogaz fermantöründen gerçek anaerobik çıkışlar kullanıldı. Çalışma, sentetik çıkışların (> %50) gerçek çıkışlara (< %20) kıyasla daha yüksek metan geri kazanımı sağladığını vurguladı ve süpürme gazı ve sıvı akış hızlarının geri kazanım verimliliği üzerindeki etkisini vurguladı. Anaerobik sindirimde, GLMC'lerin metan geri kazanımını iyileştirme potansiyeli, enerji üretimini artıracak ve sera gazı emisyonlarını azaltacaktır. Ayrıca, gerçek çıkışlarla ilgili zorlukların ele alınması için daha fazla optimizasyonun gerektiği unutulmamalıdır.

To my son—take it easy, but don't take too long.
Some things, like success, are best served fresh.

Introduction

Many ecosystems that are vital to human survival have been destroyed over the past century, due to increased industrial activity and population growth. These initiatives have not only contaminated water supplies but also increased wastewater and water contamination.

This situation calls for the development and evaluation of various wastewater management methods, particularly given the global freshwater scarcity and disaster. It is imperative to acknowledge the potential value of wastewater as a resource and to put in place sufficient water safety measures to guarantee its long-term utilization. Therefore, to ensure the proper and sustainable use of wastewater, reliable and accurate methods for evaluating water safety are crucial [1], [2]. The development strategy for wastewater treatment is motivated by four main areas, which are resource recovery, public health, environmental protection, and climate change (Fig. 1). The development of novel and sustainable wastewater treatment technologies has been primarily driven by these factors [3], [4].

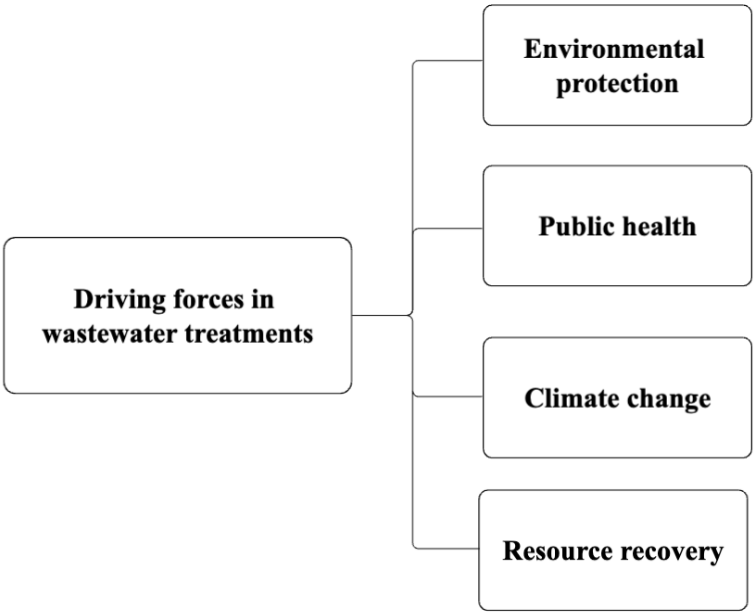


Figure 1
The main driving forces behind the development strategy of wastewater treatment

The main goal of wastewater treatment is to eliminate harmful pathogens and other contaminants to lessen the possibility of disease transmission and other detrimental health impacts, as untreated water can pose major health concerns to humans. Another important factor is environmental protection, since untreated wastewater can harm ecosystems and the surrounding environment. Prior to being released into the environment, wastewater is treated to remove various contaminants, including water pollution and heavy metals such as lead, mercury, and cadmium, organic pollutants such as pesticides and herbicides, industrial chemicals such as dyes and solvents, and nutrients like nitrogen and phosphorus [5], [6].

This approach reduces the negative effects on aquatic life and other environmental systems by ensuring that toxic compounds do not contaminate water bodies, disturb ecosystems, or pose health hazards to humans and wildlife for the reasons listed below:

- *Carbon:* Decomposing organic matter is necessary to minimize biological oxygen demand (BOD).
- *Nitrogen:* An abundance of nitrogen may result in eutrophication, which in turn can generate algal blooms that deplete water bodies of oxygen.
- *Phosphorus:* Like nitrogen, phosphorus causes eutrophication and needs to be managed.
- *Heavy metals:* Toxic substances including lead, mercury, cadmium, and others must be eliminated in order to stop bioaccumulation.
- *Organic pollutants:* Industrial chemicals, pesticides, and herbicides can be hazardous to human health and aquatic life.
- *Pathogens:* It's necessary to get rid of bacteria, viruses, and other microbes that can spread illness [5]–[7].

The development of wastewater treatment technology is also greatly impacted by climate change, which is closely related to the management of energy and water resources. As a result of climate change shifting precipitation patterns and making water scarcity more severe, there is an increasing need for efficient water management. This requires the development of improved wastewater treatment and reuse technologies to sustain water supply. Furthermore, because wastewater treatment procedures are energy-intensive, innovative approaches to lower energy use and greenhouse gas emissions are needed. Adopting sustainable and energy-efficient treatment methods can help reduce greenhouse gas (GHG) emissions and mitigate the effects of climate change. The necessity for durable and adaptable treatment systems is further highlighted by the difficulties extreme weather events, intensified by climate change, provide in maintaining constant water quality [7].

Reducing GHG emissions and lessening the consequences of climate change can be accomplished through the adoption of sustainable and energy-efficient treatment technologies [8]. The final important consideration is resource recovery, as wastewater may contain valuable resources that can be recovered and utilized in a variety of ways, including the creation of fertilizer and the production of renewable energy. These resources include nutrients (such as nitrogen, phosphorus, and potassium), organic matter, and energy (such as biogas from anaerobic digestion and thermal energy from heat recovery) [9].

1. Literature review

1.1. Anaerobic wastewater treatment – A way to biogas production

The anaerobic treatment option for wastewaters involves a complex food web, where organic components are eventually degraded with the help of a variety of microorganisms, including bacteria and archea, which produce enzymes that facilitate the breakdown of these components. Ideally, the complex organic components are converted and mineralized into mainly CH_4 and to a lesser extent to CO_2 with small quantities of hydrogen (H_2), hydrogen sulphide (H_2S), water vapour, ammonia (NH_3) by involved microbial consortia.

The composition of this complex gaseous mixture called biogas is essentially determined by the substrates used, the fermentation process, and various technical designs. Moreover, the end products of this process, such as methane, can be recovered and used as a source of renewable energy. This further contributes to the sustainability of the treatment process and reduces the overall environmental impact [10]. The anaerobic treatment process towards biogas formation consists of series and parallel steps, mainly: (*i*) hydrolysis, (*ii*) acidogenesis, (*iii*) acetogenesis, and (*iv*) methanogenesis (Fig.2) [11]. Each individual degradation step must be optimally coordinated to run the overall process smoothly.

***Hydrolysis**:* It is a pivotal step in the wastewater treatment process, where complex organic polymers are broken down into simpler monomeric and dimeric compounds. This transformation is facilitated by the action of hydrolytic bacteria, which produce extracellular enzymes that cleave the chemical bonds within the organic material. However, the efficiency of this hydrolysis process is heavily influenced by temperature and fluctuations therein, along with other factors such as pH, substrate concentration, and the presence of inhibitory substances. These factors are critical in determining the design and performance of treatment reactors. Efficient reactor design must account for maintaining optimal conditions for microbial activity, ensuring stable temperature, and managing the feedstock composition to maximize the breakdown of organic materials and enhance biogas production. Interestingly, the rate-limiting nature of hydrolysis is not primarily due to a deficiency in enzyme activity, but rather stems from factors such as the availability of free accessible surface area on particles and the overall structure of the solid substrate [12], [13]. These considerations underscore the importance of carefully optimizing environmental conditions and reactor configurations to ensure optimal hydrolysis rates, thereby facilitating subsequent stages of organic matter degradation, and ultimately enhancing the overall efficiency of the multi-step process. The design of an anaerobic reactor, specifically, with a high suspended solids (SS)/Chemical Oxygen Demand (COD) ratio, is usually dependent on the hydrolysis step [12].

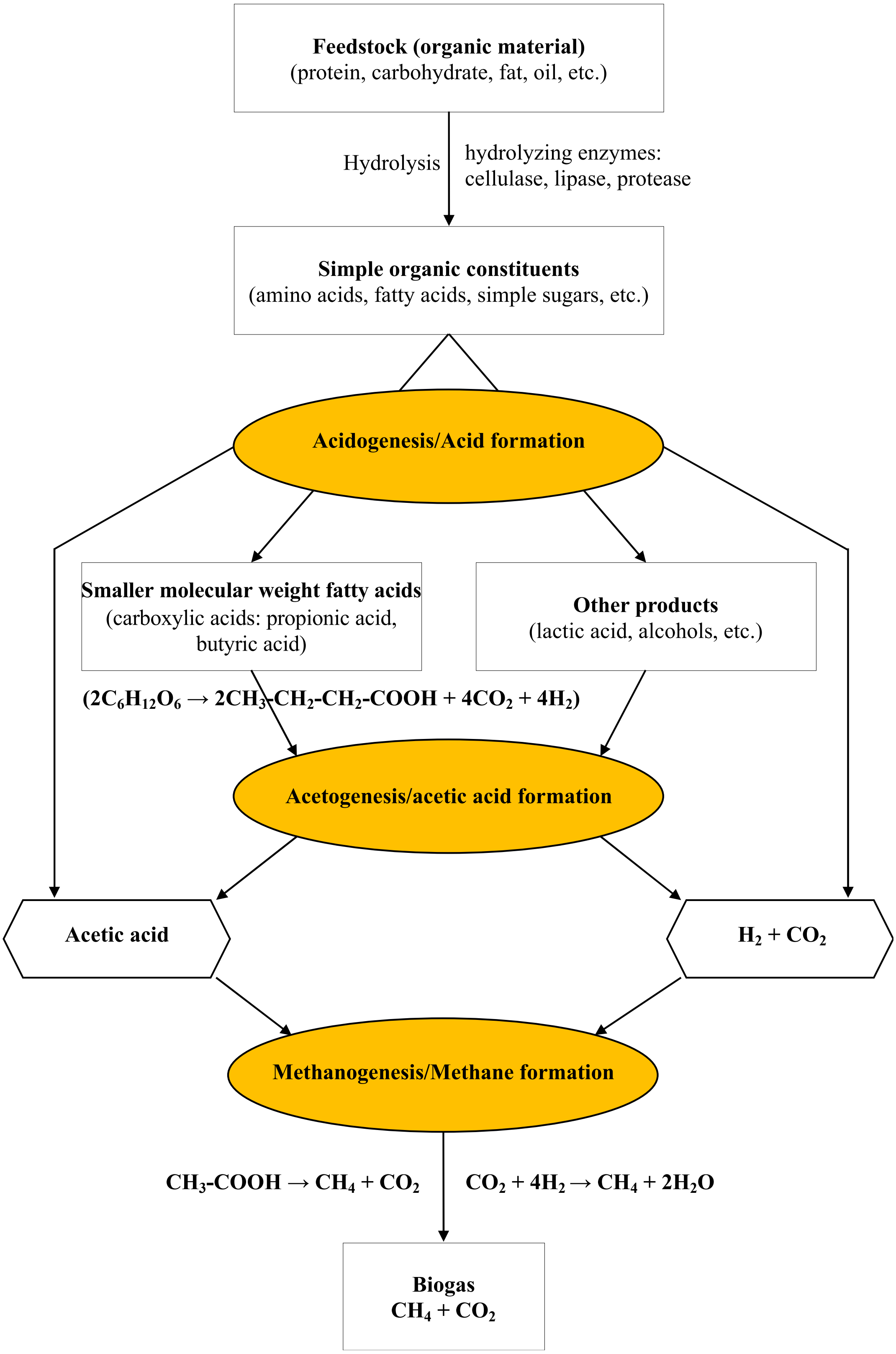


Figure 2

The four stages of the anaerobic treatment (biogas production) process: hydrolysis, acidogenesis, acetogenesis, methanogenesis [14]

Notably, primary sludge makes about 80% of domestic sewage and contains suspended matter in the range of 45-75% [15], [16]. In sewage, proteins, carbohydrates, and lipids make up the main complex organic polymers, which are hydrolysed to amino acids, simple sugars, and long-chain fatty acids (LCFAs), respectively. LCFAs originate from fats/oils, and during the degradation of triglycerides, glycerol is also produced [17], [18].

***Acidogenesis**:* The products formed via the hydrolysis step, such as amino acids, simple sugars, and LCFAs, are eventually fermented or anaerobically converted by entering the bacterial cells through the cell membrane, either by passive diffusion or active transport. Compounds generated by acidification are mainly volatile fatty acids (VFAs) such as acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, and isovaleric acid, as well as H_2, CO_2, ammonia, alcohols (e.g. methanol and ethanol) and some lactic acids. The conditions in the reactor medium, such as pH, temperature, substrate concentration, and the presence of specific microbial communities, determine the type of end products formed during anaerobic digestion. For instance, a neutral pH and mesophilic temperatures favour the production of methane, while acidic conditions can lead to higher concentrations of volatile fatty acids. Additionally, the availability of nutrients and the type of organic matter present can influence the balance between methane production and the formation of other by-products such as hydrogen and carbon dioxide [19], [20].

Theoretically, in this stage, neutral substances are transformed into carboxylic acids (VFAs) and carbonic acid. Acetate will be the predominant by-product if H_2 is efficiently removed by H_2 scavenger organisms such as hydrogenotrophic methanogens. However, further reduced compounds such as propionate and butyrate, as well as potentially even more reduced substances e.g., lactate and alcohols, are expected to occur and accumulate if methanogenesis is delayed and larger H_2 partial pressure builds up. Hence, these more reduced intermediate products are frequently present in the effluents of anaerobic reactors that are overloaded or otherwise disturbed [15], [21]. The several acidogenic reactions using sucrose as an (exemplary) substrate are listed below:

$$C_{12}H_{22}O_{11} + 9H_2O \rightarrow 4CH_3COO^- + 4HCO_3^- + 8H^+ + 8H_2 \quad (1)$$

$$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 2CH_3CH_2CH_2COO^- + 4HCO_3^- + 6H^+ + 4H_2 \quad (2)$$

$$C_{12}H_{22}O_{11} + 3H_2O \rightarrow 2CH_3COO^- + 2CH_3CH_2COO^- + 2HCO_3^- + 6H^+ + 2H_2 \quad (3)$$

The acidogenesis is the most rapid conversion stage in the anaerobic food chain and one of the most unwanted events is the over-acidification of the anaerobic digestion process characterized as an upset condition accompanied by a decrease of pH in the digestate due to the accumulation of fatty acids, resulting in a perturbated methanogenesis step (Fig. 3). High organic loading rates or existence of (methanogenic) inhibitors in the digester such as ammonia, heavy metals, sulphide, or substituted phenolic compounds can be identified as the underlying reasons [22], [23]. Once the generated acids start to consume the alkalinity, the pH begins to drop, causing a larger concentration of undissociated VFAs and drastic decline in methane production [24]. Obviously, the latter causes an even faster build-up of VFAs and a consequent pH drop and overall, an imbalanced biogas-producing ecosystem [15]. It is noteworthy that a pH shifts from the slightly alkalic to neutral range to 5-6 is commonly observed under these conditions. This pH range is indicative of inhibited methane production and often associated with higher yields of VFAs. This issue related to shift in pH reflects the need for the smoothly balanced activity of acidogenic strains and methanogenic archaea, which are sensitive to decreasing (acidic) pH levels. By carefully controlling the reactor conditions, wastewater treatment operators can minimize VFA accumulation and promote stable methane production. This optimization of process conditions helps to enhance the degradation of organic matter and improves the overall efficiency and resource recovery in anaerobic digestion systems [25].

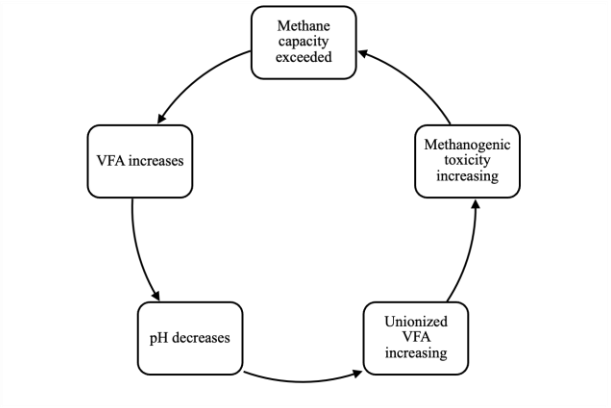


Figure 3
Effect of over-acidification on the anaerobic digestion process: accumulation of fatty acids, consequent pH reduction and methanogenesis disruption

***Acetogenesis**:* In this step, short-chain fatty acids such as propionate and butyrate are further transformed by acetogenic microorganisms to produce acetate, along with lactate, ethanol, methanol, CO_2, and H_2. These are then homoacetogenically converted to acetate, as shown in Fig. 2 [20], [24]. Acetogenic bacteria usually live in symbiosis with methanogenic bacteria. Among methanogens, one major class is hydrogen-dependent, thriving under conditions of high hydrogen partial pressure. These methanogenic organisms continuously remove hydrogen and other metabolic products produced by acetogenic bacteria, enabling the symbiotic relationship [26]. The concentration of hydrogen in the gaseous atmosphere should be balanced since it is required to produce methane. Specifically, the partial pressure of hydrogen should be kept extremely low ($\sim 10^{-4}$ atm or less) to ensure optimal conditions for methanogenesis. This low hydrogen partial pressure is necessary because it facilitates the thermodynamically favourable conversion of substrates by hydrogenotrophic methanogens, which consume hydrogen to produce methane. High hydrogen concentrations can inhibit acetogenic bacteria, thereby disrupting the production of methane and leading to process instability [27], [28]. A good symbiosis is required between the hydrogen-producing acetogenic bacteria and the hydrogen-consuming methanogenic bacteria because the thresholds of hydrogen partial pressure, which is around 10^{-4} atm or less, depend on the species of bacteria and the substrates as well [29]. Methanogens or sulphate-reducing bacteria can accomplish maintaining the hydrogen partial pressure at a very low level under stabilized digestion conditions, by effectively consuming the hydrogen. In the anaerobic digester, methanogenic archaea often use molecular hydrogen so quickly that the hydrogen partial pressure falls below 10^{-4} atm, which is sufficient to ensure the real occurrence of the hydrogen producing acetogenic process [30].

Methanogenesis**:** In principle, the four phases of anaerobic degradation take place in sequence in a single-stage process. However, the bacteria of the individual degradation steps make different demands on their habitat (e.g. pH value, temperature), so a compromise must be found here in terms of process technology. Since the methanogenic microorganisms are the weakest member of the biocenosis due to their slow growth rate and react most sensitively to disturbances, the optimum conditions must be adapted to the requirements of the methane producers [14]. Due to the action of numerous bacterial groups that are facultative or obligate anaerobes, a wide range of by-products are produced during the first three stages of anaerobic digestion [19]. However, methanogens are archaea; so far, 65 different species from 3 orders, 7 families, and 19 genus have been identified. The primary microorganisms responsible for the production of methane consists of *Methanobacterium, Methanococcus, Methanobrevibacter, Methanomicrobium, Methanosarcina*, and *Methanosaeta* [31]–[33]. During the final step of anaerobic digestion, a group of methanogenic archaea reduces carbon dioxide using hydrogen as an electron donor and decarboxylates acetate to generate methane.

Methanogens are obligate to methane production as they are strict anaerobes with a very narrow substrate spectrum. They are classified into three main functional groups: acetate converting (aceticlastic methanogens), hydrogen utilizing (hydrogenotrophic methanogens), and methylotrophic methanogens, which use methylated compounds for methane production (Table 1.). The growth rate of acetate converting methanogens is extremely low, with doubling times ranging from 4 to 9 days. This significantly poor growth rate is the reason why anaerobic reactors require a very long start-up time, often taking several weeks to months with unadopted seed material, and why high sludge concentrations are desired. However, this process generates a significant part of the total methane production (approx. 70%). The hydrogenotrophic methanogens, on the other hand, form methane from hydrogen and carbon dioxide. The methane content produced during this step makes up approximately 30% of the total methane amount [34]. On the other hand, the growth rate of hydrogenotrophic bacteria is much higher. Even though the acetate converting step is very delicate, this leads to anaerobic reactor systems to exert a exceptional stability under varying conditions [34], [35].

Table 1
Classification of methanogenesis based on the functional steps

Functional step	Reaction
Acetotrophic methanogenesis	$CH_3^-COO^- + H_2O \rightarrow CH_4 + HCO_3^-$
Hydrogenotrophic methanogenesis	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
Methylotrophic methanogens	$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$

1.2. Biogas generation potential of various feedstock

Table 2 presents estimation of biogas generation and methane content resulting from the anaerobic digestion of various organic materials. It's important to note that the actual biogas production and methane content can vary significantly based on several factors. These factors include the design and operation mode of the biogas plant, as well as the type and concentration of the substrate materials used.

Table 2
Estimated biogas generation and methane content of organic matters [36], [37]

Organic matter	Biogas yield, m^3/t dry organic matter	Methane content of biogas, V/V%
Sewage sludge	600	68
Grasses	420-540	60
Farm waste	300-420	60-70
Cow dung	90-300	65
Pig manure	350-480	65-70
Chicken manure	300-600	60

In multi-stage anaerobic digestion processes, different environmental conditions may arise within individual digester stages to enhance the overall efficiency of the process. There are some examples given as follows [38]:

Two-Stage Systems: In these systems, the first stage typically focuses on hydrolysis and acidogenesis, where complex organic materials are broken down into simpler molecules like VFAs. The second stage focuses on methanogenesis, where these simpler molecules are converted into methane and carbon dioxide. This separation allows for better control of conditions such as pH and temperature, which can be optimized for each specific microbial community involved in the process. An example of this type is the Temperature-Phased Anaerobic Digestion (TPAD) system, where the first stage operates at thermophilic temperatures (50-65 °C) to enhance hydrolysis and acidogenesis, and the second stage operates at mesophilic temperatures (30-40 °C) for methanogenesis.

Acid/Gas Phased Systems: These systems physically separate the acid forming steps (hydrolysis and acidogenesis) from the gas forming step (methanogenesis). This separation allows for optimizing the conditions for acid production in the first reactor and gas production in the second reactor, leading to increased efficiency and stability of the overall digestion process.

Advanced Two-Stage Systems: Research has shown that two-stage anaerobic digestion systems can achieve higher biogas yields and better process stability compared to single-stage systems. For example, a study highlighted that two-stage systems can enhance methane production by providing more favourable conditions for both hydrolytic/acidogenic and methanogenic phases, leading to improved organic matter degradation and pathogen reduction.

By leveraging these multi-stage designs, anaerobic digestion processes can be more effectively managed and optimized, addressing the specific needs of each microbial community involved and improving overall system performance.

These conditions can be influenced by factors such as temperature, pH, retention time, and substrate composition. These factors play key roles in general anaerobic digestion processes by determining the efficiency and stability of microbial activity. For example, temperature affects the rate of microbial reactions, pH influences enzyme activity and microbial community structure, retention time ensures adequate contact between microorganisms and substrates, and substrate composition impacts the types and rates of metabolic processes occurring within the digester. These environmental conditions, in turn, play a crucial role in shaping the composition and activity of the microbial communities (biocenosis) present in each digester stage. The metabolic activities of these microbial communities are directly impacted by the environmental conditions prevailing in their respective digester stages. Consequently, variations in environmental conditions can lead to shifts in metabolic pathways as well as population shifts among the microbial communities. Changes in temperature, pH, retention time, and substrate composition can alter the dominant microbial species, resulting in different metabolic activities and the production of various metabolic products. This highlights the importance of carefully controlling and optimizing environmental parameters throughout the anaerobic digestion process to maximize biogas production and methane content while ensuring stable and efficient operation of the biogas plant [14].

Sewage sludge stands out as a promising candidate for generating substantial amounts of biogas and methane. As a by-product of wastewater treatment, excess sewage sludge is abundant and rich in organic matter, consisting primarily of microbial cells, proteins, lipids, and other biodegradable compounds. This composition makes it an excellent substrate for anaerobic digestion, leading to the production of biogas [39], [40]. In recent years, there has been a growing emphasis on energy recovery from sewage sludge, driven by concerns regarding energy sustainability and environmental impact. Traditional methods of sludge treatment are associated with issues such as emissions of undesirable compounds and the potential contamination of soil with heavy metals and pathogens. Energy recovery from sewage sludge offers a sustainable alternative that addresses these concerns while simultaneously utilizing a valuable resource [41], [42].

1.2.1. Effects of the main operational parameters of biogas production

Several key parameters influence the operation of anaerobic biological systems for biogas production from sewage sludge [43]: Main parameters are given in order to provide a general view as follows:

- *Substrate quality and concentration*: The organic content and composition of the sewage sludge directly impact biogas yield.
- *Toxin concentration and leaching rate*: Toxins present in the sludge can inhibit microbial activity and affect biogas production.
- *Temperature*: Optimal temperature ranges are crucial for maintaining microbial activity and maximizing biogas production.

- *pH and buffer system:* Proper pH levels and buffering capacity are essential for maintaining microbial activity and stability within the system.
- *Loading rate (kg organic matter/m^3*day):* The rate at which organic matter is introduced into the system affects the efficiency and stability of biogas production.
- *Retention time (hydraulic):* Hydraulic retention time influences the duration of substrate exposure to microbial activity and thus affects biogas yield.
- *Sludge age (based on biomass):* The age of the microbial biomass within the system influences its metabolic activity and biogas production potential.
- *Nutrient to biomass ratio:* Proper nutrient levels are necessary to support microbial growth and activity.
- *Efficient mixing:* Adequate mixing ensures uniform distribution of nutrients and enhances microbial activity throughout the system.

It is frequently required to add external carbon sources to treated wastewater to meet the strict standards for lowering the concentration of nitrogen in wastewater and achieve high treatment efficiency. An examination of available waste products and semi-finished products from various food industry branches is one of the first steps in the investigation into the possibility of using alternative sources of carbon for the denitrification process. These are evaluated based on their high COD/N ratio and high content of easily degradable organic compounds. The primary inputs include waste and semi-finished products such corn syrup, glucose, molasses, glycerol, beet pulp, raw spirit, or fusel oil, as well as post-production effluent from distilleries, breweries, and fisheries [44].

To further enhance biogas production, the glycerol as a substrate was considered to be used. Glycerol is abundant and contains a high level of easily degradable carbon compounds, making it an ideal supplement to sewage sludge. The incorporation of glycerol can significantly increase the organic load available for microbial digestion, thereby boosting microbial activity and biogas yield. Furthermore, glycerol helps in balancing the carbon-to-nitrogen ratio, which is crucial for the optimal performance of anaerobic digesters. Additionally, glycerol can also be found as a by-product in other industries, which can make the anaerobic digestion process more economically viable. However, it is essential to carefully monitor glycerol concentrations to prevent potential inhibitory effects due to high organic loading or impurities present in crude glycerol [45]. When 1 and 3% (vol%) glycerol was added to sewage sludge, Fountoulakis et al. [45] reported an increase in daily biogas production of 112%, from 1106 to 2353 mL CH_4/d, as long as the proportion did not exceed 1% (vol.%).

The reaction temperature is another critical operational parameter in biogas production. Although methane fermentation can occur over a broad temperature range spanning from 10-70°C, three distinct temperature ranges are recognized: psychrophilic (below 20 °C), mesophilic (30-37 °C), and thermophilic (50-57 °C) decomposition. Psychrophilic digestion is applicable in colder climates and can be efficient under low-temperature conditions, though the process generally occurs at a slower rate. It is essential to use microbial communities that are specifically adapted to operate within the chosen temperature range. Operating at temperatures between 50-55°C offers several advantages, including a reduced risk of pathogenic microflora emergence and growth. Moreover, thermophilic microorganisms present at these conditions exhibit robust methanogenic activity, enabling shorter residence times of raw materials in fermenters and resulting in lower amounts of solid residues [46].

Therefore, maintaining optimal temperature and pH conditions is crucial for maximizing biogas production and ensuring process stability. Careful management of these parameters helps in achieving efficient and reliable biogas production while minimizing the risk of undesirable outcomes such as process upsets or the proliferation of pathogens [47].

1.3. Dissolved methane impacts and main emission sources

Fig. 4 illustrates the two main categories of microorganisms involved in the process of biogas production. The first group consists of hydrolytic and fermenter organisms, which play a crucial role in breaking down complex organic structures into simpler organic molecules. Subsequently, the second group, known as methanogenic organisms, further transforms these simpler organic molecules into methane via the formation of H_2 and CO_2.

During anaerobic digestion, the carbon in organic matter transitions between its reduced and oxidized states. The process ultimately generates biogas, a renewable and versatile fuel that can be used for various energy applications. Producing biogas offers environmental benefits, including reducing organic waste volumes, mitigating greenhouse gas emissions, and providing nutrient-rich digestate for use as fertilizer. An important source of biogas is landfill gas, produced through the anaerobic decomposition of wet organic waste in landfills. Mechanical compression from accumulated waste creates an oxygen-deprived environment, facilitating bacterial decomposition. Without proper management, landfill gas can escape into the atmosphere, posing environmental and safety risks. Methane and carbon dioxide released in this manner contribute significantly to global warming. Therefore, effective collection and treatment systems are crucial for minimizing these emissions and their associated impacts.

The Intergovernmental Panel on Climate Change (IPCC) identifies waste treatment as one of the seven sectors that contribute to global anthropogenic emissions, accounting for approximately 2.8% of all greenhouse gas (GHG) emissions [48], [49]. Remarkably, wastewater treatment and related activities account for around 9% of global methane emissions [50]. This is significant because the presence of dissolved CO_2 in water (the aqueous phase of CO_2) can influence methane solubility and behaviour, potentially effecting the methane concentrations [51], [52]. Moreover, the IPCC increased the global warming potential of CH_4 from 25 to 34 times that of CO_2, showing that CH_4 emissions have a greater environmental impact than all halocarbons combined [49]. Major sources of methane emissions, besides waste and wastewater treatment, include enteric fermentation in livestock, rice paddies, fossil fuel extraction and processing, natural gas systems, landfills, wetlands, biomass burning, and permafrost thawing [53].

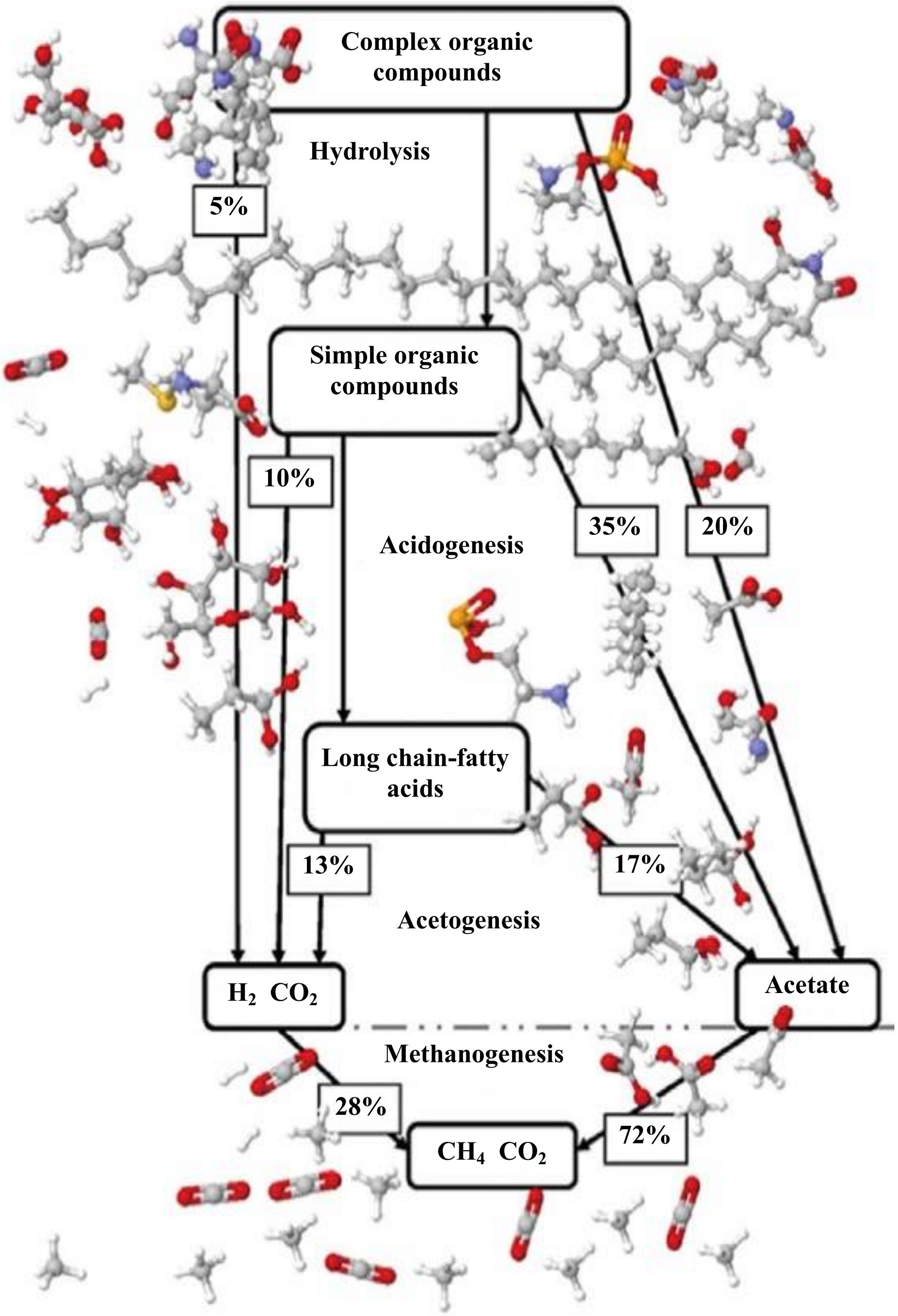


Figure 4
The microbial conversion of organic materials into biogas [54], [55]

CH_4 is considered as a valuable component in biogas with a heating value of 55 MJ/kg that can be converted to thermal and electrical energy [56]. However, during the anaerobic digestion process, part of the CH_4 produced is dissolved in the effluent and released into the environment, along with CO_2, which leads the anaerobic digestion process to be less appealing than expected. Therefore, the loss of dissolved CH_4 (D-

CH_4) in anaerobic effluents not only represents a loss of product but also contributes to the total emission of GHG, questioning the suitability of anaerobic processes [48], [57]. Methane loss as a function of the temperature of municipal wastewater containing an average soluble COD of 200 mg/L is presented in Fig. 5 [58]. Since the solubility of methane increases as the temperature decreases, the amount of dissolved methane is higher, even as high as 88% at 0 °C, at lower temperatures. Furthermore, lower and upper explosive limits of CH_4 are 4.6 vol.% and 15.8 vol.%, respectively when methane is ignited in air at 20°C and 100 kPa (relates to ambient temperature and pressure) [59], [60]. In addition to the explosive nature of CH_4, managing effluent in enclosed areas is important for environmental protection and more efficient product recovery, reducing the emission of greenhouse gases and maximizing the benefits of the anaerobic digestion process [48], [59]. The percentage of dissolved methane in the wastewater is shown in the Fig. 5, which highlights the need for advanced systems to extract the dissolved gasses. In this respect, to eliminate these drawbacks, the dissolved gases present in anaerobically-treated effluents should be removed by using alternative post-treatment processes, allowing anaerobic treatment systems to be more efficient and sustainable [57].

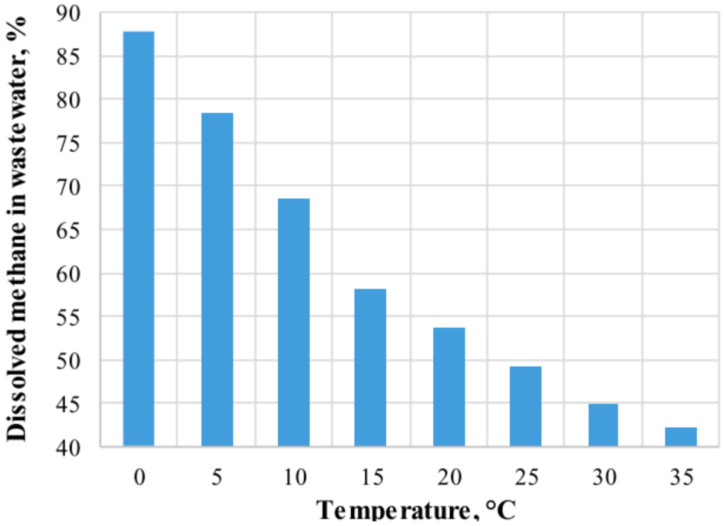


Figure 5

Dissolved methane in the wastewater as a function of temperature [58]

1.4. Degassing technologies

Various approaches have been explored to capture D-CH_4 from anaerobic effluents to enhance the energy output of anaerobic reactors and minimize atmospheric emissions. Among these post-treatment approaches, air or gas stripping and degassing membranes are widely utilized [61]–[64]. Aeration is a simple method where the high mass transfer is generated by the process of mixing carrier gases into solution and venting the gas to the outside atmosphere, and additionally helps in controlling sulphide levels. In a study, 30% CH_4 removal efficiency was attained by using air stripping in the settling compartment of up-flow anaerobic sludge blanket (UASB) reactors, followed by a dissipation chamber right after the reactor outlet [65]. However, certain disadvantages (e.g., difficulty in operation and scale-up, low CH_4 concentration in the gas outlet, potential explosion hazards, and low efficiency) needs to be considered [66]. Conversely, gas stripping, where the mass transfer area is facilitated by packing materials, is straightforward to operate and scale up. However, it provides a relatively limited mass transfer area, necessitates high gas/liquid flow rate ratios, and is susceptible to issues like flooding and foaming [67]. Among these technologies, degassing membranes represents the most potent technique for recovering dissolved biogas according to several studies, due to its advantages such as high mass transfer area, cost-effectiveness, energy-efficiency, operational robustness, and versatility. Degassing membranes have the capability to recover dissolved CH_4 in a form that is suitable for subsequent energy use with minimal site modifications and medium capital and operational cost [63], [68]–[70]. The additional treatment of recovered biogas e.g., removal of the moisture content ought to be investigated for the subsequent use. The presence of water vapour in the gaseous product stream is detrimental to the downstream processes towards gas transportation/utilization, due to issues such as corrosion problems and lowered heating value. Moreover, it is also essential to deal with the separation (recycling) of the sweep gas [71].

1.4.1. Gas-liquid and liquid-liquid membrane contactors

Gas separation from the liquid phase in membrane processes follows Fick's First Law of diffusion [72], where it is driven by the concentration gradient and the pressure drop across the membrane (Fig. 6) [67], [73]. Additionally, the hydrophobic nature of membranes serves as a barrier between the liquid and gas phases, preventing the dispersion of one phase into the other. Membrane contactors can be categorized into two main types based on their operating principles: gas-liquid and liquid-liquid membrane contactors [74], [75].

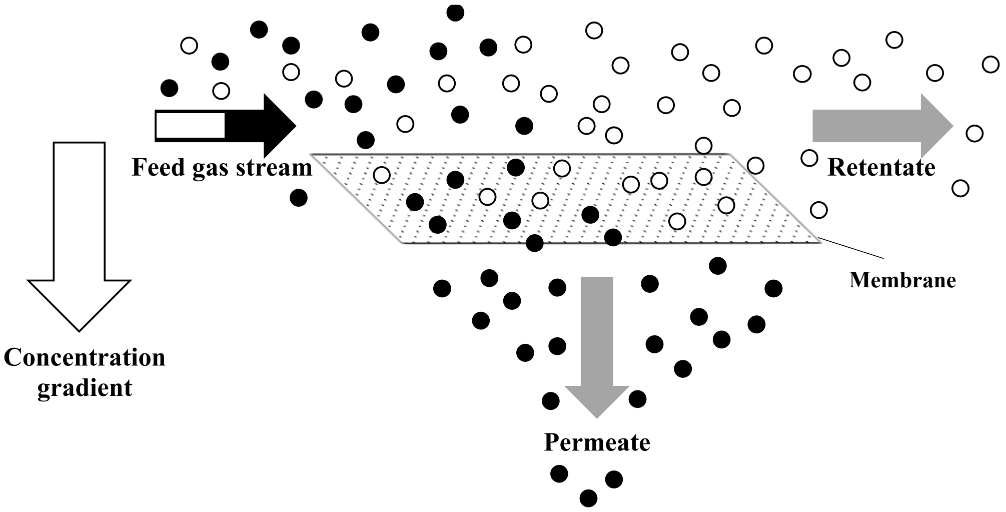


Figure 6
Theoretical scheme of the membrane gas separation process

In gas-liquid membrane contactors, a gas phase is separated from a liquid phase using a membrane. The gas molecules diffuse through the membrane pores from the gas side to the liquid side, driven by the concentration gradient and pressure differential. These systems are commonly used for gas absorption, stripping, and aeration processes. The hydrophobic nature of the membrane prevents liquid from penetrating the pores, ensuring efficient gas transfer.

In liquid-liquid membrane contactors, two immiscible liquid phases are brought into contact through a membrane. One liquid phase is typically dispersed within the membrane pores, while the other phase flows along the membrane surface. The solutes diffuse from one liquid phase to the other across the membrane, driven by concentration gradients. These contactors are used for liquid extraction, solvent recovery, and other separation processes. The membrane's wettability properties are crucial for maintaining phase separation and enhancing mass transfer efficiency. By distinguishing between these two types of membrane contactors and understanding their working principles, it becomes possible to optimize the design and operation of membrane-based separation processes for specific applications.

The maximum transfer rate is achieved when there is a significant concentration difference between the bulk solution and the membrane interface, coupled with a thin gas-liquid interface. This interface is crucial in membrane contactors, as it is the site where gas exchange occurs. Membranes inherently introduce additional resistance to mass transfer due to their thickness, compared to traditional aeration and stripping techniques. The driving force for mass transfer in these systems is the concentration gradient between the feed side and the permeate side of the membrane [51]. Another significant drawback of these conventional techniques is foaming and flooding that is caused by the direct contact of stripping gas, typically air, with the anaerobic effluents [76]. Membrane contactors are initially proposed to mitigate such operational problems by using stripping gas (or vacuum) to create a mass transfer driving force between the gas and liquid phases, which are separated by polymeric membranes as phase barriers [77]. This approach offers several advantages compared to liquid-liquid contactors. Gas-liquid membrane contactors prevent direct contact between the gas and liquid phases, reducing issues such as flooding, foaming, and phase entrainment. Additionally, they provide a larger interfacial area for mass transfer, leading to higher efficiency and better control over the separation process. In contrast, liquid-liquid contactors involve direct contact between two immiscible liquid phases, which can result in complications like emulsion formation and lower mass transfer rates due to the limited interfacial area [74], [78].

Hollow fibre modules are the most widely used membrane configuration for several reasons, including their compactness, modularity, simplicity of scaling up, high gas-liquid separation efficiency, and higher surface area. Even though membrane contactors typically use membranes with narrower module diameters to provide a substantially larger mass transfer area per unit volume, commercial hollow fibre membranes differ in terms of polymer type, porosity (non-porous, porous, microporous), geometry (inner and outer diameters, thickness, length), and number of fibres. As a result, the gas/liquid membrane contactor (GLMC) process has a lower energy consumption than traditional separation methods. Regarding liquid-liquid membrane contactors, they are less commonly discussed in the context of biogas (methane) recovery from anaerobic effluents. This is because gas-liquid membrane contactors are more suitable for separating gases like methane directly from the liquid phase. Liquid-liquid contactors are typically used for separating two immiscible liquid phases and might not offer the same advantages in terms of efficiency and effectiveness for methane recovery. However, they can still be relevant in processes where solvent extraction is involved, but this is less common for direct methane recovery from anaerobic digestion processes [70], [79]–[82].

1.4.2. D-CH_4 recovery from anaerobic effluents by membrane contactors: Flow- and Operating conditions

Membrane contactors are commonly employed for the membrane-based recovery of dissolved methane from anaerobic effluents [83]. They have a high potential to produce a product gas enriched with CH_4, thereby increasing their applicability in energy-related applications. This is due to their high packing density, which results in reduced volumes, and the non-dispersive stripping principle, which promotes mass transfer between two phases [79]. Although the methane concentrations in the sweep gas may be relatively low, the overall efficiency of the process can still be advantageous for specific applications where capturing and utilizing methane is beneficial.

Currently, most membrane contactors that are sold commercially use a hollow fibre membrane, despite the fact that various membrane contactor module geometries and configurations have been studied, including the helically wound bundle, rectangular bundle, crimped flat membrane, and vane modules [84]–[86]. Hollow fibre membrane modules are easily scalable and highly compact units that can have high packing densities with large specific membrane areas (up to 5000 m^2 m^{-3}), resulting in a favourable arrangement for gas-liquid separation [87]. These modules can have two different flow directions; one phase (such as a liquid or gas) moves within the hollow fibres (lumen side), while the other phase passes through the area between the fibres and the housing (shell side). The driving force of this membrane separation process is maintained by the constant renewal of both phases at each side of the membrane [79], [88]. When comparing the two operation modes, specifically feeding the liquid phase into the lumen or shell side of the membrane module, it has been observed by researchers that feeding the liquid into the lumen side yields better outcomes. This is attributed to more effective crossflow hydrodynamics. However, using the lumen side of the membrane modules increases the risk of clogging, especially when the effluents have a high solid content. Given this potential drawback, processing the effluents on the shell side of the membrane modules remains the preferred operation mode unless the total soluble solids (TSS) are adequately low [81], [89].

The driving force for D-CH_4 removal is generated by the concentration gradient between the feed side and the secondary side of the membrane. This gradient can be enhanced by applying a vacuum or using a sweep gas on the gas side, which helps to lower the concentration of methane on the permeate side, thereby maintaining the concentration difference that drives the mass transfer process. For the recovery and reuse of the downstream gas phase, the methane concentration in the recovered gas intended for commercial microturbines should exceed 35V/V%. Due to the fact that methane is diluted at sweep gas mode, therefore, a low gas-to-liquid flow-rate ratio (G/L) has been suggested to attain such a concentration [90]. However, this approach leads to an increase in gas phase mass transfer resistance, resulting in reduced D-CH_4 recovery efficiency [89], [91]. Vacuum operation addresses this issue, and it is recommended by some authors [92], [93]. Nonetheless, vacuum operation is less energetically efficient compared to using a sweep gas, even though the recovered methane can be directly used for thermal energy and electricity production without the need for prior enrichment. On the other hand, a greater pressure difference between the gas and liquid phases at vacuum mode could lead to pore wetting [81]. If non-porous membranes are used in vacuum operation mode, one key difference compared to porous membranes is that porous membranes generally exhibit better performance due to their lower resistance to mass transfer through the polymer. The decision to operate in vacuum or sweep gas modes for the removal of D-CH_4 depends on several factors, including D-CH_4 removal efficiency, reuse of the recovered compound, and energy consumption. Based on the results of the study carried out by Henares et al. [52], for instance, in the polydimethylsiloxane (PDMS) module, higher removal efficiency was achieved under vacuum operation compared to sweep gas operation. Conversely, in the polypropylene (PP) module, removal efficiency values were slightly higher in sweep gas operation. Vallieres and Favre [93] highlighted that at an industrial scale, sweep gas operation typically consumes less raw energy than vacuum operation, except when low vacuum pressure is feasible. Nevertheless, vacuum operation is preferred when recovering pure or high-purity components for reuse as an energy source, as sweep gas operation would necessitate a subsequent purification step, increasing overall energy consumption.

Henares et al. also investigated that in lumen mode operation, the PP microporous membrane was slightly more efficient under mild operational conditions (low liquid flow and/or vacuum pressure) but exhibited wetting under harsher conditions. In shell side mode, the PDMS membrane was more efficient, and no wetting phenomenon was observed [52]. This higher stability of dense composite fibres compared to microporous materials has been demonstrated in other absorption/desorption applications [94], where the PP module showed high sensitivity to wetting conditions. Maintaining operational conditions below the pressure where wetting occurs is crucial for stable and high-efficiency operation of the PP module at an industrial scale. Thus, selecting suitable operational conditions and membrane types is critical for this application. While microporous modules provide greater efficiency at lower flow rates (pressure), non-porous membranes perform better when higher liquid flow rates are required. The efficiency of recovery can also be improved in the combination mode of these two operational modes i.e., vacuum and sweep gas operations (Fig. 7) [95].

To enhance the quality of the outlet gas from membrane contactors, precise optimization of the operating parameters is essential. For instance, there can be a trade-off between the %CH_4 removal efficiency and the concentration of CH_4 in the gas outlet of the membrane contactor when additional stripping gas is introduced to boost the mass transfer driving force. Although this method can improve the %CH_4 removal efficiency, it inevitably reduces the CH_4 concentration in the outlet gas due to dilution [96]. Trace gases like hydrogen sulphide (H_2S), ammonia (NH_3), and water vapor must be managed effectively.

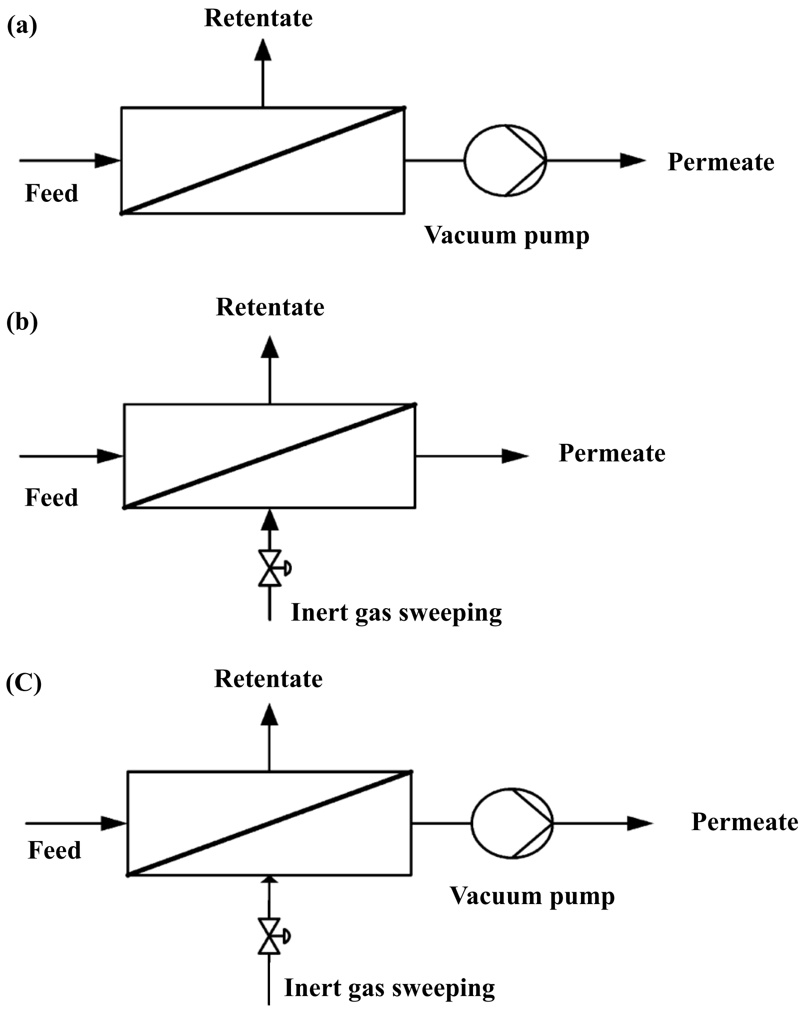


Figure 7
Three different strategies to produce a driving force: (a) vacuum pumping, (b) gas sweeping, (c) combined vacuum and gas sweeping

Removing H_2S with iron sponge or activated carbon prevents corrosion; lowering NH_3 with water scrubbing reduces health hazards; and dehumidifying biogas improves calorific value and reduces pipeline freezing risks. Addressing these trace gases enhances biogas quality for energy production and other applications [97]. Operational parameters such as gas and liquid flow rates play a crucial role in the recovery efficiency, as they have an impact on the transfer of dissolved gases from the liquid phase to the gas phase (Fig. 8).

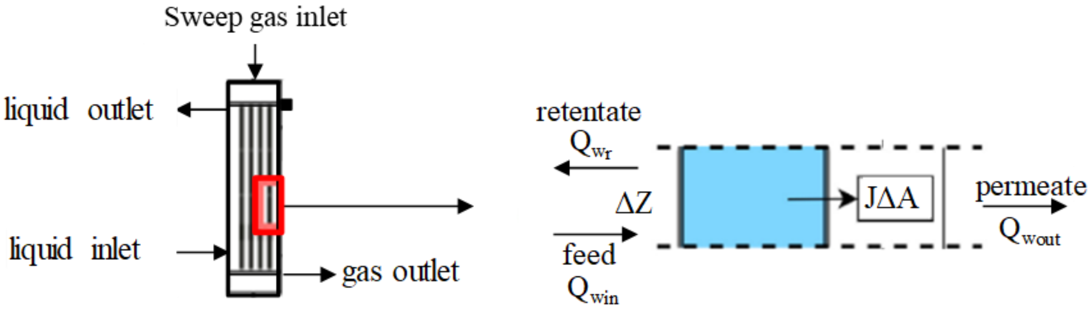


Figure 8

Scheme of the transport of the dissolved gases from the liquid phase to the gas phase: Qw_r, Qw_{in} and Qw_{out} are the mass flow rates of the retentate, feed and permeate, respectively; J=desorption flux of gas; ΔA= differential total mass transfer area;
ΔZ= differential length of the membrane

Studies have shown that as the feed liquid flow rate increases, the removal efficiency of CH_4 from the effluent also rises [82], [98], [99]. Lower flow rates allow for a longer contact time, enabling dissolved gases to remain on the surface and within the membrane for desorption. However, excessively low flows can lead to stagnation at the membrane surface, increasing resistance to the diffusion of gas through the membrane. This results in a lower CH_4 flux at lower liquid flow rates, creating a trade-off with recovery efficiency [96], [97]. In contrast, the gas phase has relatively small impact on mass transfer resistance, as the overall mass transfer is predominantly defined by the liquid phase [82], [98], [99].

1.4.3. D-CH_4 recovery from anaerobic effluents by membrane contactors: Materials

Commercial hollow fibre membranes vary in polymer type, porosity, geometry (inner and outer diameters, thickness, length), and fibre number [67], [73]. Typically, during the separation process, a microporous membrane is used as a physical barrier between the phases [74], [78]. However, utilization of hollow fibre membrane contactors with dense or composite structure (microporous support layer + dense selective layer) membranes for D-CH_4 recovery is significantly increased [62], [63], [100].

Volatile compounds in the context of biogas are those that readily vaporize at relatively low pressures and temperatures. This involves the main components of biogas, such as gases like CH_4, CO_2, H_2S, and NH_3. Contrarily, non-volatile compounds include substances like water vapor, certain organic acids, and other dissolved solids or particulates that remain in the liquid or solid phase under the same circumstances. In a microporous membrane, volatile and other gaseous compounds pass (on the upstream side) from the bulk liquid into the gas-filled micropores and then diffuse through this gaseous phase to reach the bulk gas on the secondary (downstream) side of the membrane. The mass transfer in microporous membranes is primarily influenced by the Henry's Law constant of the compound, which reflects its solubility, and specific micropore properties, including porosity, tortuosity, tube thickness, and average pore size [74]. Solubility affects the extent to which a gas dissolves in the liquid phase, while diffusivity determines the rate at which it migrates through the membrane. Additionally, the material of the membrane itself impacts the process through its hydrophobicity or hydrophilicity, although this has relatively lower importance compared to solubility and diffusivity. The mechanism of membrane separation is commonly referred to as molecular filtration, where volatile compounds like CH_4 pass from the bulk liquid into the gas-filled micropores and diffuse through the gaseous phase to reach the bulk gas [73].

The porous membranes play pivotal role in influencing wetting dynamics, despite their capacity to recover substantial quantities of dissolved methane. The hydrophobic nature of microporous membranes is instrumental in facilitating non-dispersive contact between liquid and gas phases, thereby allowing dissolved gas to diffuse freely through gas-filled pores. This unique characteristic improves efficient diffusion, a crucial aspect in various separation processes [101]. However, it is noteworthy that the wetting phenomenon introduces an additional impediment within the system, resulting an increased resistance and pressure on the lumen side. This effect becomes more pronounced with escalating liquid flow rates, as elucidated by recent studies [95], [99]. Membrane wetting occurs when water infiltrates gas-filled pores, preventing the desorption process either partially or fully. This obstruction compromises the efficacy of gas recovery mechanisms, thereby necessitating strategies to mitigate wetting effects in practical applications. Researchers are actively engaged in developing innovative solutions to address this challenge, ranging from surface modification techniques to the design of novel membrane materials with enhanced anti-wetting properties. Furthermore, the ongoing evolution of membrane technology continues to offer improvements for enhancing performance and expanding the applicability of porous membranes in diverse fields, including wastewater treatment, gas separation, and beyond. Consequently, while porous membranes hold promise in diverse applications, their utility in wastewater treatment is somewhat limited by the tendency of concentrated organic solutes in wastewater to induce membrane wetting [102].

To counteract the wetting phenomenon, nonporous membranes have been utilized as the interface between the liquid and gas phases. In a non-porous membrane, dissolved compounds such as CH_4 diffuse through the membrane structure, moving from the bulk liquid to the bulk gas. The membrane material plays a crucial role in the diffusion process, influenced by the permeability of compound within the dense membrane material. The separation of various compounds is linked to their relative transport rates through the membrane material. Consequently, dense membranes are expected to exhibit greater selectivity and higher mass transfer resistance compared to microporous membranes. The membrane separation process in dense membranes relies on the solution-diffusion mechanism [103]. In composite membranes, both the solution-diffusion and gas-phase diffusion processes occur, although the mass transfer rate of different gaseous compounds is governed primarily by the dense layer of the membrane [73]. Both Bandara et al. [62] and Cookney et al. [63] have employed nonporous membranes to recover dissolved methane from the real anaerobic effluent of UASB reactors, which are known to contain both particulate and soluble organics. In their research, Bandara et al. [62] successfully demonstrated that the recovered methane had a concentration suitable for combustion. Cookney et al. [63] conducted a preliminary investigation into the hydrodynamic conditions and found that the maximum dissolved methane removal efficiency (72%) was achieved at the lowest liquid velocity. It was suggested that dense membranes are more suitable as they have a higher capacity to obviate the pore wetting phenomenon [89]. Regarding the polymer type among nonporous membranes, the application of PDMS membrane contactors offers a promising option since it has higher gas permeability compared to other membranes such as polyamide, polypropylene or acetate cellulose, resulting in lower energy requirements for recovering the dissolved gases from the effluents [71], [104].

Collaborative efforts between academia, industry, and regulatory bodies are instrumental in driving advancements and overcoming existing limitations, ultimately paving the way for more sustainable and efficient membrane-based processes. Henares et al. [81] conducted experiments using a non-porous polydimethylsiloxane (PDMS) degassing membrane and a microporous hollow fibre membrane contactor (HFMC) composed of PP to recover D-CH_4 from anaerobic effluent. The aim was to compare the efficiency of two commercial modules with varying porosity properties (in case of PP), both suitable for industrial applications. When the liquid was directed into the lumen side, the PP membrane demonstrated greater efficiency at low liquid flow rates and/or under vacuum pressure due to its reduced resistance to mass transfer through the porous polymer. However, it exhibited pore wetting under more challenging conditions. Conversely, when the liquid flowed through the shell side, the PDMS membrane outperformed the polypropylene (PP) membrane and was not susceptible to wetting. They concluded that membrane wetting, resulting from the penetration of liquid into the pores, is a significant challenge in degassing processes due to the additional mass transfer resistance it introduces.

1.5. The objectives of the research work

Based on the literature review, it was concluded the emergence of membrane degassing technology, employing GLMCs offers a promising approach for recovering entrapped gases, primarily CH_4 in the fermentation liquor. Ideally, GLMCs are configured into hollow fibre membrane modules due to their ability to achieve higher gas desorption rates, attributed to their high volumetric mass transfer coefficients. Integrating anaerobic bioreactors with membrane separation in anaerobic membrane bioreactor systems presents a viable option for wastewater treatment.

The research objectives consisted of three parts (Fig.9):

1, The basis of research work was formed by enhancing the efficiency of dissolved gases separation from the fermentation liquor of the anaerobic digestion treatment by applying a non-porous hollow fibre membrane. The initial phase involved investigating the recovery efficiencies of CH_4 and CO_2 from model solutions. To do so, model solutions were prepared by purging CH_4/CO_2 into deionized water. I also examined the effect of gas and liquid flow rates on the gas removal (Experimental Series #1).

2, Based on the initial experimental phase, the research shifted to addressing real-world anaerobic effluents. Most studies focus on CH_4 recovery from synthetic effluents, but real effluents contain significant CO_2, posing environmental concerns. Even though there are studies carried out using real anaerobic effluents [89], [103], [105], only few of them have analysed CO_2 presence during recovery [92], [106], [107] leaving a gap in understanding the simultaneous removal of CH_4 and CO_2. This phase emphasized their binary interaction dynamics using binary gas mixtures to mimic anaerobic effluents. The study explored simultaneous CH_4 and CO_2 removal with PDMS hollow fibre membrane contactors of various sizes, compositions, and flow rates. It was also examined how different CO_2 concentrations affect methane recovery, aiming to reduce greenhouse gas emissions (Experimental Series #2).

3, In the final phase of the research, I focused on long-term recovery of biogas from real anaerobic effluents. The aim was to bridge the gap between theory and practice by conducting experiments with actual wastewater. By adjusting factors like gas and liquid flow rates as well as the methane content of the biogas, the recovery of methane from the so-obtained and prefiltered real anaerobic effluent was investigated thoroughly using a PDMS HFMC and an in-line dissolved methane sensor to directly and real-time monitor the process efficiency within the anaerobic membrane bioreactor system (Experimental Series #3).

Overall, the importance of the research work was to improve anaerobic wastewater treatment by enhancing dissolved gas separation from the fermentation liquor using membrane technology. Through a series of experiments, the differences and challenges in CH_4 recovery was emphasized by comparing the data of the current investigation using real effluent to those previously obtained with synthetic effluents applying an identical PDMS HFMC to remove the dissolved CH_4 in the fermentation liquor. My findings contribute to the advancement of sustainable wastewater treatment practices.

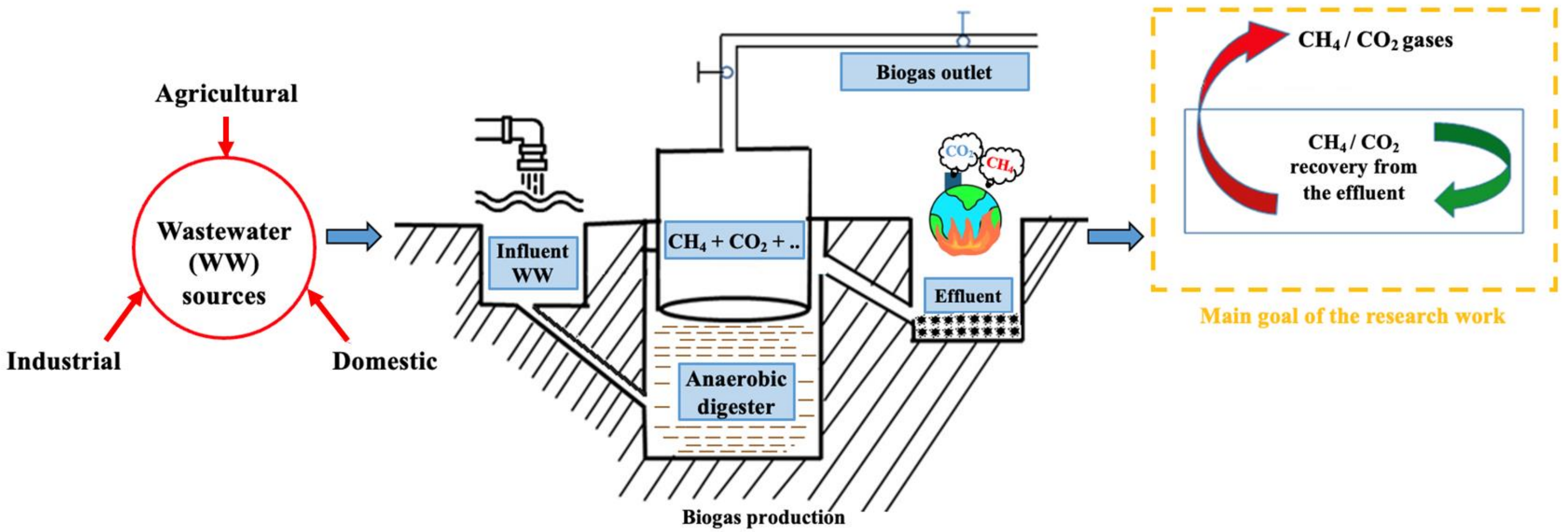


Figure 9
Visual illustration of highlights, the research purpose, and the significance of Experimental Series #2

2. Materials and methods

The primary aim of this research work is to enhance anaerobic wastewater treatment by improving the separation of dissolved gases i.e., CH_4 and CO_2 from fermentation liquor using PDMS hollow fibre membrane contactor. Another goal was to investigate the effect of varying compositions of methane and carbon dioxide in synthetic anaerobic (biogas-containing) effluents of binary gas mixtures, as well as the impact of sweep gas and feed liquid flow rates on the flux and recovery of methane.

In parallel, the study investigates a long-term recovery of biogas from real anaerobic effluents and evaluates the recovery efficiencies of methane and carbon dioxide from synthetic and real anaerobic effluents, emphasizing the importance of bridging the gap between theory and practice. To achieve these goals, three experimental series were conducted throughout the research work.

2.1. Experiments with model solutions (Experimental Series #1)

Initial experimental phase was aimed to evaluate hollow fibre membrane module for recovering the dissolved gases of pure CH_4 and CO_2 from model aqueous anaerobic effluents.

2.1.1. Preparation of model aqueous anaerobic effluents

The experiments commenced with the preparation of model solutions (MSs). Initially, 5 litres of deionized water were poured into glass bottles, followed by the purging of pure CO_2 (99%) into the deionized water using a peristaltic pump to displace air and establish an anaerobic environment. The anaerobic condition was confirmed using a dissolved oxygen analyser. Subsequently, three feed gas mixtures with different compositions (100/0, 0/100, 50/50 CH_4/CO_2 vol.%) were prepared in sealable gas bags and introduced into the glass bottles over a 3-hour period (Table 3). Saturation of each model solution was verified by monitoring the headspace composition using a gas chromatograph. At the saturation point, the concentration of CH_4/CO_2 in the headspace remained steady-state, indicating that the gas composition did not change over time.

Table 3
Composition of feed gas mixtures for Experimental Series #1

Model solutions	CH_4 (vol. %)	CO_2 (vol.%)
MS-1	100	-
MS-2	-	100
MS-3	50	50

2.1.2. Experimental apparatus

The glass bottles in which the model solutions prepared were coupled with a PermSelect® silicone, non-porous hollow fibre membrane module (from MedArray Inc.) with a surface area of 1.0 m^2. Main characteristics of the membrane module used is given in Table 4.

In the process depicted in Fig. 10, the membrane was operated with a counter current flow of the liquid on the lumen side to examine the desorption of CH_4 and CO_2 gases dissolved in the effluents. Argon (99.9%) was used as a sweep gas in the experiments with the gas flow rate adjusted between 5 and 60 mL/min using a needle valve and measured with a soap film-flow meter.

The liquid flow rate of model solutions was 15 mL/min, regulated by a peristaltic pump (Masterflex®, Cole-Parmer Instrument Co.), and monitored using a balance to measure the weight of the liquid exiting the membrane module.

Table 4
Geometric and operational characteristics of PDMS membrane module

Geometric characteristics	PDMS membrane module
Module length (cm)	14
Module diameter (cm)	6.0
Membrane area (cm^2)	10000
Number of fibres	12600
Fibre inner diameter (µm)	190
Fibre outer diameter (µm)	300
Fibre wall thickness (µm)	55
Lumen side volume (mL)	80
Shell side volume (mL)	100

2.1.3. Validation of experimental setup

The experimental apparatus comprised several components, including the PDMS module, peristaltic pump, and flow meters, which were interconnected primarily using Norprene® tubing material (Masterflex®, Cole-Parmer Instrument Co.) and Tygon® formula E-3603 laboratory tubing (Merck & Co., Inc.). Prior to measurements, leakage tests were successfully conducted to validate the reliability of the experimental apparatus. Samples were regularly taken using gastight Hamilton® syringes (300 µL) and analysed with a gas chromatograph to monitor the composition of the outlet gases from the membrane module under various experimental conditions.

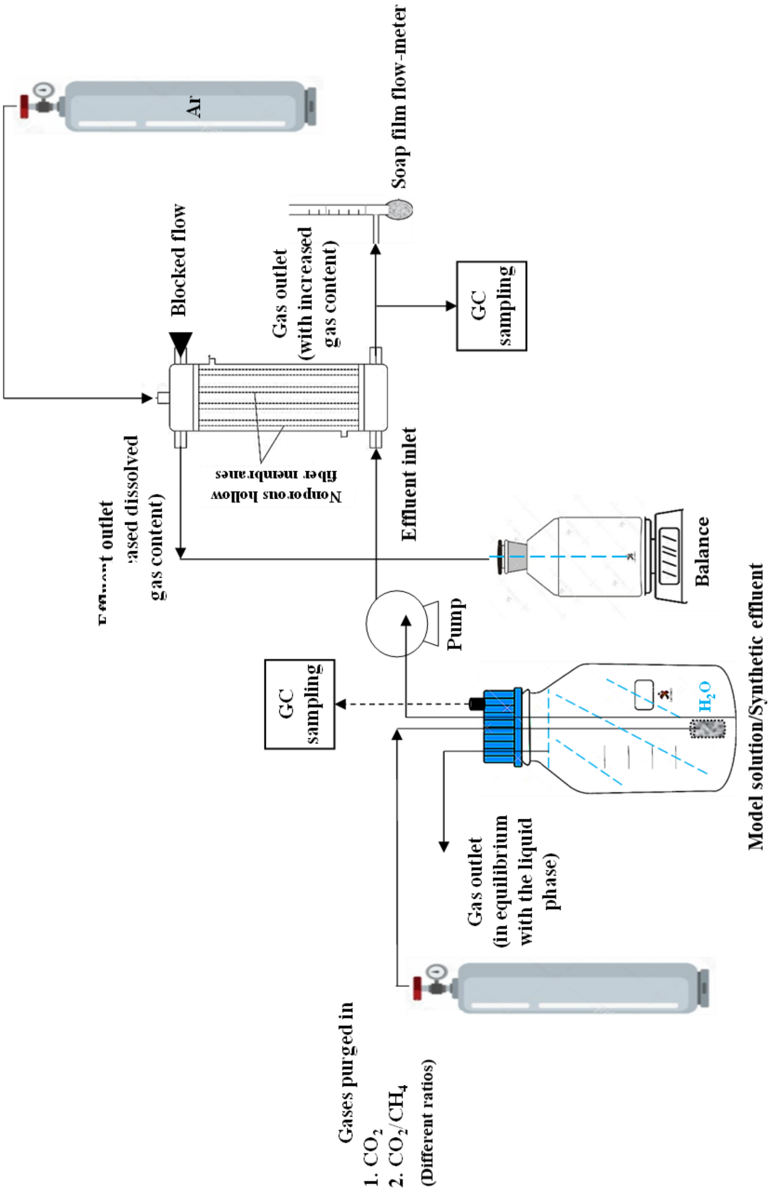


Figure 10
Scheme of the setup used during Experimental Series #1

Model solutions (MS-1, MS-2, and MS-3) were prepared according to the compositions outlined in Table 3, with a gas purging time of 3 hours into the glass bottles. The headspace composition of each model solution preparation unit was monitored using a gas chromatograph. Gas samples were extracted with a volume of 300 μL and injected at different time intervals until the change in the volume fraction of gas components became nearly constant, indicating equilibrium between dissolved gases in the effluent and those in the headspace. This equilibrium point served as the starting point for feeding the model solutions into the PDMS hollow fibre membrane contactor. At the end of each experimental period, the headspace composition was reanalysed, and no significant changes were observed, confirming the absence of alterations, such as leakage, during the experiments.

2.1.4. Analytical methods and calculations

A Hewlett Packard 5890, Series II gas chromatograph (GC) with a thermal conductivity detector (TCD) was used to monitor the compositions of the gases. Ar (99.9%) was used as the carrier gas in a Capillary Carboplot® column (Agilent Technologies, length: 60 m, internal diameter: 0.32 mm, film thickness: 1.5 mm) at a flow rate of 15 mL/min. A 100:1 split ratio was used. The injector, column oven, and detector had temperatures of 130, 90, and 115 °C, respectively.

In this study, Henry's law (Eq. 1) was used to understand the solubility of gases in liquids under specific temperature conditions. Henry's law states that the solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of that gas above the liquid. This relationship holds true under thermodynamic equilibrium conditions. According to Henry's law, as the partial pressure of a gas above the liquid increases, the solubility of the gas in the liquid also increases. Conversely, if the partial pressure decreases, the solubility of the gas decreases. This linear relationship allows for the prediction of gas solubility in liquids under equilibrium conditions, providing valuable insights into gas-liquid interactions and facilitating the design and optimization of processes such as gas absorption, dissolution, and extraction.

The partial pressure of each gas above the liquid was determined based on the results obtained from GC, while the solubility of gases in water at various temperatures was derived from literature data.

Liquid flow rates were employed to calculate the mass flow rate of gases entering the membrane module (Eq. 1).

$$S\,\mathrm{p}_i = S_i \tag{1}$$

where:

S = Henry's coefficient which is the solubility of gas component i (CH_4/CO_2) in the water at a given temperature at 1 atm (g/L)

p_i = partial pressure of the gas component i in the headspace of the glass bottle

S_i = theoretical equilibrium concentration of the gas component i in the water at p_i and a given temperature (g/L)

$$S_i\, Q_{V_L} = Q_{w_{in}} \tag{2}$$

where:

Q_{V_L} = the liquid flow rate of the dissolved gas containing model solution fed to the membrane module (mL/min)

$Q_{w_{in}}$ = the mass flow rate of the dissolved gas containing model solution fed to the membrane module (g/min)

The mass flow rate of the gases exiting the membrane module was determined by applying the ideal gas law and using the volume fraction of the gases calculated from the GC results obtained (Eq. 3).

$$x_i\, \frac{P_i Q_{V_G}}{RT}\, M_i = Q_{w_{out}} \tag{3}$$

where:

x_i = the volume fraction of the gas in the outlet of the membrane module

P_i = the pressure of the gas component (kPa)

Q_{V_G} = the gas flow rate (mL/min)

R is the gas constant (8.314 L kPa mol^{-1} K^{-1})

T = temperature (K)

M_i = molar mass of the gas component

$Q_{w_{out}}$ = mass flow rate of the gas exiting the membrane module (g/min)

Desorption fluxes of gases was calculated by Eq. 4:

$$\mathrm{J_i} = \frac{Q_{w_{out}}}{A_M} \tag{4}$$

where:

J_i = desorption flux of the gas component (g min^{-1} m^{-2})

A_M = surface area of the membrane (m^2)

Recovery efficiency of dissolved gases in each experimental point were calculated by Eq. 5.

$$\text{Recovery efficiency, \%} = \frac{Q_{w_{out}}}{Q_{w_{in}}}\,100 \tag{5}$$

2.2. Experiments with synthetic effluents (Experimental Series #2)

Following the initial experimental phase, the research direction shifted towards addressing the complexities associated with real-world anaerobic effluents, where the presence of dissolved CO_2 is significant for environmental considerations. While previous studies have mainly focused on CH_4 recovery from synthetic effluents [82], [92], [107], the simultaneous removal of both CH_4 and CO_2 remains poorly understood. In response, this research introduced binary gas mixtures mimicking anaerobic effluents to investigate their simultaneous removal using PDMS hollow fibre membrane contactors. By varying gas compositions, sweep gas and liquid flow rates, the study aimed to gain insights into the separation dynamics of CH_4 and CO_2, with a particular focus on mitigating greenhouse gas emissions. This innovative approach provided valuable experimental insights into the behaviour of these gases during separation, contributing to advancements in anaerobic wastewater treatment practices.

2.2.1. Preparation of synthetic effluents

The experiments commenced by preparing three synthetic effluents (SEs), following the procedure outlined in Experimental Series #1. Initially, 5 L of deionized water was poured into glass bottles, and pure carbon dioxide (99%, sourced from Messer Hungary Ltd.) was purged into the water using a peristaltic pump to eliminate air and establish an anaerobic environment. The anaerobic condition was verified using a dissolved oxygen analyser.

Subsequently, three different feed gas mixtures with varying compositions were prepared in sealable gas bags and introduced into the glass bottles. The composition of the binary gas mixtures used to prepare synthetic effluents was as follows: SE-1: 35/65; SE-2: 75/25; SE-3: 95/5 CH_4/CO_2 vol.% (Table 5). Based on preliminary experiments, the gas purging time was chosen to be 4 h. Saturation of each synthetic effluent was confirmed by monitoring the headspace composition using a gas chromatograph. At saturation, the concentration of CH_4/CO_2 in the headspace remained constant, indicating a stable condition where the gas composition did not fluctuate by more than ±1% over time. The methane utilized in preparing the synthetic effluents had a purity of 99.8% (obtained from Messer Hungary Ltd.).

Table 5
Composition of feed gas mixtures for Experimental Series #2

Synthetic effluents	**CH_4 (vol. %)**	**CO_2 (vol.%)**
SE-1	35	65
SE-2	75	25
SE-3	95	5

2.2.2. Experimental apparatus

The used non-porous PDMS (MedArray Inc.) membrane module was identical with the one used in the initial phase of the research (1.0 m^2) and it was integrated to the synthetic effluent-containing glass bottles. Furthermore, an additional membrane module with a surface area of 2500 cm^2 was also employed to separate dissolved gases from the effluents in order to validate the findings on a similar, but smaller-scale membrane module.

Geometric and operational characteristics of both PDMS membrane modules are listed in Table 6.

Table 6
Geometric and operational characteristics of PDMS membrane modules

Geometric characteristics	PDMS #1	PDMS #2
Module length (cm)	14	14
Module diameter (cm)	6.0	3.5
Membrane area (cm^2)	10000	2500
Number of fibres	12600	3200
Fibre inner diameter (µm)	190	190
Fibre outer diameter (µm)	300	300
Fibre wall thickness (µm)	55	55
Lumen side volume (mL)	80	21
Shell side volume (mL)	100	26

The experimental setup used in this series was identical to that employed in the initial phase of the research (Fig. 10). The membrane operated with a counter-current flow of liquid on the lumen side to assess the desorption of CH_4 and CO_2 gases. Liquid flow rates of synthetic effluents ranged from 10 to 20 mL/min, adjusted by a Masterflex® peristaltic pump from Cole-Parmer Instrument Co., and monitored using a balance to measure the weight of the liquid exiting the membrane module. Argon 99.9%) served as the sweep gas, with flow rates ranging from 10 to 20 mL/min, adjusted by a needle valve, and measured using a soap film-flow meter.

2.2.3. Validation of experimental setup

Once again, validation of the experimental apparatus followed similar steps to those in the initial phase of the research. Components such as the PDMS module, peristaltic pump, and flow meters were interconnected using Norprene® tubing from Masterflex® and Tygon® formula E-3603 tubing from Merck & Co., Inc. Leakage tests ensured the reliability of the setup. Gas samples were periodically taken with a gastight Hamilton® syringe (300 µL) and analysed using a gas chromatograph to monitor gas composition in the outlet from the membrane module.

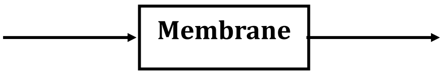
Synthetic effluents (SE-1, SE-2, and SE-3 as 35/65, 75/25, and 95/5 CH_4/CO_2 vol.%) were created by introducing (4 h) binary gas mixtures of CH_4 and CO_2 into glass bottles containing deionized water. Gas chromatography was used to monitor the headspace composition of each effluent preparation unit. Gas samples were taken periodically and injected until the gas component fractions stabilized, indicating equilibrium between dissolved gases and headspace gases. Analysis at the end of each period confirmed no significant changes, validating the experimental integrity.

2.2.4. Analytical methods and calculations

A HP 5890 (Series II) gas chromatograph with a thermal conductivity detector (TCD) and a carboplot® column was used to monitor gas compositions due to its precise separation and analysis capabilities. The measurement conditions, like column temperature, carrier gas flow rate, and injection volume, were adjusted as outlined in Section 2.1.4.

Henry's law and liquid flow rates were used to calculate the mass flow rate of gases entering the membrane module, consistent with the approach in Experimental Series #1. Meanwhile, the ideal gas law, GC results, and gas flow rates were employed to determine the mass flow rate of gases exiting the module. Recovery efficiencies of CH_4/CO_2 were then computed.

Essentially, the mass flow rates of gases entering the primary side were derived using equations based on Henry's law, while those exiting the secondary side were determined using the ideal gas law formula. Subsequently, the membrane surface area was utilized to calculate desorption fluxes, ultimately enabling the calculation of recovery efficiencies. The calculation method employed in this experimental work is summarized in Fig. 11.



Gases entering to primary side of module

$$S * p_i = S_i$$

$$S_i * Q_{V_L} = Q_{w_{in}}$$

where:

S: solubility of the gas component in the water at a given temperature at 1 atm, g/L,

pi: partial pressure of the gas component

Si: theoretical saturation of the gas component, g/L,

Qv_L: liquid flow rate, mL/min,

Qw_{in}: mass flow rate, g/min.

Gases exiting from secondary side of module

$$x_i * \frac{P_i Q_{V_G}}{RT} * M_i = Q_{w_{out}}$$

where:

x_i: volume fraction of the gas in the outlet of the membrane module

Pi: pressure of the gas component, atm

Qv_G: gas flow rate, mL/min

R: gas constant, 0.0821 L atm/mol K

Ti: temperature, K

Mi: molar mass of the gas component, g

Qw_{out}: mass flow rate of the gas exiting the membrane module, g/min.

$$\text{Desorption flux, } J_i = \frac{Q_{w_{out}}}{A_M}$$

$$\text{Recovery efficiency, \%} = \frac{Q_{w_{out}}}{Q_{w_{in}}} * 100$$

Figure 11
Summary of the calculation method used in Experimental Series #2

2.3. Biogas production and experiments with real anaerobic effluent (Experimental Series #3)

To date, most research studies have concentrated on the recovery of CH_4 from synthetic effluents [62], [71], [87], [90], [108]–[111], relying heavily on theoretical equations and calculations. However, there are far fewer examples of biogas recovery from real anaerobic effluents using membrane contactors. Sethunga et al. [112] investigated the recovery of dissolved CH_4 from both synthetic and AnMBR effluents using porous polyvinylidene difluoride (PVDF) and PDMS-modified PVDF membrane contactors. Cookney et al.[63] demonstrated the feasibility of recovering dissolved methane from low-temperature UASB reactors treating domestic wastewater with a PDMS membrane contactor. This study was expanded by integrating a polypropylene (PP) microporous membrane contactor, utilizing both synthetic and real anaerobic effluents from UASB and membrane bioreactors, and showing potential economic viability and reduced net CO_2 emissions.

Luo et al. [113] showed that a degassing membrane coupled with a UASB reactor could achieve in situ biogas upgrading, thereby lowering the dissolved CH_4 concentration in the anaerobic effluent. Despite these significant findings, further advancements are needed to fully understand the capabilities of this technology, particularly through long-term experiments with real anaerobic biogas fermentation effluents. More in-depth investigations on biogas recovery from real anaerobic digester effluents are essential for providing solid feedback and practical insights into the specific applicability of hollow fibre membrane contactors.

In this study, following long-term biogas production experiments from glycerol substrate, the desorption of methane from the prefiltered real anaerobic effluent was thoroughly investigated using a PDMS HFMC and an in-line dissolved methane sensor (Fig. 12). This setup allowed for direct and real-time monitoring of process efficiency within the anaerobic membrane bioreactor system. The study emphasizes the differences and challenges in CH_4 recovery by comparing data from real effluents to those obtained with synthetic effluents, which were previously explained in-depth (see sections 2.1 and 2.2) and published in prior studies [71], [111], using an identical PDMS HFMC. This comparative analysis represents the main innovation of this work and provides notable added value to the existing literature.

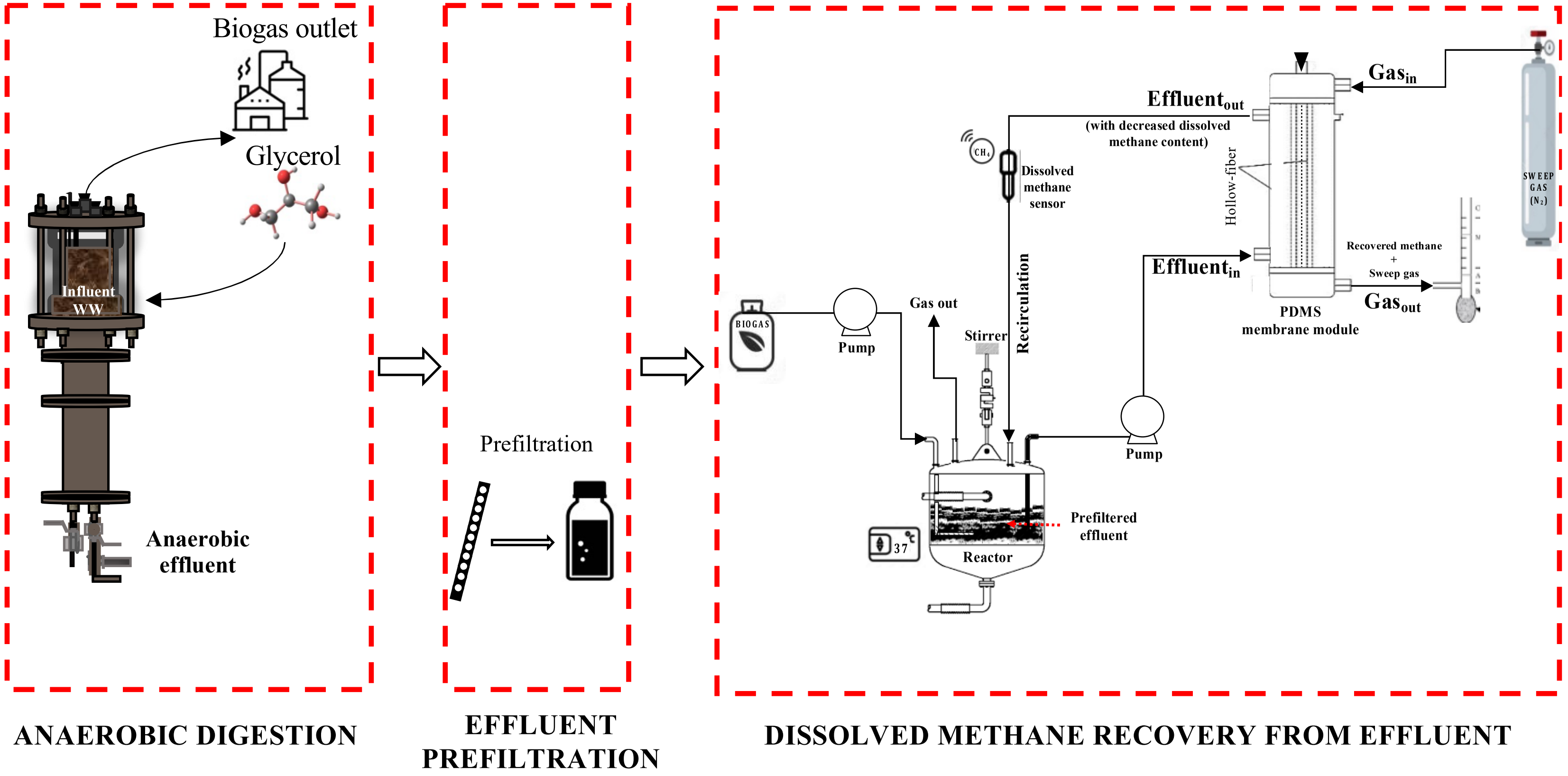


Figure 12
Visual representation of the main highlights for Experimental Series #3

Anaerobic digestion of the organic matter was conducted under mesophilic conditions, maintaining a stable temperature of approximately 35-38 °C. This temperature range is optimal for the activity of mesophilic microorganisms, which play a crucial role in breaking down organic materials and producing biogas. Before initiating the anaerobic digestion process, leakage tests were carried out meticulously to confirm the integrity of the experimental apparatus. These tests ensured that there were no leaks that could compromise the anoxic conditions or lead to the loss of biogas, thereby validating the reliability of the setup for accurate experimental results.

As it is shown in Fig.12, glycerol, with a purity of over 99.5%, served as the sole source of organic material for the anaerobic digestion process. To ensure that the bacterial community had sufficient nutrients and nitrogen source for growth, yeast extract was supplemented every two weeks at a concentration of 2 g/L. This setup facilitated the efficient conversion of glycerol into biogas, with continuous monitoring and adjustments to maintain optimal conditions for anaerobic digestion. The addition of yeast extract helped support the metabolic need of microbial community, promoting sustained biogas production over the experimental period.

Previous studies that have demonstrated the efficacy of glycerol in producing methane and generating power [114]. To optimize the anaerobic digestion process, initial tests were conducted to determine the maximum glycerol load that the microbial community could tolerate without experiencing inhibition. Since glycerol is readily metabolized by acidogenic bacteria, there is a potential risk that the subsequent steps of acetogenesis and methanogenesis could become limiting factors when the substrate is overloaded [115].

Scheme of the experimental setup of fed-batch anaerobic bioreactor where the anaerobic digestion of the organic matter was conducted is shown in Figs. 13 and 14.

Figure 13
Fed-batch anaerobic bioreactor used during the experiments

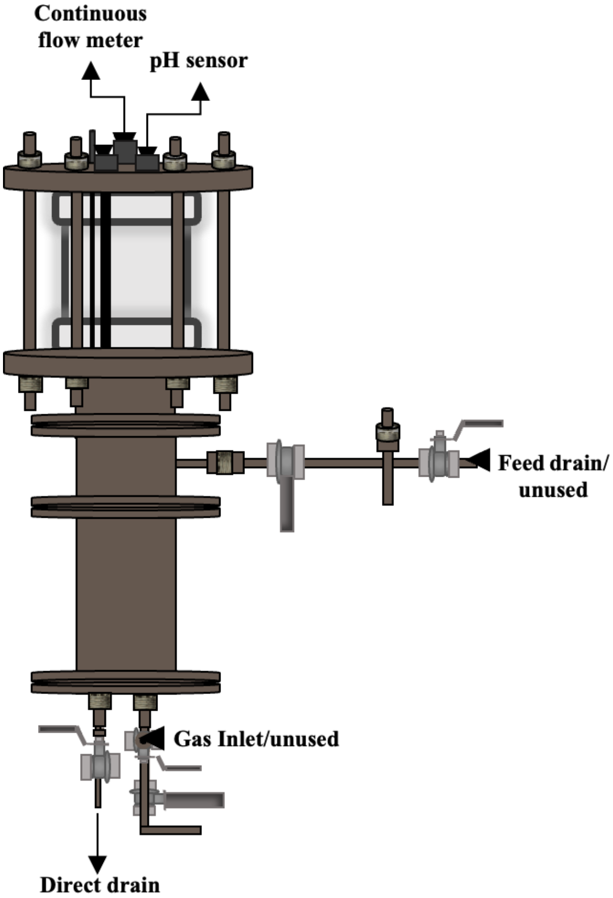


Figure 14
Scheme of the experimental setup of fed-batch anaerobic bioreactor

Acidogenic bacteria rapidly convert glycerol into volatile fatty acids (VFAs), which then need to be further processed by acetogenic bacteria into acetic acid, hydrogen, and carbon dioxide. These intermediates are finally converted into methane by methanogenic archaea. If the rate of glycerol degradation by acidogenic bacteria exceeds the capacity of acetogenic and methanogenic bacteria to process these intermediates, it can lead to an accumulation of VFAs. This imbalance can cause a drop in pH and inhibit the overall anaerobic digestion process, highlighting the importance of carefully balancing the substrate load to maintain stable and efficient digestion.

Biogas production was measured using a U-tube manometer, with gas flow data recorded and logged via Measurement Computing (MC) USB-5100 software. This software continuously tracked and monitored the gas flow, providing real-time data on biogas production.

Since maintaining an optimal pH level in the medium is crucial for achieving a higher biomass energy yield [116], a pH sensor was attached to the bioreactor to monitor pH values throughout the anaerobic digestion process. Following the initial setup, the bioreactor operated in fed-batch mode for a duration of 120 days to produce biogas. During this period, occasional internal biogas recirculation was performed to ensure proper mixing of the reactor contents, thereby enhancing the efficiency of the anaerobic digestion process. The total gas production was calculated by summing the daily gas production over the entire experiment.

To determine the composition of the produced biogas, gas samples were taken from the bioreactor headspace at regular intervals using a gastight Hamilton® syringe (300 μL). These samples were then analysed with a gas chromatograph. The analysis provided detailed information on the biogas composition, including the concentrations of methane, carbon dioxide, and other gases present. This comprehensive monitoring and analysis ensured accurate assessment of the biogas production process and its efficiency over the 120-day operational period.

Furthermore, microbial community samples were collected at various stages during the fermentation process to monitor the composition and behaviour of the microbial communities, including archaea. These samples were sent to Novogene, a next-generation sequencing (NGS) service provider, for detailed analysis.

For the detailed microbial community testing, samples were taken from different parts of the bioreactor, including the inoculum, the lower section, and the upper section, to capture a comprehensive view of the microbial dynamics throughout the biogas production process. The sequencing analysis provided insights into the diversity and abundance of microbial species present at each stage of fermentation, allowing for a better understanding of how these communities contributed to consistent biogas production. This detailed microbial profiling helped identifying key microorganisms involved in the anaerobic digestion process and their roles in the biochemical pathways leading to biogas production.

2.3.1. Dissolved gas recovery with integrated membrane technology

After 120 days of continuous operation of the bioreactor in fed-batch mode, the anaerobic effluent was first filtered by using a 1 mm sieve to remove suspended solids, which could potentially clog the membranes. The prefiltered anaerobic effluent was kept in a refrigerator for 3 days (technically until the next use) to maintain its stability in a low-temperature (4 ◦C) environment by slowing down microbial growth and enzymatic activity and then, was placed in a stirred tank bioreactor with a working volume of 2 L coupled by a non-porous PDMS membrane (MedArray Inc., product reference code: PDMSXA-1.0) with a 1.0 m^2 surface area to separate the dissolved gases from the real effluent (Table 4).

This initial filtration step was crucial to ensure the proper functioning and longevity of the membrane contactors by preventing blockages that could impede the recovery process. Storing the filtered effluent at low temperature (4 °C) helped preserve its composition and minimize microbial activity until it could be utilized in the subsequent experiments. These experiments aimed to recover dissolved methane, enhancing the overall efficiency and yield of the anaerobic digestion process. The use of PDMS hollow fibre membrane contactors in this phase was instrumental in effectively separating dissolved methane from the liquid phase, thereby optimizing the biogas recovery.

The investigation into the recovery of dissolved CH_4 in the effluent involved a counter-current flow setup, where the liquid was supplied on the shell side of the membrane module, while the sweep gas entered the membrane module through the hollow fibre capillaries. Although this membrane module had been utilized in previous studies [71], [111], there is insufficient information available regarding its efficiency and behaviour when exposed to treating real effluent. It is important to note that the prefiltering process using a 1 mm sieve resulted in the partial removal of microorganisms that actively participate in biogas production. Consequently, to simulate fermentation conditions accurately and align with the parameters of our previous research paper [71], binary CO_2/CH_4 mixtures with varying ratios (70/30 CO_2/CH_4 vol.%; 50/50 CO_2/CH_4 vol.%; 30/70 CO_2/CH_4 vol.%) were used (Table 7).

Table 7
Composition of feed gas mixtures for Experimental Series #3 for creating simulated fermentation conditions

Feed gas mixtures	CH_4 (vol. %)	CO_2 (vol.%)
1	30	70
2	50	50
3	70	30

The use of these gas mixtures allowed for a controlled comparison of methane recovery efficiency under different simulated fermentation conditions. By analysing the performance of the PDMS hollow fibre membrane contactors with these specific gas mixtures, it was possible to evaluate and compare the effectiveness of methane recovery. Consequently, the system was operated with a controlled gas inflow rate of 0.7 mL/min, a value corresponding to the average gas production capacity of 1 litre per day. This controlled inflow rate ensured that the consistency and stability throughout the duration of experiment is maintained. To monitor the biogas output accurately, a U-tube gas flow meter was employed, providing real-time measurements of gas production. In addition to monitoring biogas production, a dissolved methane sensor (Pro-Oceanus Digital Mini CH_4, Pro-Oceanus System Inc., Canada) was integrated into the recirculation side of the module. This sensor allowed for precise measurement of methane concentration in the effluent returning to the reactor after the degassing process. Periodically, the dissolved methane probe was disconnected from this position and directly inserted into the reactor to measure the actual methane concentration in the filtered effluent, which served as the feed for the PDMS HFMC module. Data collected from the dissolved methane probe were continuously logged onto a computer system to track methane concentration over time. This comprehensive monitoring approach ensured that the efficiency of the dissolved methane recovery process could be accurately assessed and optimized throughout the experiment. A peristaltic pump (Masterflex®, Cole-Parmer Instrument Co.) was used to adjust the liquid flow rate of real effluent between 10-20 mL/min, in accordance with our previous paper [71]. Nitrogen (99.9%) was used to create anoxic condition in the system and as the sweep gas in the experiments; the sweep gas flow rate was regulated using a needle valve, varied between 10-20 mL/min and measured with a soap film flowmeter, similar to our previous work [71]. The Norprene® tubing material (Masterflex®, Cole-Parmer Instrument Co.) and Tygon® formula E-3603 laboratory tubing (Merck & Co., Inc.) were primarily used to connect the various components of the experimental equipment including the PDMS module, peristaltic pump, and flow meter. The methane recovery experiments using the PDMS membrane module were conducted at a temperature of 37 °C over a period of 12 days. Throughout the experimentation process, various effluent and sweep gas flow rates were adjusted to achieve different gas-to-liquid flow ratios (G/L). This allowed for the investigation of the impact of membrane operational parameters, as well as the methane proportion in the binary gas mixture, on the efficiency of CH_4 recovery. The experimental plan, detailing the adjustments made to assess the recovery efficiency of dissolved CH_4 from the filtered fermentation effluent under steady-state conditions, is provided in Table 8. This plan outlined the specific parameters varied during the experiments to systematically evaluate the performance of the PDMS membrane module in recovering CH_4. Additionally, the schematic representation of the experimental setup, illustrating the arrangement of components and flow pathways, is depicted in Fig. 15. This visual representation facilitated a clear understanding of how the various elements of the experimental apparatus were interconnected and operated to facilitate methane recovery from the filtered fermentation effluent. Together, the experimental plan and setup scheme provided a comprehensive framework for conducting and understanding the CH_4 recovery experiments, enabling systematic exploration of key operational parameters and their impact on methane recovery efficiency. The validity and reliability of the experimental apparatus were ensured through meticulous testing, including the successful completion of leakage tests prior to commencing measurements. These tests were conducted to verify the integrity of the experimental setup and ensure that no leaks were present, which could compromise the accuracy of the measurements or affect experimental outcomes.

Table 8
The operating parameters of the PDMS membrane contactor for recovering dissolved methane from the filtered real anaerobic effluent under the various (70/30 CH_4/CO_2 vol.%, 50/50 CH_4/CO_2 vol.% and 30/70 CH_4/CO_2 vol.%) binary gas supply conditions

G/L ratio	Liquid (effluent) flow rate mL/min	(Sweep) gas flow rate mL/min
1*	15	15
1	10	10
2	10	20
1*	15	15
1	20	20
0.5	20	10
1*	15	15

*: repeated (centre point) settings

To monitor the performance of the membrane module and assess the efficiency of methane recovery under different experimental settings, gas samples were extracted from the headspace of the bioreactor at consistent intervals. This was achieved using a gastight Hamilton® syringe (300 μL), which enabled precise sampling without introducing any external contaminants. The extracted gas samples were then analysed using a gas chromatograph to determine the composition of the outlet gases of the membrane module, specifically focusing on the sweep gas side. This analysis provided valuable insights into the concentration of methane and other gases present in the recovered gas stream under various experimental conditions.

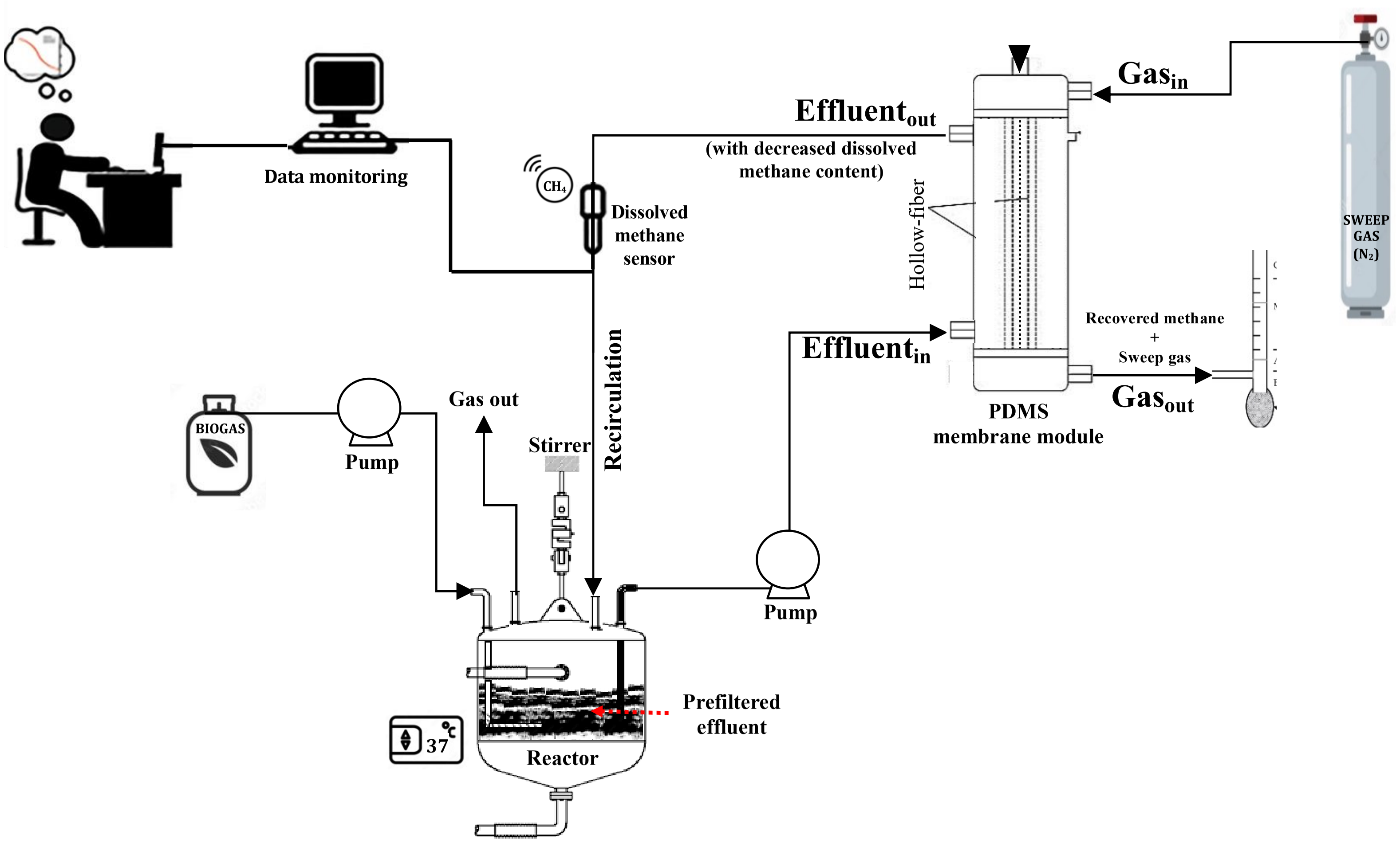


Figure 15
Experimental setup using membrane contactors to recover CH_4 from the real anaerobic effluent

2.3.2. Analytical methods and calculations

HP 5890 (Series II) GC equipped with a thermal conductivity detector (TCD) and a carboplot® column was employed to monitor the compositions of the gases. This setup was chosen for its ability to accurately separate and analyse the different components of the gas mixture. The measurement conditions, including parameters such as column temperature, carrier gas flow rate, and injection volume, were adapted as detailed in the Section 2.1.4 above. These conditions were optimized to ensure optimal separation and detection of the gases of interest, allowing for precise quantification of their concentrations.

The analysis of VFAs content was conducted using the GC. Prior to injection, all samples underwent centrifugation at 13000 rpm for 10 minutes to eliminate suspended particles. Quantification was performed using the internal standard method with n-butanol (1 g/L). Injection volume was maintained at 1 µl. The injection port, FID, and column temperatures were set at 240 °C, 250 °C, and 70 °C, respectively. The DB-FFAP column was initially held at 70 °C for 1 minute, then ramped up to 150 °C at a rate of 10 °C 1/min, and finally held at 150 °C for 1 minute.

Total solids (TS) and volatile solids (VS) of the filtered sludge were determined using gravimetric analysis according to the standard American Public Health Association (APHA) methods 2540 B (total solids dried at 103–105 °C) and 2540 E (volatile solids ignited at 550°C), respectively [117]. The chemical oxygen demand (COD) regarding the sample coming from the liquid phase was measured by the potassium dichromate ($K_2Cr_2O_7$) standard method [118]. This is a general COD determination that uses potassium dichromate in excess in an acidic medium with the aid of silver sulphate and a photometer (PF-12 Macherey-Nagel GmbH & Co. KG, Düren, Germany).

CH_4 recovery calculations were based on data obtained from both the dissolved CH_4 probe and GC results (Fig. 15) under steady-state conditions. The dissolved CH_4 concentrations (mg/L) were measured by the probe, providing real-time data on the methane content in the liquid phase. In parallel, the mass flow rate of CH_4 exiting the membrane module was determined using Eq. (3) as given in Section 2.1.4. This equation is essential for calculating the amount of methane recovered from the effluent through the PDMS hollow fibre membrane contactors.

The combined data from the dissolved CH_4 probe and the GC analysis allowed for a comprehensive assessment of methane recovery efficiency. The probe provided direct measurements of dissolved methane, while the GC results offered detailed insights into the composition of the gas phase, including the quantity of methane exiting the membrane module. By integrating these data sources, the recovery calculations accounted for both dissolved and gaseous methane, ensuring an accurate and reliable evaluation of the methane recovery process.

This dual-measurement approach enabled precise tracking of methane recovery performance, facilitating the optimization of experimental conditions and operational parameters to maximize the efficiency of the methane recovery system. Representative flow sheet of dissolved methane recovery is given in Fig. 16.

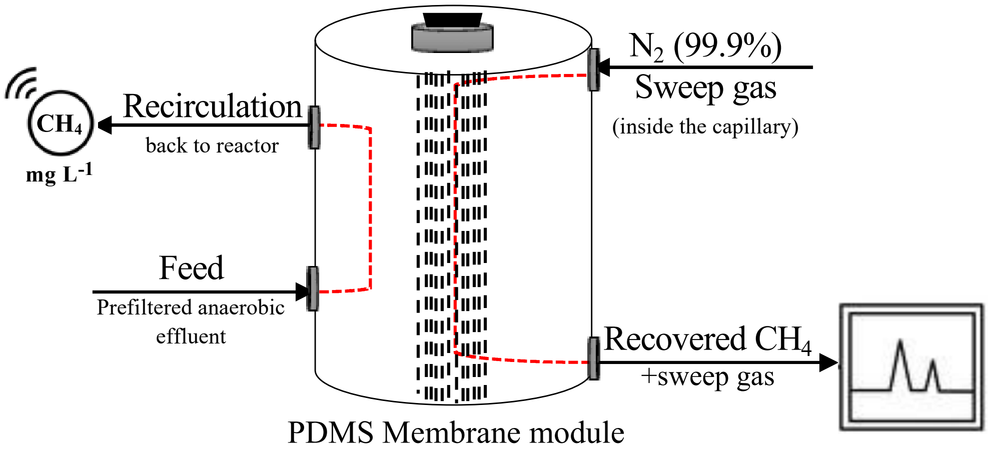


Figure 16
Flow sheet of dissolved methane recovery

3. Results and discussion

3.1. Recovery of dissolved gases (CH_4, CO_2) from model solutions using PDMS membrane contactor

This section presents the results of the initial experimental phase, referred to as Experimental Series #1, aiming to evaluate hollow fibre membrane module for recovering the dissolved gases of CH_4 and CO_2 from model aqueous anaerobic effluents with different compositions (100/0, 0/100, 50/50 CH_4/CO_2 vol.%).

The recovery efficiencies of CH_4/CO_2 from MS-1/MS-2 as a function of the sweep gas flow rate at a liquid flow rate of 15 mL/min are displayed in Tables 9 and 10, and their summarized representation is depicted in Fig. 17.

Table 9
Recovery efficiency of CH_4 from MS-1 (100/0 vol% CH_4/CO_2) as a function of the sweep gas flow rate

Gas containing liquid flow rate (mL/min)	Sweep gas flow rate (mL/min)	Recovery efficiency of CH_4 (%)
15	5	**57.1**
15	10	**58.0**
15	20	**58.6**
15	60	**35.9**

Table 10
Recovery efficiency of CO_2 from MS-2 (0/100 vol% CH_4/CO_2) as a function of the sweep gas flow rate

Gas containing liquid flow rate (mL/min)	Sweep gas flow rate (mL/min)	Recovery efficiency of CO_2 (%)
15	5	**9.2**
15	10	**29.0**
15	20	**47.6**
15	60	**61.6**

The results indicated that the recovery efficiency of CH_4 remained relatively constant (57.1-58.6%) across sweep gas flow rates of 5-20 mL/min but declined rapidly to 35.9% as the gas flow rate increased to 60 mL/min. This observation aligns with findings reported by Cookney et al. [89], who noted minimal impact on the mass transfer coefficient of CH_4 with increasing gas flow rates, attributed to mass transfer being controlled by resistance in the liquid phase.

Similarly, Rongwong et al. [82], [119] observed dilution of CH_4 concentration in the outlet gas at higher gas flow rates, a phenomenon also evident in this study. While the recovery efficiency of CO_2 increased with the sweep gas flow rate, these values were notably lower than those observed for CH_4, except at a gas flow rate of 60 mL/min.

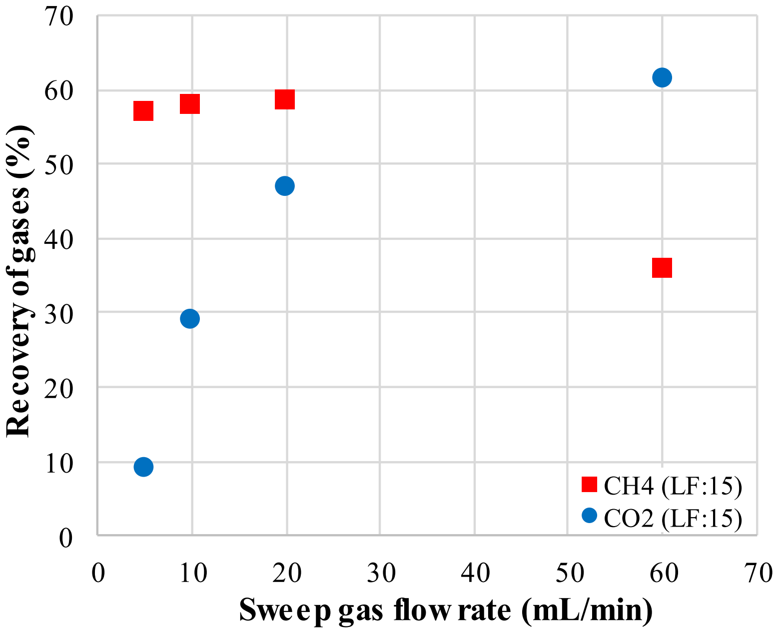


Figure 17
Recovery efficiencies of CH_4/CO_2 from MS-1 and MS-2 as a function of the sweep gas flow rate at 15 mL/min liquid flow rate

To further explore the impact of gas mixture composition on recovery efficiencies of membrane module, MS-3 was created by purging a 50:50 mixture of CH_4 and CO_2 gases into deionized water for 3 hours. The results from MS-3 were then compared with those obtained from model solutions prepared with pure gases. The recovery efficiencies of CH_4 and CO_2 as a function of the sweep gas flow rate are presented in Table 11 and Fig. 18.

The results obtained from MS-3 exhibited a similar trend to those observed with individual gases. Specifically, the recovery efficiency of CO_2 increased from 36.2% to 62.9% with an increase in the sweep gas flow rate, while for CH_4 the recovery efficiency ranged from 53.1% to 61.3% at gas flow rates of 10-20 mL/min, but significantly dropped to 11.9% by applying a gas flow rate of 60 mL/min. Notably, at this higher gas flow rate, the recovery efficiency of CH_4 from MS-1 was 35.9%, indicating a potential negative impact of CO_2 presence in the model solution on CH_4 recovery. Nevertheless, employing a sweep gas flow rate of 20 mL/min resulted in both gases achieving recovery efficiencies exceeding 50%.

Table 11
Recovery efficiencies of CH_4 and CO_2 from MS-3 (50/50 vol% CH_4/CO_2) as a function of the sweep gas flow rate

Liquid flow rate (mL/min)	**Sweep gas flow rate (mL/min)**	**Recovery efficiency of CH_4 (%)**	**Recovery efficiency of CO_2 (%)**
15	10	**61.3**	**36.2**
15	20	**53.1**	**55.0**
15	60	**11.9**	**62.9**

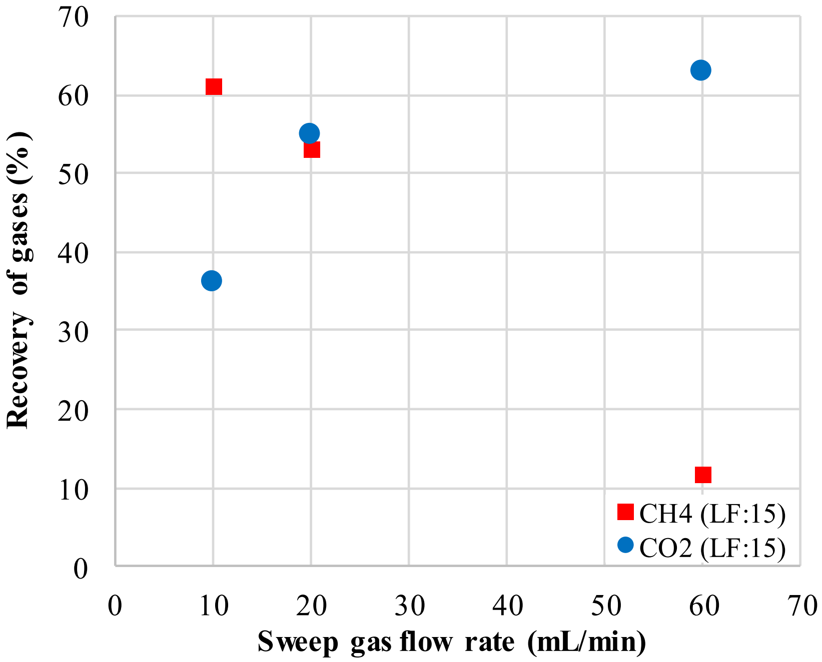


Figure 18
Recovery efficiencies of CH_4/CO_2 from MS-3 as a function of the sweep gas flow rate at 15 mL/min liquid flow rate

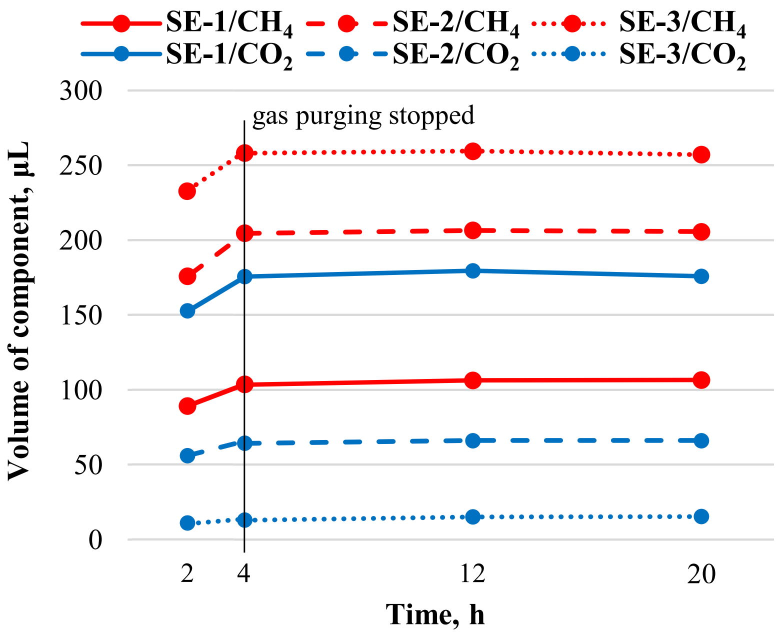
3.2. Degassing of synthetic effluents using different scale PDMS membrane modules

In this section, the findings of Experimental Series #2 are presented. The primary objective was to assess the performance of a hollow fibre membrane modules of various sizes in recovering dissolved CH_4 and CO_2 gases from synthetic effluents with varying compositions (SE-1:35/65, SE-2:75/25, and SE-3:95/5 CH_4/CO_2 vol.%). The other aim was to understand the simultaneous removal of CH_4 and CO_2 and the effect of their binary interaction on transmembrane transport of both gases. Furthermore, the impact of sweep gas and feed liquid flow rates on the recovery of both gases was thoroughly investigated.

3.2.1. Preparation and stabilization of synthetic effluents

Synthetic effluents (SE-1, SE-2 and SE-3) were prepared by purging binary gas mixtures with different compositions of CH_4 and CO_2 into deionized water-containing glass bottles. Based on preliminary experiments the gas purging time was chosen to be 4 hours. The composition of the binary gas mixtures used to prepare synthetic effluents is listed in Table 5. The headspace composition of each synthetic effluent preparation unit was monitored with a gas chromatograph, gas samples were taken with a volume of 300 μL and injected at different time periods.

Fig. 19 shows the change in volume of gas components in the headspace as a function of time. It can be seen that after 4 hours, the change in the volume of gas components was near-constant, indicating that the dissolved gases in the effluent are in equilibrium with the gases in the headspace [119]. Gas purging was stopped, and the glass bottles were sealed for the following 8 hours. Fig. 19 shows that the stability of synthetic effluents remained steady-state, therefore, experiments of simultaneous CH_4 and CO_2 removal were commenced by feeding the stabilized synthetic effluents into the PDMS hollow fibre membrane contactor. At the end of 8 hours experimental period, the composition of the headspace was analysed again, and no significant change was observed, which indicates that there was no alteration e.g., leakage during the experiments.



SE-1: 35%/65% CH_4/CO_2; **SE-2**: 75%/25% CH_4/CO_2; **SE-3:** 95%/5% CH_4/CO_2

Figure 19
Change in the volume of gas components in the headspace as a function of time

3.2.2. Evaluation of gas (CO_2, CH_4) fluxes under fixed G/L ratio

Gas separation experiments were conducted within the temperature range of 21-23 °C and under atmospheric pressure conditions. Desorption fluxes of methane (J_{CH_4}) and carbon dioxide (J_{CO_2}) served as key operational parameters indicating process efficiency, calculated using Eq. 4.

Both sweep gas and liquid flow rates, along with the corresponding gas-to-liquid (G/L) ratios, were adjusted as detailed in Table 12. Figs. 20 and 21 depict the desorption fluxes of CH_4 and CO_2, respectively, as a function of liquid flow rate (at a G/L of 1) in the case of different synthetic effluents (SE-1, SE-2, SE-3).

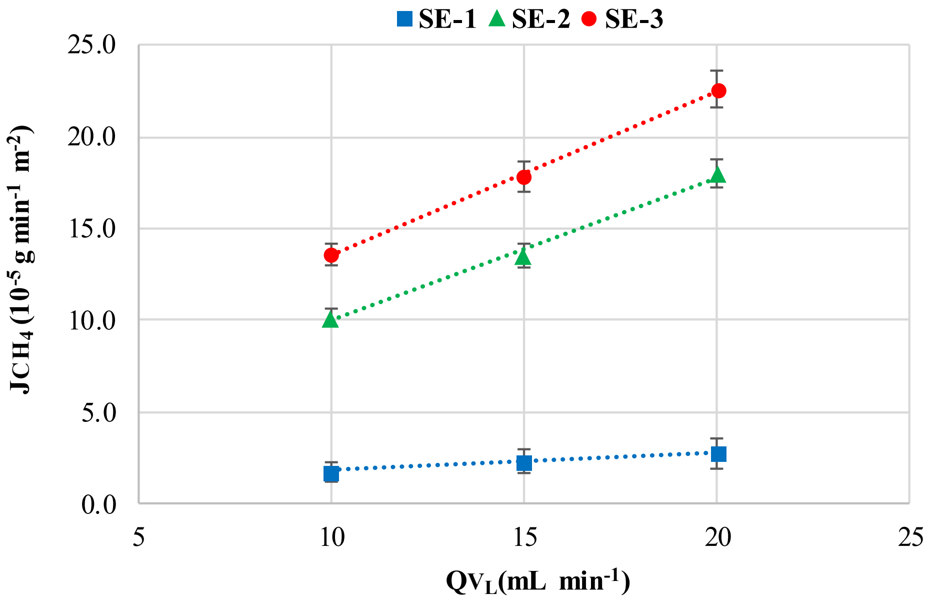


Figure 20
Desorption fluxes of methane as a function of liquid flow rate (G/L ratio= 1)

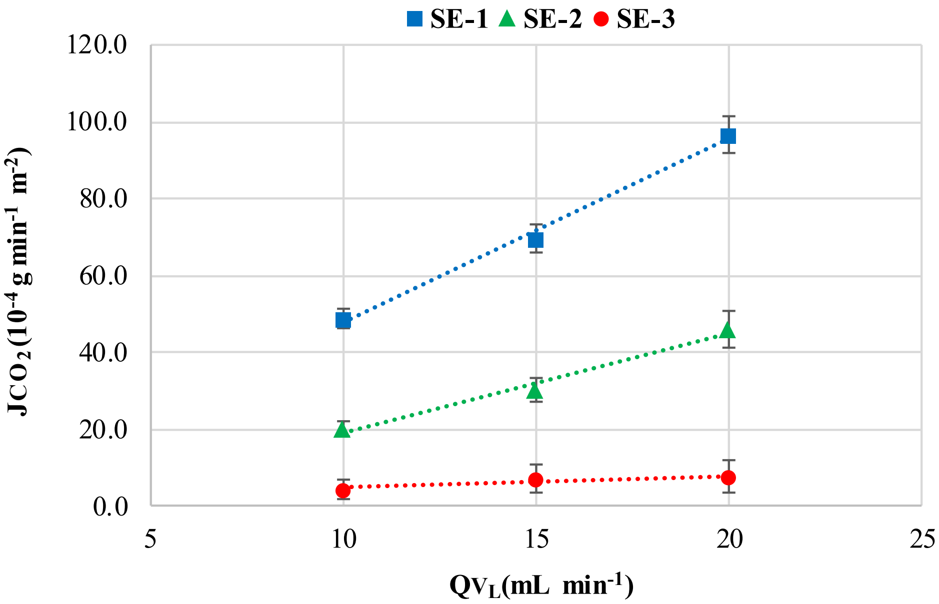


Figure 21
Desorption fluxes of carbon dioxide as a function of liquid flow rate (G/L ratio= 1)

The results show that CO_2 fluxes were much higher than those of CH_4 regardless of the synthetic effluent composition. This can be attributed to the fact that CO_2, being polar, is about 50–70 times more soluble in water than CH_4, allowing it to dissolve more readily [82], [120]. The desorption flux of each gas increased with the proportion of that gas in the binary mixtures used to create the synthetic effluents. Consequently, CH_4 flux increased in the order of SE-1 < SE-2 < SE-3, while CO_2 flux increased in the order of SE-3 < SE-2 < SE-1. However, the increase in CO_2 flux was more pronounced than that of CH_4.

The desorption process through dense membranes, such as the one used in these experiments, typically follows a solution-diffusion mechanism. The permeate flux is usually reduced by the thin selective dense layer due to its resistance to gas passage [91]. Nonetheless, higher liquid flow rates can intensify the desorption of gases. As shown in Figs. 20 and 21, the desorption fluxes of both CH_4 and CO_2 increased with rising liquid flow rates across all three synthetic effluents. This may be explained by the fact that the mass transfer resistance at the liquid boundary layer is important in the transport of gases with relatively small values of Henry's law constants in hollow fibre membrane contactors [57], [63], [90]. Similar findings have been reported by other researchers as well [82], [90], [108].

Table 12
Desorption fluxes of CH_4 as a function of liquid and sweep gas flow rates

QV_L (mL/min)	QV_G (mL/min)	G/L ratio	JCH_4 (g/(min m^2))		
			SE-1	**SE-2**	**SE-3**
10	10	1.0	$1.78\ 10^{-5}$	$1.01\ 10^{-4}$	$1.36\ 10^{-4}$
10	20	2.0	$2.62\ 10^{-6}$	$6.17\ 10^{-5}$	$9.98\ 10^{-5}$
20	10	0.5	$5.03\ 10^{-5}$	$1.88\ 10^{-4}$	$1.82\ 10^{-4}$
20	20	1.0	$2.76\ 10^{-5}$	$1.80\ 10^{-4}$	$2.22\ 10^{-4}$

Table 12 summarizes the effect of the sweep gas flow rate on the gas fluxes observed in this research. At a liquid flow rate of 10 mL/min, increasing the sweep gas flow rate from 10 to 20 mL/min significantly reduced the CH_4 flux. This reduction is attributed to the dilution effect of the sweep gas, which lowers the CH_4 concentration. However, this effect was less pronounced when the dissolved CH_4 concentration in the synthetic effluent was higher (SE-1 < SE-3). At a liquid flow rate of 20 mL/min, in the case of SE-1, the CH_4 flux was also decreased to a high extent when the gas flow rate was increased from 10 mL/min to 20 mL/min. However, in the case of SE-2 and SE-3, the flux was only slightly influenced. Since the G/L ratio was 0.5 in the second case due to the two times higher liquid flow rate, the mass transfer resistance was reduced and the dilution effect of the sweep gas had a lower influence on the CH_4 flux, especially at higher CH_4 concentrations (SE-2 and SE-3). These observations suggest that the G/L ratio is a critical parameter influencing CH_4 flux and should not be overlooked. Interestingly, Cookney et al. [89] investigated the effect of the sweep gas flow rate on the degassing efficiency of CH_4 in the anaerobically treated effluents, and no influence on the CH_4 flux was observed.

In addition to Cookney et al. [89], Henares et al. [52] also investigated the recovery of dissolved CH_4 from anaerobic effluent by using a PDMS membrane contactor to support the desorption of dissolved methane and using nitrogen as a sweep gas. Cookney et al. [89] concluded that the mass transfer of gaseous methane was not governed by the gaseous phase boundary layer but by the diffusivity within dense membrane material, therefore lower recovery efficiency was obtained by increasing the liquid flow rate and no effect of sweep gas flow rate was found. Due to the low partial pressure of CH_4 in the nitrogen sweep gas, vacuum was proposed to control the gas side as an alternative to the sweep gas [89]. In the latter work, PDMS was found to be more efficient, due to the fact that no pore wetting phenomenon and the consequent hindrance of gas transfer was observed [52]. In particular, Sethunga et al. [121] examined the use of dense membranes for recovering dissolved methane from anaerobic reactor effluents. They noted that porous membranes are susceptible to pore-clogging when treating anaerobic effluent. High mass transfer area and larger inner diameter were suggested to improve the efficiency of gas recovery.

3.2.3. Effect of gas and liquid flow rates on the recovery of dissolved CH_4 and CO_2

The recovery of dissolved CH_4 and CO_2 was calculated using Eq. (5). Fig. 22 shows the methane recovery as a function of liquid flow rate for the different synthetic effluents at a G/L ratio of 1. An increase in the liquid flow rate led to a decrease in CH_4 recovery for all synthetic effluents. Similar observations were made by Sethunga et al. [112]. This can be explained by the fact that membrane contactors may have a liquid flow rate limit, which reduces their effectiveness by deforming and compressing the membrane fibres [92]. The presence of CO_2 in the synthetic effluents also had an adverse impact on CH_4 recovery; however, the recovery improved by increasing the methane proportion in the binary gas mixtures used to prepare the synthetic effluents.

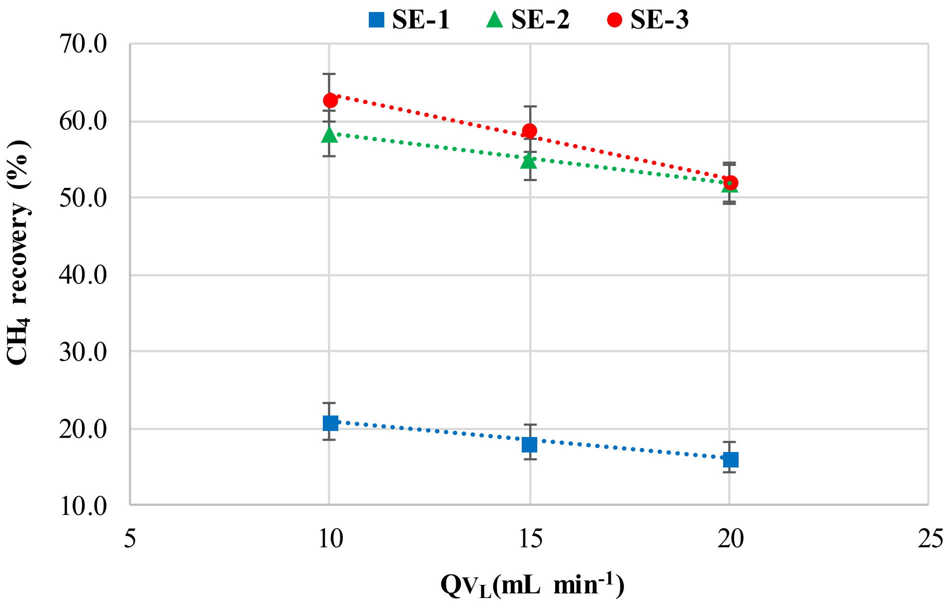
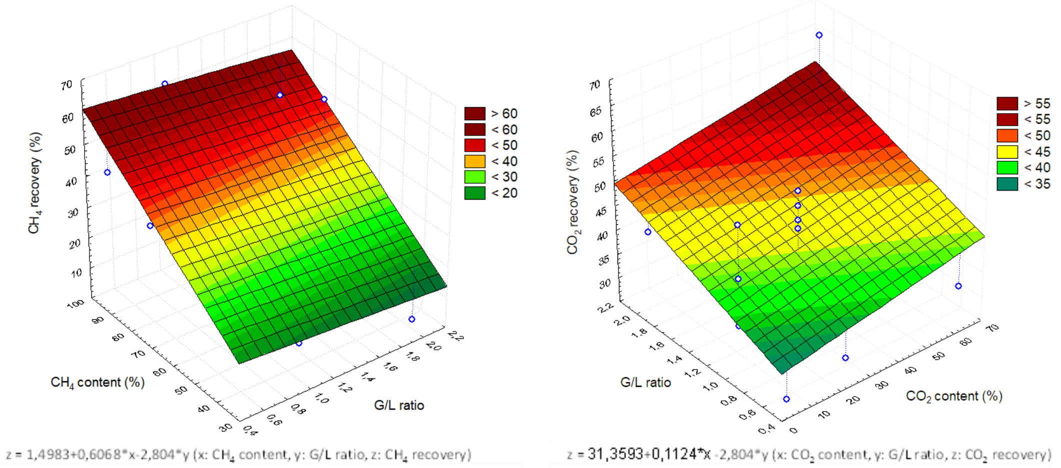


Figure 22
Methane recovery as a function of liquid flow rate (G/L ratio = 1)

A response surface, assuming linearity for simplicity, is illustrated in Fig. 23 to visualize the influence of binary gas mixture composition and the G/L ratio on the recovery of the respective components. The results indicate that a lower G/L ratio and higher CH_4 content in the binary gas mixtures used to prepare the synthetic effluents favour enhanced CH_4 recovery. Conversely, a higher G/L ratio and higher CO_2 content in the binary gas mixtures were advantageous for achieving higher CO_2 recovery.

In summary, the experimental outcomes suggest that increasing the liquid flow rate relative to the sweep gas flow rate (resulting in a lower G/L ratio) is more beneficial for CH_4 recovery, while the opposite is true for CO_2 recovery. These results align with the conclusions of the study by Sohaib et al. [108]. Regarding the impact of CH_4 and CO_2 contents in the synthetic effluents, higher inlet (dissolved) component concentrations can generate a higher partial driving force, positively contributing to the actual component flux and consequently enhancing the respective recovery values.

As for the time-stability of the membrane separation process, each experiment took 10–12 hours, and the overall study spanned approximately 2–3 months, considering repetitions and turnaround times. During this extended period, there was no observable loss of performance in the membrane module, indicating reliable and steady operation of the system.



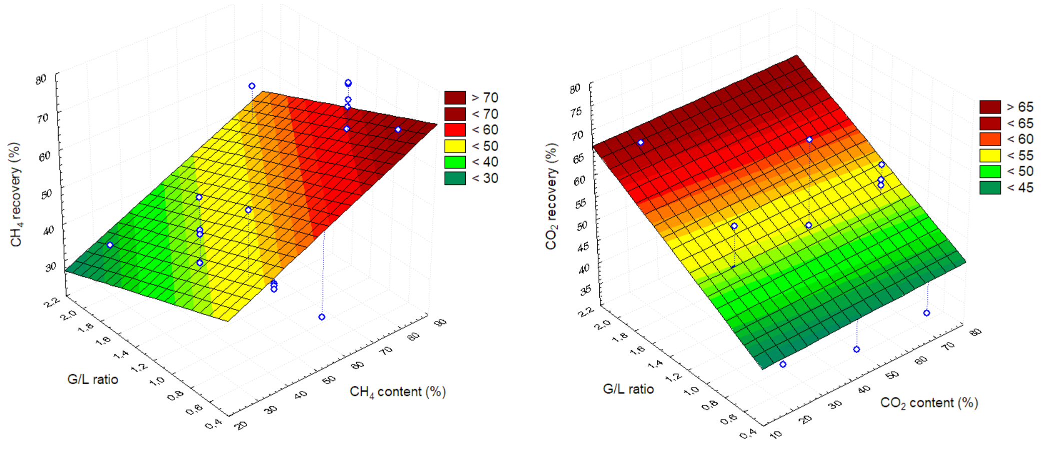
(a) (b)

Figure 23
Response surface for CH_4 (a) and CO_2 (b) recovery as a function of G/L ratio and the share of the respective component content in the binary gas mixtures ($A_{PDMS\ module} = 1\ m^2$).
The plain response surfaces were fitted in Statistica 8

3.2.4. Impact of membrane size on the recovery of dissolved CH_4 and CO_2

To verify whether the findings in Fig. 24 could be generalized and validated on a smaller-scale PDMS module with different effective surfaces, synthetic effluents (SE-1, SE-2, and SE-3) were pumped through a non-porous PDMS membrane module with a 2500 cm² surface area (Table 6).

Fig. 24 demonstrates the impact of the binary gas mixture composition and the G/L ratio on the recovery of the respective components. Based on the results from this smaller membrane, it was concluded that similar observations could be made regardless of the membrane module size, suggesting the findings are independent of the membrane size. Specifically, CH_4 recovery was enhanced by decreasing the G/L ratio and increasing the CH_4 content in the binary gas mixtures, while higher CO_2 content in the binary gas mixtures and applying a higher G/L ratio improved CO_2 recovery.



z = 42,1778+0,3721*x-10,1978*y (x: CH_4 content, y: G/L ratio, z: CH_4 recovery)

(a)

z = 37,3647+0,0245*x+13,071*y (x: CO_2 content, y: G/L ratio, z: CO_2 recovery)

(b)

Figure 24
Response surface for CH_4 (a) and CO_2 (b) recovery as a function of G/L ratio and the share of the respective component content in the binary gas mixtures ($A_{PDMS\ module}$= 2,500 cm^2).
The plain response surfaces were fitted in Statistica 8

3.3. Conversion of glycerol into biogas and the removal of CH_4 from prefiltered anaerobic effluent

The primary objective of the study was to assess the performance of the PDMS hollow fibre membrane module in recovering CH_4 dissolved in the anaerobic effluent generated after biogas production in the fed-batch bioreactor. Within this framework, the focus was on evaluating the long-term performance of biogas fermentation and the subsequent recovery of dissolved methane. To achieve this, the effluent was first prefiltered to remove larger particles and prevent immediate clogging, which could otherwise lead to module failure. Once prefiltered, recovery experiments for dissolved CH_4 were initiated using the PDMS hollow fibre membrane module, as highlighted earlier in Fig. 12. The forthcoming discussion will highlight the differences and challenges encountered in CH_4 recovery by comparing the data from this investigation, which utilized real effluent, with previous findings obtained using synthetic effluents but employing the identical membrane module. This comparison aims to elucidate the performance discrepancies between real and synthetic effluents, shedding light on the practical challenges and potential solutions for optimizing methane recovery from real-world anaerobic digestion processes. By examining the variations in methane recovery efficiency and identifying specific operational hurdles, the study seeks to provide a comprehensive understanding of the performance of membrane module in realistic conditions, ultimately contributing to the advancement of biogas production and recovery technologies.

3.3.1. The optimum glycerol load for enhanced methanogenic activity

During the preliminary experiments, pure glycerol was added to the bioreactor to achieve substrate loadings ranging from 6.7 to 33.3 g/L. Analysis of the fermentation broth revealed an imbalance in the metabolic activities of the microbial community. Specifically, the organic acids produced by fermentative acidogenic bacteria were not consumed by the acetogenic or methanogenic bacteria at the same rate as they were produced. This imbalance indicated that while the acidogenic bacteria efficiently converted glycerol into organic acids, the subsequent steps involving acetogenesis and methanogenesis were slower, leading to an accumulation of these intermediate organic acids. Such an accumulation can disrupt the pH balance of the system and potentially inhibit the overall anaerobic digestion process. To address this issue, further optimization of the substrate loading rate and the operational conditions may be necessary to enhance the activity and growth of the acetogenic and methanogenic bacteria, ensuring a more balanced and efficient biogas production process. As a result of that accumulation of organic acids resulted from an organic (substrate) overload, a significant drop in pH from 7.1 ± 0.1 to 5.8 ± 0.1 was observed. The dominant volatile fatty acids (VFAs) identified in the fermentation broth were caproic acid (C6) and valeric acid (C5). In addition to these, lower quantities of propionic acid (C3), butyric acid (C4), and acetic acid (C2) were also observed. Analysis results of the over-produced organic acids is listed in Table 13 (as indicated in Fig. 25, the day #5).

Table 13
The over-produced organic acids during fermentation (120 days)

Organic acids	Value, g/L
Acetic acid	0.6
Propionic acid	1.8
Butyric acid	1.7
Valeric acid	5.8
Caproic acid	11.1

Leng et al. [122] demonstrated that caproic acid production can be enhanced by enriching *Eubacterium limosum* with glycerol as a substrate, showing a synergistic effect with *Clostridium kluyveri*. The latter uses the metabolic products of acetic acid and ethanol for chain elongation, which helps explaining the relatively low acetic acid content observed in the system. Additionally, the acidification of the anaerobic digester increased hydrogen gas concentration, as the system favoured hydrogen production over methane production under these conditions [123]. This shift towards hydrogen production is due to the inhibitory effects of the accumulated organic acids on methanogenic activity. The production of VFAs, such as caproic acid and valeric acid, needs to be carefully controlled due to their significant inhibitory effects on methanogenic bacteria. The accumulation of these metabolites can lead to system malfunctioning [124]. Based on the results obtained from these preliminary experiments conducted over three weeks, it was evident that the system required intervention to address the pH imbalance caused by substrate overload. To mitigate this issue, one-third of the bioreactor content was drawn off and replaced with fresh anaerobic sludge. This fresh sludge helped offset the pH imbalance by leveraging the alkalinity present in the bulk inoculum. After the initial adjustment and acclimation period, the bioreactor operation was modified to ensure more stable conditions. The bioreactor was subsequently supplemented with 3.3 g/L of pure glycerol as a substrate loading at regular intervals of every 4–5 days. This controlled feeding strategy aimed to maintain a balanced microbial community and prevent the overproduction of VFAs, thereby stabilizing the anaerobic digestion process and enhancing methane production efficiency.

3.3.2. Cumulative biogas production analysis

Fig. 25 presents the biogas production rate (mL/h) and cumulative biogas volume over time, emphasizing the timing of substrate addition (SA). At the beginning of the study, low biogas production was observed, which was predicted due to the direct correlation between the rate of biogas production and the specific growth rate of methanogenic bacteria [125]. The inhibition of this growth was linked to the organic overload of the system, resulting in notable hydrogen production rather than methane in the initial 5 days. A similar investigation on anaerobic digestion performance by Abubakar and Ismail [126] reported slow initial biogas production primarily due to the lag phase of microbial growth.

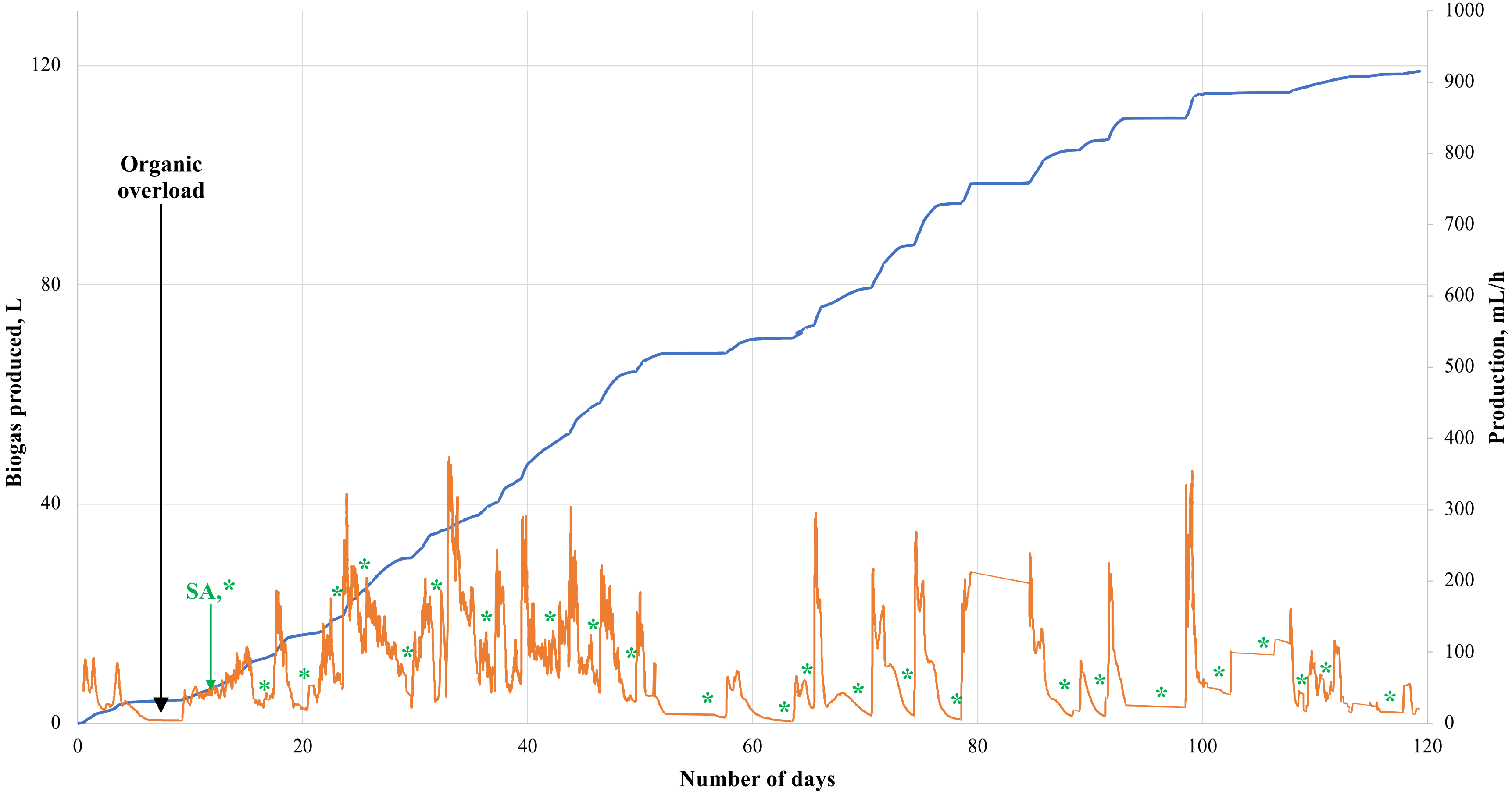


Figure 25

Production rate and cumulative volume of biogas over time, including the timing of substrate addition (SA), reactor volume: 2L

After completing the preliminary experiments, an optimal glycerol dose was established after 5-6 days of observation. This led to a substantial increase in biogas production as methanogens entered their exponential growth phase. The anaerobic digestion performance, shown in the cumulative biogas production in Figure 26, demonstrated that the bioreactor produced a total of 120 litres of biogas over 120 days, averaging 1 L/d as indicated earlier in Section 2.3.1.

During the experimental period, the pH stabilized between 6.5 and 7.5, with an average value of 7.1. Under stable conditions, the GC results of daily samples taken from the bioreactor headspace exhibited a gas composition of:

- 55-75% CH_4, 25-45% CO_2, and 0-0.2% H_2

The average cumulative biogas composition was:

- CH_4: 67.4 ± 10.3%, CO_2: 32.5 ± 10.3%, and H_2: 0.1 ± 0.1%

Theoretical methane production from the anaerobic digestion of glycerol is estimated to be 605 mL/d using the Buswell formula (Eq. 6) and the ideal gas law [127]:

$$C_3H_5(OH)_3 \rightarrow 1.75CH_4 + 1.25CO_2 + H_2O \tag{6}$$

Experimental results showed a methane production rate of 674 mL/d, which not only approached but exceeded the theoretical estimate by about 10%. This indicates complete digestion of glycerol, further promoting active biomass growth in the system. This suggests that glycerol was completely digested, further enhancing the growth of active biomass in the system. This observation aligns with previous work investigating the effect of glycerol on anaerobic digestion [45], highlighting the complete digestion of glycerol and significant enhancement in the growth of active biomass, facilitating methane production in the system.

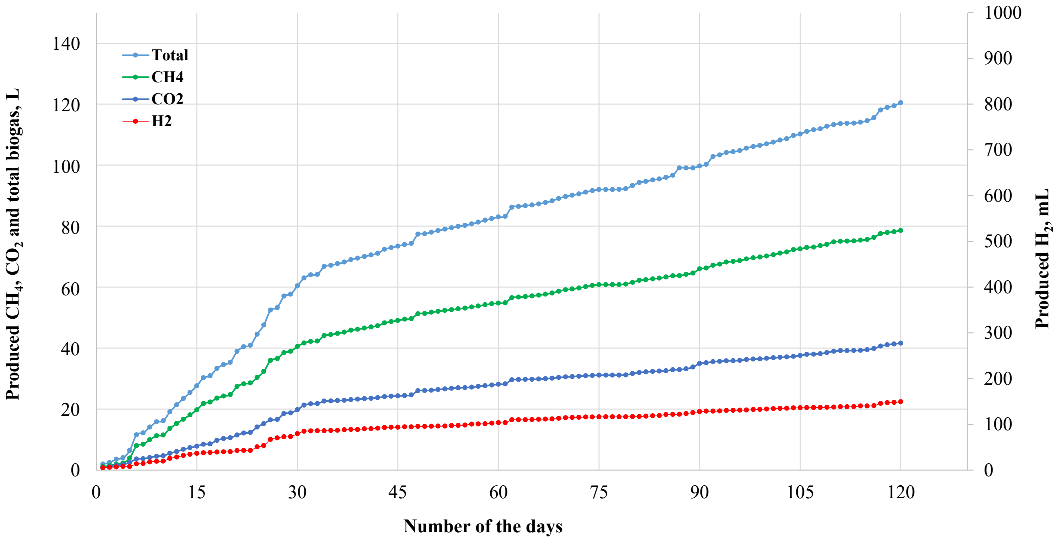


Figure 26
Cumulative biogas production during 120 days of operation

3.3.3. Recovery of dissolved CH_4 from filtered effluent by using PDMS hollow fibre membrane contactor

After 120 days of biogas production, the effluent obtained from the bioreactor was filtered using a 1 mm sieve to prevent potential membrane clogging due to suspended solids in the anaerobic effluent. The primary characteristics of the homogenized sludge after filtering were as follows:

- TS: 1.0% (w/w)
- VS: 0.67% (w/w)
- COD: 18.5 ± 1.5 gO_2/dm^3
- VS/TS Ratio: 67%, indicating high organic content

It's important to note that prefiltration removed a significant portion of the original active biomass, which had been responsible for the biogas production over the 120-day period. To reinforce biogas production in the recirculating membrane reactor, external "biogas" was introduced, using a binary mixture of methane and carbon dioxide in various compositions. Initially, a biogas mixture consisting of 70% CH_4 and 30% CO_2 vol.% was prepared to replicate the composition of the biogas produced during the anaerobic digestion process. The sweep gas and liquid flow rates were varied between 10 and 20 mL/min.

For a comprehensive analysis, additional biogas mixtures with different methane to carbon dioxide ratios (50/50 and 30/70 CH_4/CO_2 vol.%) were also prepared. Methane recovery experiments were conducted using a PDMS hollow fibre membrane contactor. This approach allowed for a detailed assessment of the biogas production and methane recovery processes, providing insights into optimizing biogas yields and improving the performance of the membrane contactor system under different operating conditions. The results of these experiments were then compared with previous research work to evaluate the efficiency and effectiveness of methane recovery under varying conditions [71].

Fig. 27 illustrates methane recovery as a function of the gas to liquid flow rate ratio for various methane/carbon dioxide mixtures supplied to the reactor system. The results indicate that the methane concentration in the biogas mixture had a small impact on methane recovery. However, an increase in the G/L ratio led to a slight decrease in CH_4 recovery. This suggests that a higher G/L ratio significantly influences CH_4 transport compared to the biogas composition. This phenomenon is attributed to the shorter residence time of the effluent within the membrane module at higher liquid flow rates. Shorter residence times reduce the contact time between the gas and liquid phases, thereby affecting the efficiency of methane transfer. This behaviour highlights the crucial role of mass transfer resistance at the liquid boundary layer in the transport of gases within hollow fibre membrane contactors. Although the permeate flux is diminished due to resistance to gas transfer, increasing the liquid flow rate helps to mitigate this resistance by enhancing mass transfer [63], [89], [91], [103]. These findings are consistent with previous studies by various researchers [69], [89], [106], [128], which also reported similar observations regarding the impact of G/L ratio and flow rates on gas transport in membrane contactors. Therefore, optimizing the G/L ratio and liquid flow rate is essential to improving methane recovery efficiency in membrane-based biogas upgrading systems.

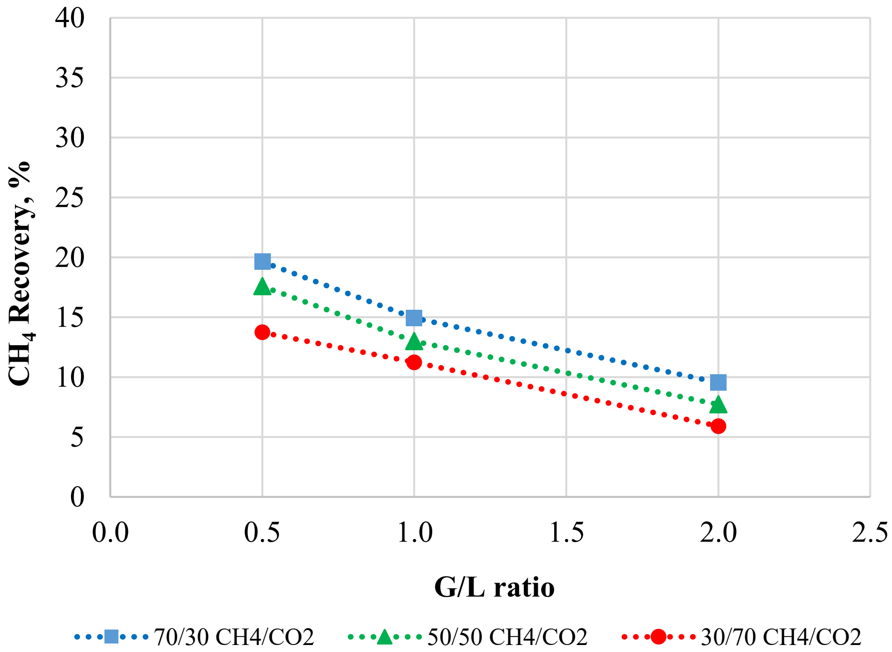


Figure 27
Methane recovery from different effluents as a function of gas to liquid flow ratio

The study also concluded that the higher CH_4 composition in the biogas mixture directly correlated with slightly increased CH_4 recovery percentages, as depicted in Fig. 27. Notably, this effect was found to be considerably more significant compared to findings from a previous study conducted under similar operational conditions, specifically focusing on synthetic effluent [71].

Fig. 28 provides a detailed comparative analysis of methane degassing experiments, incorporating both synthetic effluents from previous research [71] and real effluents examined in the current study. Despite the anticipation of potential differences between synthetic and real effluents, the results reveal no substantial increase in CH_4 recovery across the datasets.

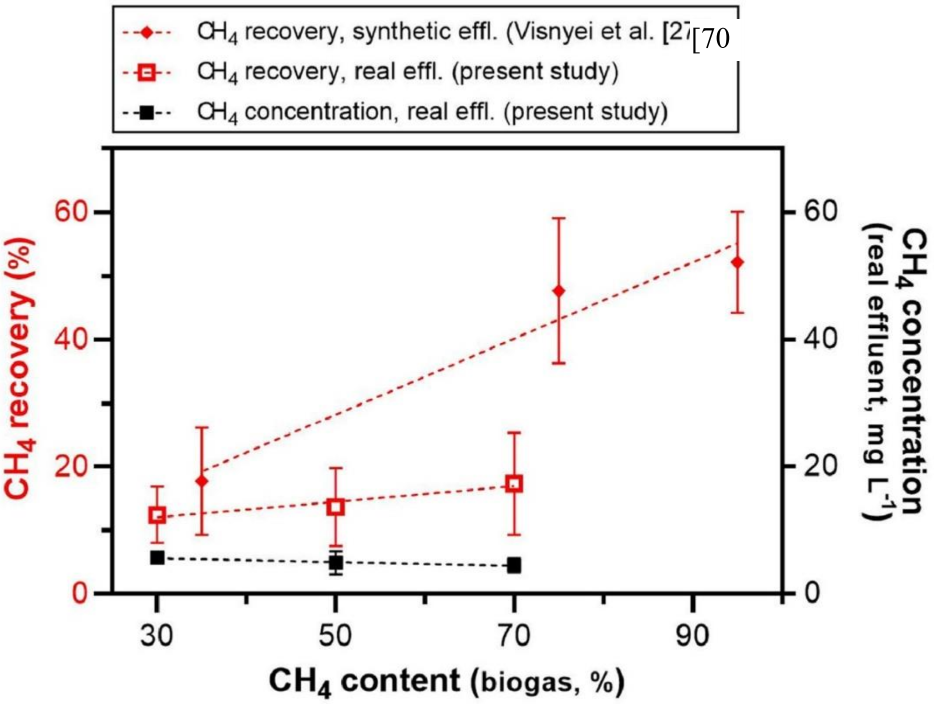


Figure 28
Comparative data on CH_4 recovery in real and synthetic effluents (G/L=1)

The findings indicate that, despite variations in CH_4 concentration within the biogas (30%, 50%, 70%), there was no significant increase in CH_4 recovery rates (12.4±4.4%, 13.6±6.1%, 17.3±8.0%) observed. However, the impact of CH_4 concentration on CH_4 recovery rates was notably more pronounced in the case of synthetic effluent (17.8±8.4%, 47.6±11.4%, 52.2±7.9%). Additionally, the study revealed that there were no substantial changes in the dissolved CH_4 concentration of the prefiltered effluent supplied to the membrane (5.7±0.8 mg/L, 4.9±1.8 mg/L, 4.5±1.1 mg/L) across different experimental settings (30%, 50%, 70%). This suggests that the driving force to enhance the dissolved CH_4 recovery remained relatively consistent between the shell and lumen side of the module.

The research findings, based on real effluent, indicate that regardless of the CH_4 content in the biogas mixture, there were no significant variations observed in either the recovery of CH_4 or the dissolved CH_4 concentration in the feed. The study demonstrates that, under all tested conditions, methane dissolution occurred notably faster than methane desorption through the PDMS membrane. Essentially, a constant concentration of dissolved methane was sustained in the feed stream of the membrane, specifically in the prefiltered effluent purged with various external binary methane/carbon dioxide mixtures at a flow rate of 1 L/day. As a result, the performance of the membrane module remained unaffected by this factor. Additionally, despite the continuous extraction of methane from the effluent through the membrane extraction process, it was observed to be slower compared to methane dissolution into the effluent. This slower extraction compensated for the recovery percentages of CH_4, which were measured as 12.4±4.4%, 13.6±6.1%, and 17.3±8.0% for increasing CH_4 concentrations in the real effluent at 30%, 50%, and 70%, respectively.

The 3D diagrams presented in Figure 29 depict the influence of the G/L ratio and CH_4 content in the biogas mixture on CH_4 recovery. These diagrams showcase response surfaces for both synthetic effluents from previous research [71] and real effluents from the current study, assuming a linear relationship between the independent and dependent variables.

From the visualised tendencies in Fig. 29a-b, it is to conclude in both cases that operating the membrane process under lower G/L ratios in a fermenter where there is a higher concentration (partial pressure) of CH_4 in the biogas (meaning concurrently a higher dissolved methane concentration in the fermentation liquor too as long as the Henry's law is followed) could lead to improved CH_4 recovery efficiency from the effluent.

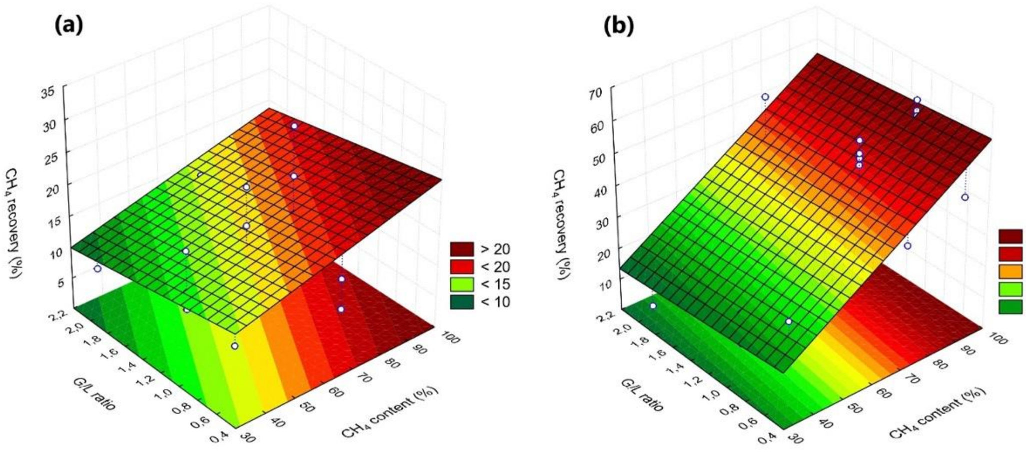


Figure 29
Response surface for CH_4 recovery as a function of G/L ratio and share of CH_4 content in the gas mixtures produced from real anaerobic effluent (a) and previously done synthetic effluent (b) ($A_{PDMS\ module}$= 1 m^2). The Fig. 29b was taken from our previous paper [71]**.**
White dots: Experimental data.
The plain response surfaces were fitted in Statistica 8

It is important to clarify that a linear relationship was assumed because Henry's Law indicates that increasing the concentration of a gas component in biogas leads to a proportional increase in its dissolved concentration when partial pressure is raised (as explained in Section 2.1.4). This assumption was supported by results with pure gases, where the effect of liquid flow rate on component fluxes was observed to follow a linear trend in all synthetic gas mixtures (Figs. 20 and 21). Even in a synthetic effluent, a nearly linear pattern was exhibited by CH_4 and CO_2. Based on these observations, the application of linear response surface fitting was justified, as the results aligned with both theoretical expectations and experimental data from initial tests.

The methane recovery data obtained with the synthetic effluent notably exceeded that of the real effluent (Fig. 29b compared to Fig. 29a). I attribute this difference to various factors related to the effluent, such as its complexity or compositional differences between synthetic and real effluents. Additionally, factors related to the flow regime and feeding conditions in the membrane module, such as lumen-to-shell operation (as in the case of synthetic effluent in Visnyei et al. [71], reflecting our previous work) versus shell-to-lumen operation (as in the case of the real effluent in the present study, aimed at preventing internal clogging of the capillaries), may have contributed to this variation.

This observation, wherein higher methane recovery was achievable with synthetic effluent compared to real effluent, aligns with findings from previous studies conducted by other researchers [71], [90], [128]. Towards the end of the gas recovery experiments (spanning 12 days in total), we also noted the emergence of membrane fouling as a noteworthy phenomenon, despite prefiltering the sludge. Thus, addressing membrane fouling poses a significant challenge that warrants attention, and the development of an appropriate cleaning strategy for the module should be considered in future studies to restore its efficiency.

4. Summary

The process of converting organic waste into well-stabilized sludge through anaerobic digestion of wastewater is a widely used technique for producing biogas. The major objective of this study was to improve the efficiency of separating dissolved gases, specifically CH_4 and CO_2, from the fermentation liquor in anaerobic digestion process using GLMCs. This study was divided into three experimental series, each of which focused on one particular aspect of the recovery process utilizing synthetic and real effluent.

The first experimental series focused on the removal of dissolved gases from model solutions. The investigation showed that using a PDMS non-porous hollow fibre membrane contactor was effective in recovering CH_4 and CO_2 from model solutions. The results showed that in a 50:50 CH_4/CO_2 mixture, the nearly stable recovery of CH_4 dropped significantly to 11.9% at 60 mL/min. At this higher flow rate, experiment with pure CH_4 recovery was 35.9%, indicating a potential negative impact of CO_2 presence on CH_4 recovery. Another result was that these findings highlighted the potential of GLMCs in improving gas recovery, resulting in enhanced anaerobic energy production and lower greenhouse gas emissions.

Through the use of PDMS hollow-fibre membrane contactors, second experimental series progressed the study by examining the simultaneous removal of CH_4 and CO_2 from synthetic effluents. An increase in the liquid flow rate (10, 15, 20 mL/min) decreased the CH_4 recovery for all synthetic effluents (20.9, 18.2, 16.2%; 58.3, 55.0, 51.8%; 63.0, 58.9, 52.1% for the synthetic effluents of 35:65 CH_4/CO_2; 75:25 CH_4/CO_2 ; 95:5 CH_4/CO_2). The study examined the dynamics between CH_4 and CO_2 recovery, indicating that a higher liquid flow rate facilitated CH_4 transport whereas a higher gas flow rate favoured CO_2 transport. Furthermore, it was discovered that CO_2 had a detrimental effect on CH_4 recovery. These understandings are essential for maximizing the removal of gases by membrane contactors simultaneously, addressing issues related to energy recovery and environmental issues.

The objective of third experimental series was to successfully bridge the gap between laboratory and real-life applications by centering on the long-term recovery of biogas from real anaerobic effluents. As a first step of this experimental series; the fed-batch anaerobic bioreactor was built up with a 2L volume using sludge from anaerobic digester treating secondary sludge from a municipal wastewater treatment plant and operated for 120 days. This time period resulted with a total of 120 litres of biogas produced. The pure glycerol with an amount of 3.3 g/L was supplemented as a substrate loading to the bioreactor at regular intervals of every 4–5 days. An in-line dissolved methane sensor and a PDMS hollow-fibre membrane contactor were used in the study to carefully analyse the effects of different operating factors on methane recovery. The outcomes showed that real and synthetic effluents had significantly different gas recovery efficiency, with real effluents presenting different challenges like fouling. This stage focused on the necessity of practical and sustainable techniques for treating anaerobic wastewater, emphasizing the significance of overcoming operational issues to enable broader utilization of this technology. The results indicated that the methane concentration in the biogas mixture had a small impact on methane recovery. However, an increase in the G/L ratio led to a slight decrease in CH_4 recovery. The study also concluded that the higher CH_4 composition in the biogas mixture directly correlated with slightly increased CH_4 recovery percentages.

All considered, this study shows that adding GLMCs to anaerobic membrane bioreactor systems is a viable way to improve wastewater dissolved gas recovery. The series of experiments that were carried out delivers valuable data that advances sustainable wastewater treatment techniques. However, further study is needed to address issues with cost, technological readiness, and legislation before this technology can be widely adopted.

5. Thesis Statements

I. I have demonstrated that the recovery percentages of CH_4 from model solutions using a non-porous PDMS hollow fibre membrane contactor was influenced by significant presence of CO_2 in the mixture (50:50 CH_4/CO_2%) and the sweep gas flow rate.

a. In the case of model solution consisting pure CH_4; CH_4 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 CH_4/CO_2%), the recovery percentages of CH_4 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.

b. CH_4 recovery was negatively affected by CO_2 presence in the model solutions.

c. CO_2 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 CO_2 vol.%) and model solution-3 (50:50 CH_4/CO_2%).

d. Applying a sweep gas flow rate of 20 mL/min, the recovery rate of both gases from model solution-3 (50:50 CH_4/CO_2%) exceeded 50%.

Related publication:

M. Visnyei, P. Bakonyi, N. Nemestóthy, and K. Bélafi-Bakó, “Separation of Dissolved Gases from Aqueous Anaerobic Effluents Using Gas-Liquid Membrane Contactors,” Hungarian J. Ind. Chem., vol. 50, no. 2, pp. 23–26, 2022.

II. I have proven that gas transport and recovery percentages of dissolved gases in synthetic effluents (CH_4/CO_2) 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 CH_4 transport, while a higher sweep gas flow rate is preferable for the CO_2 transport over CH_4.

a. As it is aligning with the previous Thesis Statement I., a negative impact of CO_2 on the CH_4 recovery was observed once again. However, I have shown that this effect can be mitigated by increasing the CH_4 concentration in the gas mixture.

b. Depending on the actual biogas composition and the CO_2 content of the effluent (associated with the actual composition of biogas), the CH_4 recovery could be improved up to 63 % under steady-state conditions.

c. Experiments with 1.0 m^2 and 2500 cm^2 demonstrated an independency of the membrane size on the recovery percentages of CH_4 and CO_2, indicating that similar observations could be made regardless of the membrane module surface area.

Related publication:

M. Visnyei, P. Bakonyi, K. Bélafi-Bakó, and N. Nemestóthy, "Integration of gas–liquid membrane contactors into anaerobic digestion as a promising route to reduce uncontrolled greenhouse gas (CH_4/CO_2) emissions," Bioresour. Technol., vol. 364, p. 128072, Nov. 2022.

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.

a. Digestion of glycerol significantly enhanced biomass activity, achieving stability with a pH of 7.1. Moreover, the averaged cumulative biogas composition was CH_4: 67.4 ± 10.3 %; CO_2: 32.5 ± 10.3 %; H_2: 0.1 ± 0.1 %.

b. 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.

c. After 120 days, 120 litres of biogas were produced, averaging 1 L/day.

Related publication:

M. Visnyei, P. Bakonyi, T. Rózsenberszki, L. Koók, P. Komáromy, K. Bélafi-Bakó, N. Nemestóthy, "Mitigated CH_4 release of anaerobic waste fermentation is enabled through effluent degassing system equipped with a polydimethylsiloxane membrane contactor" Chem. Eng. J. Adv, Vol. 18, 100607, May, 2024.

IV. I have demonstrated the recovery of dissolved CH_4 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% CH_4/CO_2). The ratio of sweep gas (N_2) to effluent flow rates (G/L) impacted the degassing efficiency.

a. The higher G/L ratio had a greater impact on CH_4 transport compared to the composition, while higher CH_4 composition in the biogas mixture corresponded to the slightly higher CH_4 recovery percentages. This effect was higher in synthetic effluent experiments carried out in similar operating conditions.
b. The CH_4 recovery as 12.4 ± 4.4%, 13.6 ± 6.1%, 17.3 ± 8.0% was observed as the CH_4 concentration increased in the biogas (30, 50 and 70 vol%), while the dissolved CH_4 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.
c. No significant changes in CH_4 recovery or dissolved CH_4 concentration in the feed were observed, regardless of CH_4 content of the biogas.
d. 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 CH_4 content in the gas mixtures are favourable to enhance the CH_4 recovery.

Related publication:

M. Visnyei, P. Bakonyi, T. Rózsenberszki, L. Koók, P. Komáromy, K. Bélafi-Bakó, N. Nemestóthy, “Mitigated CH_4 release of anaerobic waste fermentation is enabled through effluent degassing system equipped with a polydimethylsiloxane membrane contactor” Chem. Eng. J. Adv, Vol. 18, 100607, May, 2024.

References

[1] M. Qadir, D. Wichelns, L. Raschid-Sally, P. G. Mccornick, and P. Drechsel, “The Challanges of Wastewater Irrigation in Developing Countries,” *Agric. Water Manag.*, vol. 97, pp. 561–568, Dec. 2010, doi: 10.1016/j.agwat.2008.11.004.

[2] M. Qadir, P. Drechsel, B. Jiménez Cisneros, Y. Kim, A. Pramanik, P. Mehta, and O. Olaniyan, “Global and regional potential of wastewater as a water, nutrient and energy source,” 2020, doi: 10.1111/1477-8947.12187.

[3] J. Hughes, K. Cowper-Heays, E. Olesson, R. Bell, and A. Stroombergen, “Impacts and implications of climate change on wastewater systems: A New Zealand perspective,” *Clim. Risk Manag.*, vol. 31, p. 100262, Jan. 2021, doi: 10.1016/J.CRM.2020.100262.

[4] M. J. Kacprzak and I. Kupich, “The specificities of the circular economy (CE) in the municipal wastewater and sewage sludge sector—local circumstances in Poland,” *Clean Technol. Environ. Policy*, vol. 25, no. 2, pp. 519–535, Aug. 2021, doi: 10.1007/S10098-021-02178-W/FIGURES/6.

[5] J. A. Silva, “Wastewater Treatment and Reuse for Sustainable Water Resources Management: A Systematic Literature Review,” *Sustain.*, vol. 15, no. 14, p. 10940, Jul. 2023, doi: 10.3390/SU151410940/S1.

[6] M. H. Isa, L. P. Wong, and N. M. Mubarak, “Editorial: Advances in removal of toxic substances from wastewater,” *Front. Environ. Sci.*, vol. 11, p. 1165882, Mar. 2023, doi: 10.3389/FENVS.2023.1165882/BIBTEX.

[7] P. Shumbula, C. Maswanganyi, N. Shumbula, P. Shumbula, C. Maswanganyi, and N. Shumbula, “Type, Sources, Methods and Treatment of Organic Pollutants in Wastewater,” Dec. 2021, doi: 10.5772/INTECHOPEN.101347.

[8] L. Lu, J. S. Guest, C. A. Peters, X. Zhu, G. H. Rau, and Z. J. Ren, “Wastewater treatment for carbon capture and utilization,” *Nat. Sustain. 2018 112*, vol. 1, no. 12, pp. 750–758, Dec. 2018, doi: 10.1038/s41893-018-0187-9.

[9] UNESCO, “The United Nations World Water Development Report 2022: groundwater: making the invisible visible; executive summary,” 2022.

[10] E. Aparicio, R. M. Rodríguez-Jasso, A. Lara, A. Loredo-Treviño, C.N. Aguilar, E.T. Kostas, and H.A. Ruiz, “Biofuels production of third generation biorefinery from macroalgal biomass in the Mexican context: An overview,” *Sustain. Seaweed Technol. Cultiv. Biorefinery, Appl.*, pp. 393–446, Jan. 2020, doi: 10.1016/B978-0-12-817943-7.00015-9.

[11] A. Sikora, A. Detman, A. Chojnacka, and M.K. Błaszczyk, “Anaerobic Digestion: I. A Common Process Ensuring Energy Flow and the Circulation of Matter in Ecosystems. II. A Tool for the Production of Gaseous Biofuels,” *Ferment. Process.*, Feb. 2017, doi: 10.5772/64645.

[12] C. E. Manyi-Loh and R. Lues, “Anaerobic Digestion of Lignocellulosic Biomass: Substrate Characteristics (Challenge) and Innovation,” *Ferment.*

2023, Vol. 9, Page 755, vol. 9, no. 8, p. 755, Aug. 2023, doi: 10.3390/FERMENTATION9080755.

[13] R. Banu J, S. Sugitha, S. Kavitha, Y. Kannah R, J. Merrylin, and G. Kumar, “Lignocellulosic Biomass Pretreatment for Enhanced Bioenergy Recovery: Effect of Lignocelluloses Recalcitrance and Enhancement Strategies,” *Front. Energy Res.*, vol. 9, p. 646057, Nov. 2021, doi: 10.3389/FENRG.2021.646057/BIBTEX.

[14] G. Zur Nutzung, “Leitfaden Biogas - Von der Gewinnung zur Nutzung,” 2016, Accessed: Apr. 13, 2023. [Online]. Available: www.dbfz.de

[15] Z. Van Lier, Jules B.; Nidal, Mahmoud.;Grietje, *Anaerobic wastewater treatment*. IWA Publishing, 2020. doi: 10.2166/9781789060362_0701.

[16] Y. Özoguz, “Efficient management of wastewater, its treatment and reuse in the mediterranean countries,” 2009.

[17] J. Ma, C. Frear, Z.W. Wang, L. Yu, Q. Zhao, X. Li, and S, Chen, “A simple methodology for rate-limiting step determination for anaerobic digestion of complex substrates and effect of microbial community ratio,” *Bioresour. Technol.*, vol. 134, pp. 391–395, Apr. 2013, doi: 10.1016/J.BIORTECH.2013.02.014.

[18] M. Ramos-Suarez, Y. Zhang, and V. Outram, “Current perspectives on acidogenic fermentation to produce volatile fatty acids from waste,” *Rev. Environ. Sci. Bio/Technology 2021 202*, vol. 20, no. 2, pp. 439–478, Feb. 2021, doi: 10.1007/S11157-021-09566-0.

[19] C. . Vasmara, S. Galletti, S. . Cianchetta, and E. . Ceotto, “Advancements in Giant Reed (Arundo donax L.) Biomass Pre-Treatments for Biogas Production: A Review.,” *Energies*, vol. 16, no. 949, 2023, Accessed: Feb. 27, 2023. [Online]. Available: https://www.researchgate.net/profile/Ciro-Vasmara/publication/367168254_Advancements_in_Giant_Reed_Arundo_donax_L_Biomass_Pre-Treatments_for_Biogas_Production_A_Review/links/63c530ca6fe15d6a5724daa3/Advancements-in-Giant-Reed-Arundo-donax-L-Biomass-Pre-Treatments-for-Biogas-Production-A-Review.pdf

[20] P. Wang, H. Wang, Y. Qiu, L. Ren, and B. Jiang, “Microbial characteristics in anaerobic digestion process of food waste for methane production–A review,” *Bioresour. Technol.*, vol. 248, pp. 29–36, Jan. 2018, doi: 10.1016/J.BIORTECH.2017.06.152.

[21] S. Agnihotri, D.M. Yin, A. Mahboubi, T. Sapmaz, S. Varjani, W. Qiao, D.Y. Koseoglu-Imer, and M.J. Taherzadeh, “A Glimpse of the World of Volatile Fatty Acids Production and Application: A review,” *Bioengineered*, vol. 13, no. 1, p. 1249, 2022, doi: 10.1080/21655979.2021.1996044.

[22] J. E. Hernandez and R. G. J. Edyvean, “Inhibition of biogas production and biodegradability by substituted phenolic compounds in anaerobic sludge,” *J. Hazard. Mater.*, vol. 160, no. 1, pp. 20–28, Dec. 2008, doi:

10.1016/J.JHAZMAT.2008.02.075.

[23] T. Lienen, A. Kleyböcker, M. Brehmer, M. Kraume, L. Moeller, K. Görsch, and H. Würdemann, "Floating layer formation, foaming, and microbial community structure change in full-scale biogas plant due to disruption of mixing and substrate overloading," *Energy, Sustain. Soc. 2013 31*, vol. 3, no. 1, pp. 1–14, Oct. 2013, doi: 10.1186/2192-0567-3-20.

[24] X. Goux, M. Calusinska, S. Lemaigre, M. Marynowska, M. Klocke, T. Udelhoven, E. Benizri, and P. Delfosse, "Microbial community dynamics in replicate anaerobic digesters exposed sequentially to increasing organic loading rate, acidosis, and process recovery," *Biotechnol. Biofuels*, vol. 8, no. 1, pp. 1–18, Aug. 2015, doi: 10.1186/S13068-015-0309-9/TABLES/1.

[25] J. Sun, L. Zhang, and K. C. Loh, "Review and perspectives of enhanced volatile fatty acids production from acidogenic fermentation of lignocellulosic biomass wastes," *Bioresour. Bioprocess. 2021 81*, vol. 8, no. 1, pp. 1–21, Aug. 2021, doi: 10.1186/S40643-021-00420-3.

[26] B. E. L. Morris, R. Henneberger, H. Huber, and C. Moissl-Eichinger, "Microbial syntrophy: interaction for the common good," *FEMS Microbiol. Rev.*, vol. 37, no. 3, pp. 384–406, May 2013, doi: 10.1111/1574-6976.12019.

[27] Y. Song, W. Qiao, M. Westerholm, G. Huang, M. J. Taherzadeh, and R. Dong, "Microbiological and Technological Insights on Anaerobic Digestion of Animal Manure: A Review," *Ferment. 2023, Vol. 9, Page 436*, vol. 9, no. 5, p. 436, May 2023, doi: 10.3390/FERMENTATION9050436.

[28] T. Kong and W. Zhang, "Enhanced Anaerobic Digestion Using Conductive Materials through Mediation of Direct Microbial Interspecies Electron Transfer: A Review," *Ferment. 2023, Vol. 9, Page 884*, vol. 9, no. 10, p. 884, Sep. 2023, doi: 10.3390/FERMENTATION9100884.

[29] D. Deublein and A. Steinhauser, "Biogas from Waste and Renewable Resources: An Introduction, Second Edition," *Biogas from Waste and Renewable Resources: An Introduction, Second Edition*, 2010. https://books.google.pl/books?hl=en&lr=&id=CJiMmmxu2tcC&oi=fnd&pg=PT13&dq=Deublein,+D.+et+al.+2008&ots=ImoAhSgWOi&sig=4bPugBIzdO4vLcn25qgQy0aoeZ8&redir_esc=y#v=onepage&q=symbiosis&f=false (accessed Feb. 27, 2023).

[30] D. Feng, A. Xia, Y. Huang, X. Zhu, X. Zhu, and Q. Liao, "Effects of carbon cloth on anaerobic digestion of high concentration organic wastewater under various mixing conditions," *J. Hazard. Mater.*, vol. 423, p. 127100, Feb. 2022, doi: 10.1016/J.JHAZMAT.2021.127100.

[31] H. Imachi, S. Sakai, A. Ohashi, H. Harada, S. Hanada, Y. Kamagata, and Y. Sekiguchi, "Pelotomaculum propionicicum sp. nov., an anaerobic, mesophilic, obligately syntrophic, propionate-oxidizing bacterium", doi: 10.1099/ijs.0.64925-0.

[32] D. Z. Sousa, H. Smidt, M. M. Alves, A. J. M. Stams, and C. M. M. Alves, “Syntrophomonas zehnderi sp. nov., an anaerobe that degrades long-chain fatty acids in co-culture with Methanobacterium formicicum”, doi: 10.1099/ijs.0.64734-0.

[33] S. Harirchi, S. Wainaina, T. Sar, S.A. Nojoumi, M. Parchami,S. Varjani, S.K. Khanal, J. Wong, M.K. Awasthi, and M.J. Taherzadeh, “Microbiological insights into anaerobic digestion for biogas, hydrogen or volatile fatty acids (VFAs): a review,” 2022, doi: 10.1080/21655979.2022.2035986.

[34] R. Conrad, M. Klose, P. Claus, and A. Enrich-Prast, “Methanogenic pathway, 13C isotope fractionation, and archaeal community composition in the sediment of two clear-water lakes of Amazonia.,” *Limnol. Oceanogr.*, vol. 55, no. 2, pp. 689–702, 2010.

[35] T. Fenchel, G. M. King, and T. H. Blackburn, “Bacterial Metabolism,” in *Bacterial Biogeochemistry*, Academic Press, 2012, p. 19. doi: 10.1016/B978-0-12-415836-8.00001-3.

[36] Y. Zhang, S. Kusch-Brandt, A. M. Salter, and S. Heaven, “Estimating the Methane Potential of Energy Crops: An Overview on Types of Data Sources and Their Limitations,” *Process. 2021, Vol. 9, Page 1565*, vol. 9, no. 9, p. 1565, Sep. 2021, doi: 10.3390/PR9091565.

[37] J. Liu and S. R. Smith, “The link between organic matter composition and the biogas yield of full-scale sewage sludge anaerobic digestion,” *Water Sci. Technol.*, vol. 85, no. 5, pp. 1658–1672, Mar. 2022, doi: 10.2166/WST.2022.058.

[38] “Fact Sheet: Multi-Stage Anaerobic Digestion | US EPA.” https://www.epa.gov/biosolids/fact-sheet-multi-stage-anaerobic-digestion (accessed Jun. 11, 2024).

[39] M. H. Romdhana, A. Hamasaiid, B. Ladevie, and D. Lecomte, “Energy valorization of industrial biomass: Using a batch frying process for sewage sludge,” *Bioresour. Technol.*, vol. 100, no. 15, pp. 3740–3744, Aug. 2009, doi: 10.1016/J.BIORTECH.2009.01.043.

[40] H. B. Goyal, D. Seal, and R. C. Saxena, “Bio-fuels from thermochemical conversion of renewable resources: A review,” *Renew. Sustain. Energy Rev.*, vol. 12, no. 2, pp. 504–517, Feb. 2008, doi: 10.1016/J.RSER.2006.07.014.

[41] Y. Cao and A. Pawłowski, “Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: Brief overview and energy efficiency assessment,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 3, pp. 1657–1665, Apr. 2012, doi: 10.1016/J.RSER.2011.12.014.

[42] Y. J. Suh and P. Rousseaux, “An LCA of alternative wastewater sludge treatment scenarios,” *Resour. Conserv. Recycl.*, vol. 35, no. 3, pp. 191–200, 2002, doi: 10.1016/S0921-3449(01)00120-3.

[43] A. Karlsson, A. Björn, S. Yekta, and B. H. Svensson, “IMPROVEMENT OF THE BIOGAS PRODUCTION PROCESS Explorative project (EP1),”

Sweeden, 2014. Accessed: Apr. 13, 2023. [Online]. Available: www.liu.se/brc

[44] J. Smyk and K. Ignatowicz, "The influence of glycerin on nitrogen removal in wastewater treatment with activated sludge," *E3S Web Conf.*, vol. 22, Nov. 2017, doi: 10.1051/E3SCONF/20172200161.

[45] M. S. Fountoulakis, I. Petousi, and T. Manios, "Co-digestion of sewage sludge with glycerol to boost biogas production," *Waste Manag.*, vol. 30, no. 10, pp. 1849–1853, Oct. 2010, doi: 10.1016/j.wasman.2010.04.011.

[46] C. Shi, X. Yan, F. Guo, and R. Peng, "Comparison of the mesophilic and thermophilic anaerobic sludge digestion from an energy perspective," *J. Residuals Sci. Technol. vol. 18, núm. 2*, vol. 14, no. 3, pp. 81–87, 2011, Accessed: Apr. 13, 2023. [Online]. Available: https://upcommons.upc.edu/handle/2117/116990

[47] I. Ferrer, F. Vázquez, and X. Font, "Comparison of the Mesophilic and Thermophilic Anaerobic Sludge Digestion from an Energy Perspective," 2011.

[48] V. Gupta and R. Goel, "Managing dissolved methane gas in anaerobic effluents using microbial resource management-based strategies," *Bioresour. Technol.*, vol. 289, p. 121601, Oct. 2019, doi: 10.1016/J.BIORTECH.2019.121601.

[49] A. Lawson and F. M. Ahmad, "OVERVIEW CLIMATE INNOVATION," 2018, Accessed: Apr. 13, 2023. [Online]. Available: https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2015.

[50] P. Velasco, V. Jegatheesan, and M. Othman, "Recovery of dissolved methane from anaerobic membrane bioreactor using degassing membrane contactors," *Front. Environ. Sci.*, vol. 6, no. DEC, Dec. 2018, doi: 10.3389/FENVS.2018.00151.

[51] P. Velasco, V. Jegatheesan, K. Thangavadivel, M. Othman, and Y. Zhang, "A focused review on membrane contactors for the recovery of dissolved methane from anaerobic membrane bioreactor (AnMBR) effluents," *Chemosphere*, vol. 278, Sep. 2021, doi: 10.1016/j.chemosphere.2021.130448.

[52] M. Henares, M. Izquierdo, J. M. Penya-Roja, and V. Martínez-Soria, "Comparative study of degassing membrane modules for the removal of methane from Expanded Granular Sludge Bed anaerobic reactor effluent," *Sep. Purif. Technol.*, vol. 170, pp. 22–29, Oct. 2016, doi: 10.1016/J.SEPPUR.2016.06.024.

[53] M. R. Morgan, *Climate change 2001*, vol. 59, no. 8. 2004. doi: 10.1256/wea.58.04.

[54] S. Kotelnikova, "Microbial production and oxidation of methane in deep subsurface," *Earth-Science Rev.*, vol. 58, no. 3–4, pp. 367–395, Oct. 2002, doi: 10.1016/S0012-8252(01)00082-4.

[55] E. L. Iannotti, J. R. Fischer, and D. M. Sievers, "Characterization of Bacteria from a Swine Manure Digester," *Appl. Environ. Microbiol.*, vol. 43, no. 1, pp. 136–143, Jan. 1982, doi: 10.1128/AEM.43.1.136-143.1982.

[56] M. M. Noor, A. P. Wandel, and T. Yusaf, “Design and Development of MILD Combustion Burner,” *J. Mech. Eng. Sci.*, vol. 5, pp. 662–676, Dec. 2013, doi: 10.15282/JMES.5.2013.13.0064.

[57] B. C. Crone, J. L. Garland, G. A. Sorial, and L. M. Vane, “Significance of dissolved methane in effluents of anaerobically treated low strength wastewater and potential for recovery as an energy product: A review,” *Water Research*, vol. 104. Elsevier Ltd, pp. 520–531, Nov. 01, 2016. doi: 10.1016/j.watres.2016.08.019.

[58] Z. H. Liu, H. Yin, Z. Dang, and Y. Liu, “Dissolved methane: A hurdle for anaerobic treatment of municipal wastewater,” *Environ. Sci. Technol.*, vol. 48, no. 2, pp. 889–890, 2014, doi: 10.1021/es405553j.

[59] S. Kundu, J. Zanganeh, and B. Moghtaderi, “A review on understanding explosions from methane-air mixture,” *J. Loss Prev. Process Ind.*, vol. 40, pp. 507–523, Mar. 2016, doi: 10.1016/J.JLP.2016.02.004.

[60] L. Huang, Y. Wang, S. Pei, G. Cui, L. Zhang, S. Ren, Z. Zhang, and N. Wang, “Effect of elevated pressure on the explosion and flammability limits of methane-air mixtures,” *Energy*, vol. 186, p. 115840, Nov. 2019, doi: 10.1016/J.ENERGY.2019.07.170.

[61] K. Hartley and P. Lant, “Eliminating non-renewable CO2 emissions from sewage treatment: An anaerobic migrating bed reactor pilot plant study,” *Biotechnol. Bioeng.*, vol. 95, no. 3, pp. 384–398, Oct. 2006, doi: 10.1002/BIT.20929.

[62] W. M. K. R. T. W. Bandara, H. Satoh, M. Sasakawa, Y. Nakahara, M. Takahashi, and S. Okabe, “Removal of residual dissolved methane gas in an upflow anaerobic sludge blanket reactor treating low-strength wastewater at low temperature with degassing membrane,” *Water Res.*, vol. 45, no. 11, pp. 3533–3540, May 2011, doi: 10.1016/J.WATRES.2011.04.030.

[63] J. Cookney, E. Cartmell, B. Jefferson, and E. J. McAdam, “Recovery of methane from anaerobic process effluent using poly-di-methyl-siloxane membrane contactors,” *Water Sci. Technol.*, vol. 65, no. 4, pp. 604–610, Feb. 2012, doi: 10.2166/wst.2012.897.

[64] P. L. McCarty, J. Bae, and J. Kim, “Domestic wastewater treatment as a net energy producer-can this be achieved?,” *Environ. Sci. Technol.*, vol. 45, no. 17, pp. 7100–7106, Sep. 2011, doi: 10.1021/ES2014264/ASSET/IMAGES/LARGE/ES-2011-014264_0001.JPEG.

[65] R. M. Glória, C. L. Souza, C. A. L. Chernicharo, M. E. A. Do Carmo, and P. V. O. Silva, “Effectiveness of a Desorption Chamber for the Removal of Dissolved Gases from Anaerobic Effluents,” 2016.

[66] D. T. Mai, C. Kunacheva, and D. C. Stuckey, “A review of posttreatment technologies for anaerobic effluents for discharge and recycling of wastewater,” *Crit. Rev. Environ. Sci. Technol.*, vol. 48, no. 2, pp. 167–209, Jan. 2018, doi:

10.1080/10643389.2018.1443667.

[67] V. Stazi and M. C. Tomei, “Dissolved methane in anaerobic effluents: A review on sustainable strategies for optimization of energy recovery or internal process reuse,” *J. Clean. Prod.*, vol. 317, p. 128359, Oct. 2021, doi: 10.1016/j.jclepro.2021.128359.

[68] W. Rongwong, K. Goh, G. S. M. D. P. Sethunga, and T. H. Bae, “Fouling formation in membrane contactors for methane recovery from anaerobic effluents,” *J. Memb. Sci.*, vol. 573, pp. 534–543, Mar. 2019, doi: 10.1016/J.MEMSCI.2018.12.038.

[69] P. Velasco, V. Jegatheesan, and M. Othman, “Effect of long-term operations on the performance of hollow fiber membrane contactor (HFMC) in recovering dissolved methane from anaerobic effluent,” *Sci. Total Environ.*, vol. 841, no. February, p. 156601, 2022, doi: 10.1016/j.scitotenv.2022.156601.

[70] P. Sanchis-Perucho, Á. Robles, F. Durán, J. Ferrer, and A. Seco, “PDMS membranes for feasible recovery of dissolved methane from AnMBR effluents,” *J. Memb. Sci.*, vol. 604, p. 118070, Jun. 2020, doi: 10.1016/J.MEMSCI.2020.118070.

[71] M. Visnyei, P. Bakonyi, K. Bélafi-Bakó, and N. Nemestóthy, “Integration of gas–liquid membrane contactors into anaerobic digestion as a promising route to reduce uncontrolled greenhouse gas (CH4/CO2) emissions,” *Bioresour. Technol.*, vol. 364, p. 128072, Nov. 2022, doi: 10.1016/J.BIORTECH.2022.128072.

[72] D. R. Poirier and G. H. Geiger, “Transport phenomena in materials processing,” *Transp. Phenom. Mater. Process.*, pp. 1–659, Jan. 2016, doi: 10.1007/978-3-319-48090-9/COVER.

[73] E. Centeno Mora and C. de L. Chernicharo, “Use of membrane contactors for removing and recovering dissolved methane from anaerobic reactors effluents: state-of-the-art, challenges, and perspectives,” *Rev. Environ. Sci. Biotechnol.*, vol. 19, no. 3, pp. 673–697, 2020, doi: 10.1007/s11157-020-09546-w.

[74] H. Kreulen, C. A. Smolders, G. F. Versteeg, and W. P. M. Van Swaaij, “Determination of mass transfer rates in wetted and non-wetted microporous membranes,” *Chem. Eng. Sci.*, vol. 48, no. 11, pp. 2093–2102, Jan. 1993, doi: 10.1016/0009-2509(93)80084-4.

[75] P. Luis, “Membrane contactors,” *Fundam. Model. Membr. Syst. Membr. Process Perform.*, pp. 153–208, Jan. 2018, doi: 10.1016/B978-0-12-813483-2.00005-8.

[76] S. Heile, C. A. L. Chernicharo, E. M. F. Brandt, and E. J. McAdam, “Dissolved gas separation for engineered anaerobic wastewater systems,” *Sep. Purif. Technol.*, vol. 189, no. May, pp. 405–418, 2017, doi: 10.1016/j.seppur.2017.08.021.

[77] W. Rongwong, J. Lee, K. Goh, H. E. Karahan, and T. H. Bae, “Membrane-based technologies for post-treatment of anaerobic effluents,” *npj Clean Water*,

vol. 1, no. 1. 2018. doi: 10.1038/s41545-018-0021-y.

[78] A. Gabelman and S. T. Hwang, “Hollow fiber membrane contactors,” *J. Memb. Sci.*, vol. 159, no. 1–2, pp. 61–106, Jul. 1999, doi: 10.1016/S0376-7388(99)00040-X.

[79] S. Heile, C. A. L. Chernicharo, E. M. F. Brandt, and E. J. McAdam, “Dissolved gas separation for engineered anaerobic wastewater systems,” *Sep. Purif. Technol.*, vol. 189, pp. 405–418, 2017, doi: 10.1016/j.seppur.2017.08.021.

[80] A. Gabelman and S.-T. Hwang, “Hollow ®ber membrane contactors”.

[81] M. Henares, M. Izquierdo, J. M. Penya-Roja, and V. Martínez-Soria, “Comparative study of degassing membrane modules for the removal of methane from Expanded Granular Sludge Bed anaerobic reactor effluent,” *Sep. Purif. Technol.*, vol. 170, pp. 22–29, 2016, doi: 10.1016/j.seppur.2016.06.024.

[82] W. Rongwong, S. Wongchitphimon, K. Goh, R. Wang, and T. H. Bae, “Transport properties of CO2 and CH4 in hollow fiber membrane contactor for the recovery of biogas from anaerobic membrane bioreactor effluent,” *J. Memb. Sci.*, vol. 541, pp. 62–72, 2017, doi: 10.1016/j.memsci.2017.06.090.

[83] M. Mulder, *Basic Principles of Membrane Technology*, Second edi. Springer Netherlands, 1997. Accessed: Apr. 03, 2024. [Online]. Available: https://books.google.hu/books?hl=tr&lr=&id=y2_wCAAAQBAJ&oi=fnd&pg=PA1&ots=X9cYlh_mLP&sig=O1c7nbZFvK81d2lFtpheLZ8mAVk&redir_esc=y#v=onepage&q&f=false

[84] S. R. Wickramasinghe, M. J. Semmens, and E. L. Cussler, “Mass transfer in various hollow fiber geometries,” *J. Memb. Sci.*, vol. 69, no. 3, pp. 235–250, May 1992, doi: 10.1016/0376-7388(92)80042-I.

[85] S. R. Wickramasinghe, M. J. Semmens, and E. L. Cussler, “Hollow fiber modules made with hollow fiber fabric,” *J. Memb. Sci.*, vol. 84, no. 1–2, pp. 1–14, Sep. 1993, doi: 10.1016/0376-7388(93)85046-Y.

[86] M. G. De Angelis, M. Minelli, L. Sun, G. Panagakos, and G. Lipscomb, “Effect of Packing Nonuniformity at the Fiber Bundle–Case Interface on Performance of Hollow Fiber Membrane Gas Separation Modules,” *Membr. 2022, Vol. 12, Page 1139*, vol. 12, no. 11, p. 1139, Nov. 2022, doi: 10.3390/MEMBRANES12111139.

[87] S. Wongchitphimon, W. Rongwong, C. Y. Chuah, R. Wang, and T. H. Bae, “Polymer-fluorinated silica composite hollow fiber membranes for the recovery of biogas dissolved in anaerobic effluent,” *J. Memb. Sci.*, vol. 540, pp. 146–154, Oct. 2017, doi: 10.1016/J.MEMSCI.2017.06.050.

[88] A. Gugliuzza and A. Basile, “Membrane contactors: fundamentals, membrane materials and key operations,” *Handb. Membr. React.*, vol. 2, pp. 54–106, Jan. 2013, doi: 10.1533/9780857097347.1.54.

[89] J. Cookney, A. Mcleod, V. Mathioudakis, P. Ncube, A. Soares, B. Jefferson, and E.J. McAdam, “Dissolved methane recovery from anaerobic effluents using hollow fibre membrane contactors,” *J. Memb. Sci.*, vol. 502, pp. 141–150, 2016,

doi: 10.1016/j.memsci.2015.12.037.

[90] A. McLeod, B. Jefferson, and E. J. McAdam, “Toward gas-phase controlled mass transfer in micro-porous membrane contactors for recovery and concentration of dissolved methane in the gas phase,” *J. Memb. Sci.*, vol. 510, pp. 466–471, Jul. 2016, doi: 10.1016/J.MEMSCI.2016.03.030.

[91] J. M. Vadillo, L. Gómez-Coma, A. Garea, and A. Irabien, “Hollow Fiber Membrane Contactors in CO2Desorption: A Review,” *Energy and Fuels*, vol. 35, no. 1, pp. 111–136, Jan. 2021, doi: 10.1021/acs.energyfuels.0c03427.

[92] M. Henares, M. Izquierdo, P. Marzal, and V. Martínez-Soria, “Demethanization of aqueous anaerobic effluents using a polydimethylsiloxane membrane module: Mass transfer, fouling and energy analysis,” *Sep. Purif. Technol.*, vol. 186, pp. 10–19, Oct. 2017, doi: 10.1016/J.SEPPUR.2017.05.035.

[93] C. Vallieres and E. Favre, “Vacuum versus sweeping gas operation for binary mixtures separation by dense membrane processes,” *J. Memb. Sci.*, vol. 244, no. 1–2, pp. 17–23, Nov. 2004, doi: 10.1016/J.MEMSCI.2004.04.023.

[94] E. Chabanon, D. Roizard, and E. Favre, “Membrane Contactors for Postcombustion Carbon Dioxide Capture: A Comparative Study of Wetting Resistance on Long Time Scales,” *Ind. Eng. Chem. Res.*, vol. 50, no. 13, pp. 8237–8244, Jul. 2011, doi: 10.1021/IE200704H.

[95] R. Jiménez-Robles, C. Gabaldón, V. Martínez-Soria, and M. Izquierdo, “Simultaneous application of vacuum and sweep gas in a polypropylene membrane contactor for the recovery of dissolved methane from water,” *J. Memb. Sci.*, vol. 617, p. 118560, Jan. 2021, doi: 10.1016/J.MEMSCI.2020.118560.

[96] C. Kalakech, Q. Sohaib, G. Lesage, and J. P. Mericq, “Progress and challenges in recovering dissolved methane from anaerobic bioreactor permeate using membrane contactors: A comprehensive review,” *J. Water Process Eng.*, vol. 50, p. 103218, Dec. 2022, doi: 10.1016/J.JWPE.2022.103218.

[97] Y. Lee, K. H. Yun, D. Sethunga, and T. H. Bae, “Membrane contactors for maximizing biomethane recovery in anaerobic wastewater treatments: Recent efforts and future prospect,” *Appl. Sci.*, vol. 11, no. 4, pp. 1–16, Feb. 2021, doi: 10.3390/app11041372.

[98] G. S. M. D. P. Sethunga, W. Rongwong, R. Wang, and T. H. Bae, “Optimization of hydrophobic modification parameters of microporous polyvinylidene fluoride hollow-fiber membrane for biogas recovery from anaerobic membrane bioreactor effluent,” *J. Memb. Sci.*, vol. 548, pp. 510–518, Feb. 2018, doi: 10.1016/J.MEMSCI.2017.11.059.

[99] C. Kalakech, Q. Sohaib, G. Lesage, and J.-P. Mericq, “Progress and challenges in recovering dissolved methane from anaerobic bioreactor permeate using membrane contactors: A comprehensive review,” *J. Water Process Eng.*, vol. 50, pp. 2214–7144, 2022, doi: 10.1016/j.jwpe.2022.103218.

[100] G. Luo, W. Wang, and I. Angelidaki, “A new degassing membrane coupled

upflow anaerobic sludge blanket (UASB) reactor to achieve in-situ biogas upgrading and recovery of dissolved CH 4 from the anaerobic effluent," *Appl. Energy*, vol. 132, pp. 536–542, Nov. 2014, doi: 10.1016/j.apenergy.2014.07.059.

[101] S. Heile, S. Rosenberger, A. Parker, B. Jefferson, and E. J. McAdam, "Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO2 separation during biogas upgrading," *J. Memb. Sci.*, vol. 452, pp. 37–45, Feb. 2014, doi: 10.1016/J.MEMSCI.2013.10.007.

[102] S. Goh, J. Zhang, Y. Liu, and A. G. Fane, "Fouling and wetting in membrane distillation (MD) and MD-bioreactor (MDBR) for wastewater reclamation," *Desalination*, vol. 323, pp. 39–47, Aug. 2013, doi: 10.1016/J.DESAL.2012.12.001.

[103] B. C. Crone, J. L. Garland, G. A. Sorial, and L. M. Vane, "Significance of dissolved methane in effluents of anaerobically treated low strength wastewater and potential for recovery as an energy product: A review," *Water Res.*, vol. 104, pp. 520–531, 2016, doi: 10.1016/j.watres.2016.08.019.

[104] P. Bakonyi, G. Buitrón, I. Valdez-Vazquez, N. Nemestóthy, and K. Bélafi-Bakó, "A novel gas separation integrated membrane bioreactor to evaluate the impact of self-generated biogas recycling on continuous hydrogen fermentation," *Appl. Energy*, vol. 190, pp. 813–823, 2017, doi: 10.1016/j.apenergy.2016.12.151.

[105] V. Stazi and M. C. Tomei, "Dissolved methane in anaerobic effluents: A review on sustainable strategies for optimization of energy recovery or internal process reuse," *Journal of Cleaner Production*, vol. 317. Elsevier Ltd, Oct. 01, 2021. doi: 10.1016/j.jclepro.2021.128359.

[106] W. Rongwong, S. Wongchitphimon, K. Goh, R. Wang, and T. H. Bae, "Transport properties of CO2 and CH4 in hollow fiber membrane contactor for the recovery of biogas from anaerobic membrane bioreactor effluent," *J. Memb. Sci.*, vol. 541, no. March, pp. 62–72, 2017, doi: 10.1016/j.memsci.2017.06.090.

[107] D. Hidalgo, S. Sanz-Bedate, J. M. Martín-Marroquín, J. Castro, and G. Antolín, "Selective separation of CH4 and CO2 using membrane contactors," *Renew. Energy*, vol. 150, pp. 935–942, May 2020, doi: 10.1016/J.RENENE.2019.12.073.

[108] Q. Sohaib, C. Kalakech, C. Charmette, J. Cartier, G. Lesage, and J. P. Mericq, "Hollow-Fiber Membrane Contactor for Biogas Recovery from Real Anaerobic Membrane Bioreactor Permeate," *Membranes (Basel).*, vol. 12, no. 2, Feb. 2022, doi: 10.3390/membranes12020112.

[109] Liu, T., Li, J., Khai Lim, Z., Chen, H., Hu, S., Yuan, Z. and Guo, J., "Simultaneous Removal of Dissolved Methane and Nitrogen from Synthetic Mainstream Anaerobic Effluent," *Environ. Sci. Technol.*, vol. 54, no. 12, pp. 7629–7638, Jun. 2020, doi: 10.1021/acs.est.0c00912.

[110] H. Yeo, J. An, R. Reid, B. E. Rittmann, and H. S. Lee, “Contribution of Liquid/Gas Mass-Transfer Limitations to Dissolved Methane Oversaturation in Anaerobic Treatment of Dilute Wastewater,” *Environ. Sci. Technol.*, vol. 49, no. 17, pp. 10366–10372, Sep. 2015, doi: 10.1021/ACS.EST.5B02560/ASSET/IMAGES/LARGE/ES-2015-02560U_0003.JPEG.

[111] M. Visnyei, P. Bakonyi, N. Nemestóthy, and K. Bélafi-Bakó, “Separation of Dissolved Gases from Aqueous Anaerobic Effluents Using Gas-Liquid Membrane Contactors,” *Hungarian J. Ind. Chem.*, vol. 50, no. 2, pp. 23–26, 2022, doi: 10.33927/hjic-2022-14.

[112] G. S. M. D. P. Sethunga, H. E. Karahan, R. Wang, and T. H. Bae, “PDMS-coated porous PVDF hollow fiber membranes for efficient recovery of dissolved biomethane from anaerobic effluents,” *J. Memb. Sci.*, vol. 584, pp. 333–342, Aug. 2019, doi: 10.1016/j.memsci.2019.05.016.

[113] G. Luo, W. Wang, and I. Angelidaki, “A new degassing membrane coupled upflow anaerobic sludge blanket (UASB) reactor to achieve in-situ biogas upgrading and recovery of dissolved CH4 from the anaerobic effluent,” *Appl. Energy*, vol. 132, pp. 536–542, Nov. 2014, doi: 10.1016/j.apenergy.2014.07.059.

[114] G. Luo, L. Xie, Q. Zhou, and I. Angelidaki, “Enhancement of bioenergy production from organic wastes by two-stage anaerobic hydrogen and methane production process,” 2011, doi: 10.1016/j.biortech.2011.02.012.

[115] M. B. Viana, A. V. Freitas, R. C. Leitão, G. A. S. Pinto, and S. T. Santaella, “Anaerobic digestion of crude glycerol: a review,” *Environ. Technol. Rev.*, vol. 1, no. 1, pp. 81–92, Nov. 2012, doi: 10.1080/09593330.2012.692723.

[116] C. Zhang, H. Ye, F. Liu, Y. He, W. Kong, and K. Sheng, “Determination and Visualization of pH Values in Anaerobic Digestion of Water Hyacinth and Rice Straw Mixtures Using Hyperspectral Imaging with Wavelet Transform Denoising and Variable Selection,” 2016, doi: 10.3390/s16020244.

[117] L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, *Standard methods for the examination of water and wastewater*, 20th editi. Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation, 1998.

[118] L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, *Standard methods for the examination of water and wastewater*, 19th editi. Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation, 1995.

[119] W. Rongwong, K. Goh, and T. H. Bae, “Energy analysis and optimization of hollow fiber membrane contactors for recovery of dissolve methane from anaerobic membrane bioreactor effluent,” *J. Memb. Sci.*, vol. 554, pp. 184–194, May 2018, doi: 10.1016/J.MEMSCI.2018.03.002.

[120] P. Velasco, V. Jegatheesan, and M. Othman, “Recovery of dissolved methane

from anaerobic membrane bioreactor using degassing membrane contactors," *Frontiers in Environmental Science*, vol. 6, no. DEC. Frontiers Media S.A., Dec. 17, 2018. doi: 10.3389/fenvs.2018.00151.

[121] G. S. M. D. P. Sethunga, J. Lee, R. Wang, and T. H. Bae, "Influences of operating parameters and membrane characteristics on the net energy production in dense, porous, and composite hollow fiber membrane contactors for dissolved biomethane recovery," *J. Memb. Sci.*, vol. 610, Sep. 2020, doi: 10.1016/j.memsci.2020.118301.

[122] L. Leng, M. K. Nobu, T. Narihiro, P. Yang, G.-Y. A. Tan, and P.-H. Lee, "Shaping microbial consortia in coupling glycerol fermentation and carboxylate chain elongation for Co-production of 1,3-propanediol and caproate: Pathways and mechanisms," 2018, doi: 10.1016/j.watres.2018.10.063.

[123] P. Sivagurunathan, G. Kumar, P. Bakonyi, S.H. Kim, T. Kobayashi, K.Q. Xu, G. Lakner, G. Tóth, N. Nemestóthy, and K. Bélafi-Bakó, "A critical review on issues and overcoming strategies for the enhancement of dark fermentative hydrogen production in continuous systems," *Int. J. Hydrogen Energy*, vol. 41, no. 6, pp. 3820–3836, Feb. 2016, doi: 10.1016/J.IJHYDENE.2015.12.081.

[124] M. B. Viana, A. V. Freitas, R. C. Leitão, G. A. S. Pinto, and S. T. Santaella, "Anaerobic digestion of crude glycerol: a review," *Environ. Technol. Rev.*, vol. 1, no. 1, pp. 81–92, Nov. 2012, doi: 10.1080/09593330.2012.692723.

[125] A. Nopharatana, P. C. Pullammanappallil, and W. P. Clarke, "Kinetics and dynamic modelling of batch anaerobic digestion of municipal solid waste in a stirred reactor," *Waste Manag.*, vol. 27, no. 5, pp. 595–603, 2007, doi: 10.1016/J.WASMAN.2006.04.010.

[126] A. Umar, Shehu, Ibn and N. Ismail, "ANAEROBIC DIGESTION OF COW DUNG FOR BIOGAS PRODUCTION," vol. 7, no. 2, 2006, Accessed: Nov. 19, 2023. [Online]. Available: www.arpnjournals.com

[127] L. Vinet and A. Zhedanov, "A 'missing' family of classical orthogonal polynomials," *J. Phys. A Math. Theor.*, vol. 44, no. 8, p. 085201, Feb. 2011, doi: 10.1088/1751-8113/44/8/085201.

[128] Q. Sohaib, C. Kalakech, C. Charmette, J. Cartier, G. Lesage, and J.-P. Mericq, "Hollow-Fiber Membrane Contactor for Biogas Recovery from Real Anaerobic Membrane Bioreactor Permeate membranes Hollow-Fiber Membrane Contactor for Biogas Recovery from Real Anaerobic Membrane Bioreactor Permeate," *Membranes (Basel).*, vol. 2022, no. 2, p. 112, 2022, doi: 10.3390/membranes12020112ï.

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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 (CH_4/CO_2) emissions”, Bioresource Technology, 2022, 364, 128072 **(IF: 11.40)**

2. **Visnyei, M.,** Bakonyi, P., Rózsenberszki, T., Koók, L., Komáromy, P., Bélafi-Bakó, K., Nemestóthy, N.: „Mitigated CH_4 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**)

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Merve Visnyei