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Mitigated CH_4 release of anaerobic waste fermentation is enabled through effluent degassing system equipped with a polydimethylsiloxane membrane contactor

Merve Visnyei, Péter Bakonyi *, Tamás Rózsenberszki, László Koók, Péter Komáromy, Katalin Bélafi-Bakó, Nándor Nemestóthy

Research Group on Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary

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ABSTRACT

In this study, first, a fed-batch biogas fermenter was established using anaerobic digester sludge treating secondary sludge from a municipal wastewater treatment plant and operated for 120 days on glycerol as the sole substrate. Then, the prefiltered effluent of the anaerobic digester unit was loaded subsequently into a stirred-tank coupled with a hollow-fibre, polydimethylsiloxane (PDMS) gas-liquid membrane contactor and a dissolved methane sensor for studying the gas recovery process under continuous biogas supply, consisting of CH_4 and CO_2 in different proportions (70/30 CH_4/CO_2 vol.%; 50/50 CH_4/CO_2 vol.%; 30/70 CH_4/CO_2 vol.%.). Experiments showed that besides the actual composition of the internal biogas, the ratio (0.5–2) of sweep gas (N_2) and effluent (liquid) volumetric flow rates (G/L) could be a crucial operating factor with influence on the degassing efficiency attainable by the 1 m^2 PDMS membrane module. Results were compared to the performance of the same PDMS membrane module working with synthetic anaerobic digester effluents, indicating the dissolved methane recoveries observed with the synthetic effluents (>50 %) considerably surpassed those with the real effluent (<20 %) where the dissolved methane concentrations, at G/L of 1, were in the range of 12.4 to 17.3 mg L^{-1}.

1. Introduction

One of the greatest contributions to greenhouse gases (GHGs) may come from the lost part of the methane production during biogas fermentation [1,2]. The emission of 1 kg of methane to the environment yields a similar impact on global warming as emitting 28 kg of carbon dioxide over a span of 100 years [3]. This issue carries substantial importance as it plays a pivotal role in reducing the fugitive emissions and maximising the energy production of the facilities by recovering the methane entrapped in the anaerobic digester effluent [4–6]. Therefore, the selection of suitable post-treatment layouts that can manage this problem seems critical in advancing the establishment of biogas reactors at larger-scales [7,8].

So far, different technologies such as free-fall jet towers [9,10], spray aeration [11], packed columns [12], tray aeration [13], diffused aeration [14], and membrane contactors (MCs) [15–17] have been studied for removing or recovering dissolved methane contained in the anaerobic effluents. Among these alternatives, gas-liquid membrane contactors (GL-MCs), have gained noteworthy attention in various fields [18] mainly due to their non-dispersive stripping principle, the capacity for a high packing density resulting in reduced unit volumes, and the potential for generating a product gas stream enriched with CH_4 [19–22]. Hollow-fibre membrane contactors (HFMC) have been identified and found suitable for transferring dissolved CH_4 from liquids into a gaseous phase [23–25] in line with the research efforts towards the design and implementation of contemporary anaerobic wastewater management approaches. In particular, hydrophobic microporous as well as non-porous materials are available to fabricate HFMC for degassing processes. Although the hydrophobic membrane with microporous structure promotes non-dispersive interaction between the contacting gaseous and liquid phases, membrane fouling and pore wetting may occur when integrated into complex wastewater treatment systems, significantly reducing the mass transfer and achievable selectivity [16].

Hence, to avoid these adverse effects, non-porous polymeric membranes, such as those made of polydimethylsiloxane (PDMS) can be utilized. PDMS membrane contactors present a compelling choice

* Corresponding author.
E-mail address: bakonyi.peter@mk.uni-pannon.hu (P. Bakonyi).

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thanks to their superior gas permeating capability in contrast to alternative membranes i.e., polyamide, cellulose acetate or polypropylene. This increased gas permeability reduces the energy needed to extract dissolved gases from effluents, making PDMS membrane contactors an attractive option [26–28].

During the extraction of methane from the liquid phase across a membrane, vacuum or a sweep (usually nitrogen) is applied on the secondary side of the membrane module. Selecting between the desorption or degassing modes requires evaluation of various factors, including the expenses and demand of energy for methane degassing or the processability of the operations [28,29]. Salient gas recovery performances (70–90 %) could typically be attained under sweep-gas operation [30,31]. In contrast, applying vacuum mode with 800 mbar pressure vacuum, 80 % recovery was achieved using 50 L h^{-1} liquid flow rate and a dense PDMS membrane [32].

The differences between the effectiveness of the two approaches were pointed out by Cookney et al. [28], indicating a 72 % recovery efficiency when applying sweep gas and the lowest possible liquid velocity, while this value was around 80 % under 308 mbar vacuum. Furthermore, employing vacuum can lead to less significant dilution on the gas-side, while the use of a sweep gas can be accompanied by a dilutive effect. This was evidenced by the purity of only 0.028 (v/v%) recovered methane in the gaseous phase. The proper choice of the flow rates – both in terms of the liquid and the sweep gas – is pivotal in maximizing the efficiency of methane recovery within membrane contactor systems, as demonstrated by the significant impact on the recovery rates observed in the experiments. For this reason, numerous studies analysed the effects of liquid and sweep gas flow rates on the composition of the gas phase as well as on the achievable dissolved gas recovery performance [17,28,29,31,33]. In the study of Henares et al. [30], higher gas flux along with an increased liquid flow rate resulted in improved gas recovery, which observation is in line the experiences of Visnyei et al. [27]: the CH_4 transport was enhanced in response to adjusting higher liquid flow rates, meanwhile the CO_2 transport was favoured when higher gas flow rates were set. Sethunga et al. [34] documented the same effect: the CH_4 recovery was decreased by operating under higher liquid flow rates.

To date, however, the majority of research studies have primarily concentrated on methane recovery from simple (model) effluents based on theoretical equations and calculations [35–40], while there are far less examples concerning the applicability of membrane contactors for dissolved methane/carbon dioxide (biogas) recovery using effluent from biogas fermenters. In one particular instance, Sethunga et al. [34] used porous PVDF and PDMS-modified PVDF membrane contactors to regain methane from the effluent of anaerobic membrane bioreactor. Additionally, Cookney et al. [28] demonstrated the feasibility of dissolved methane recovery from the effluent of wastewater-processing anaerobic bioreactor by using membrane contactor made of PDMS material. This study was further expanded by integrating a microporous membrane contactor made of polypropylene for the treatment of real anaerobic bioreactor effluents containing dissolved biogas [17]. In another report, Luo et al. [41] showed that a membrane module attached to a UASB reactor was capable of real effluent degassing and lower consequently the concentration of dissolved methane in the feed stream.

Although these above works delivered important findings, further advances are still required to understand this technology and its capabilities, regarding in particular the long-term experiments employing real anaerobic, biogas fermentation effluents. In other words, there is a need for more in-depth investigations on biogas recovery from real anaerobic digester effluents that would lead to more solid feedback and useful experiences about the specific applicability of the HFMCs under practical conditions.

Therefore, in this study, following long-term biogas production experiments from glycerol substrate, 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. By investigating operational variables such as sweep gas and liquid flow rates, as well as the methane content of the biogas, the study highlights the importance of the gas-to-liquid flow ratio in optimizing methane recovery. In parallel, the study emphasizes the differences and challenges in CH_4 recovery by comparing the data of the current investigation using real effluent to those previously obtained with synthetic effluents applying an identical PDMS HFMC in order to remove the dissolved CH_4 in the fermentation liquor [27], which altogether, stand as the main innovation of this work and represent in our opinion of notable added-value to the already published literature.

2. Materials and methods

2.1. Anaerobic bioreactor setup for real effluent preparation

A laboratory-scale, fed-batch anaerobic bioreactor with a working volume of 2 L was inoculated with 1.5 L of sludge. The inoculum with an initial pH value of 7.1 ± 0.1 was collected from an anaerobic digester unit treating the excess sludge of municipal wastewater treatment plant in the town of Veszprém, Hungary. In the start-up period, the system was flushed using nitrogen gas (>99.9 vol%) to maintain anoxic conditions and conduct the anaerobic digestion of the organic matter under mesophilic conditions at 37 °C. Glycerol (>99.5 %) was used as the substrate source for biogas fermentation, by considering it as an organic substance that is easily digestible and storable for extended periods and can be used to enhance biogas production. It was already proven as a suitable organic matter to produce methane in earlier investigations [42]. Preliminary experiments were carried out to find the sufficient load of glycerol tolerated well by the underlying microbial community [43]. Based on the results of preliminary experiments (detailed in Section 3.1.1), 3.3 g L^{-1} pure glycerol was routinely supplemented to the bioreactor in every 4–5 days interval. The anaerobic digestion process was operated under mesophilic conditions at 37°C. In addition to the glycerol (>99.5%) as the sole substrate, yeast extract (Sigma-Aldrich) was supplemented every two weeks (2 g L^{-1}) to ensure nutrients and N-source for the growth of microorganisms.

Biogas production was quantified using a U-tube, while the data for gas flow measurements and logging was recorded by using Measurement Computing (MC) USB-5100 software. This software was used to track and monitor the gas flow continuously. Since an optimum pH value of the media results in a higher yield of biomass energy [44], a pH sensor was coupled to the bioreactor to track the pH values. After the initial procedures, the bioreactor was put into fed-batch operation mode and allowed to run for 120 days to produce biogas with occasionally scheduled internal biogas recirculation to ensure the mixing of the bioreactor content. The cumulative gas production was determined by adding together the daily gas production values throughout the experimental duration. Gas samples were extracted from the headspace of the bioreactor at consistent intervals using a gastight Hamilton® syringe (300 μL) and analysed using a gas chromatograph to observe the composition of the generated biogas.

2.2. 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 prevent potential membrane clogging caused by suspended solids present in the anaerobic effluent. 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 1). The recovery of the CH_4 dissolved in the effluent was investigated with a counter-current flow, where the liquid was fed on the shell side of the membrane module, while the sweep gas was entering the membrane module in the hollow-fibre capillaries. This membrane module had been used in previous work [27], however, there is not enough information about its efficiency and behaviour when subjected to treat real effluent.

It is noteworthy that the prefiltering process through the 1 mm sieve resulted in the (partial) removal of the microorganisms participating actively in the production of biogas and consequently, there was a need for the use of binary CO_2/CH_4 mixtures with different ratios of the two gases (70/30 CH_4/CO_2 vol.%; 50/50 CH_4/CO_2 vol.%; 30/70 CH_4/CO_2 vol.%) to mimic the fermentation conditions in this sense and comply with the settings of our previous research paper [27] used later on for methane recovery efficiency comparison (Fig. 7).

Therefore, the system was operated at a controlled flow rate of 0.7 mL min^{-1} gas inflow (equivalent to the 1 L d^{-1} averaged gas production capacity experienced with the biogas fermenter according to Section 3.1.2). To ensure consistency and stabilization of the experiment, biogas output was measured using a U-tube gas flow meter. Furthermore, a dissolved methane sensor (Pro-Oceanus Digital Mini CH_4, Pro-Oceanus System Inc., Canada) was built-in the recirculation side of the module in order to measure the CH_4 concentration in the effluent returning to the reactor after the degassing step. Occasionally, the dissolved methane probe was disconnected from this position and put directly into the reactor to measure the actual methane concentration in the filtered effluent that is the feed of the PDMS HFMC. The dissolved CH_4 probe was connected to a computer for continuous data logging to monitor the dissolved CH_4 as a function of time.

A peristaltic pump (Masterflex®, Cole-Parmer Instrument Co.) was used to adjust the liquid flow rate of real effluent between 10 and 20 mL min^{-1}, in accordance with our previous paper [27]. Nitrogen (99.9 %) was utilized 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 and 20 mL min^{-1} and measured with a soap film flowmeter, similar to our previous work [27].

Norprene® and Tygon® formula E-3603 laboratory tubings (Masterflex®, Cole-Parmer Instrument Co.; Merck & Co., Inc.) were used to connect the various components of the experimental equipment including the PDMS module, peristaltic pump, and flow meter.

The methane recovery experiments with the PDMS membrane module were carried out at 37 °C under in 12 days in total. By varying the effluent and sweep gas flow rates, different gas-to-liquid flow ratios (G/L) were adjusted and the effect of this membrane operational parameter could be sought along with the impact of the methane proportion in the binary gas. The completed experimental plan to assess the recovery efficiency of dissolved methane from the filtered fermentation effluent under steady-state conditions is given in Table 2, while the scheme of the experimental setup is illustrated in Fig. 1.

The validity and reliability of the experimental apparatus were confirmed by the successful completion of leakage tests prior to the measurements. Gas samples were extracted from the headspace of the bioreactor at consistent intervals using a gastight Hamilton® syringe (300 µL) and analysed using a gas chromatograph to observe the actual composition of the outlet gases of the membrane module on the sweep gas side.

Table 1
Characteristics of the non-porous polydimethylsiloxane (PDMS) contactor module.

Geometric characteristics	Value
Module length (cm)	14
Module diameter (cm)	6.0
Membrane area (m^2)	1.0
Number of fibres	12,600
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

Table 2
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^{-1})	(Sweep) gas flow rate (mL min^{-1})
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

2.3. Analytical methods and calculations

To monitor the compositions of the gases, HP 5890 (Series II) GC equipped with a TCD and a carboplot® column was used. The measurement conditions were adapted from our work and can be found in details in our previous publication [27].

The VFAs content was followed by a gas chromatograph (Hewlett Packard series II 5890) equipped with FID detector. Before the injection, all the samples were centrifuged at 13,000 rpm for 10 min to avoid suspended particles. Determination was made with the internal standard method using n-butanol (1 g L^{-1}). The injection volume was 1 µl. The temperatures of the injection port, FID, and column were set at 240 °C, 250 °C, and 70 °C, respectively. The initial temperature of the DB-FFAP column was set at 70 °C for 1 min, then increased to 150 °C at a heating rate of 10 °C min^{-1}, and maintained at 150 °C for 1 min.

The total solids (TS) and volatile solids (VS) of the filtered sludge were determined by following the protocol of APHA [45]. 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 [46].

CH_4 recovery calculations were based on the data obtained from both the dissolved CH_4 probe and GC results (Fig. 2) under steady-state conditions. The dissolved CH_4 concentrations (mg L^{-1}) were measured by the probe and in parallel, the mass flow rate of CH_4 exiting the membrane module was determined according to Eq. (1) [27].

$$x_i{}^{*}\frac{P_i Q_{V_G}{}^{*}}{RT} M_i = Q_{w_{out}} \quad (1)$$

where x_i volume fraction of methane in the outlet of the membrane module, P_i pressure of methane, QV_G gas flow rate, R universal gas constant, T temperature, M_i molar mass of methane, Qw_{out} mass flow rate of methane exiting the membrane module.

The actual methane recovery performance was obtained by Eq. (2):

$$\text{Recovery efficiency}, \% = \frac{Q_{w_{out}}}{Q_{w_{in}}} * 100 \quad (2)$$

3. Results and discussion

The primary objective of the study was to assess the performance of the PDMS membrane module in recovering methane (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. Subsequently, the effluent

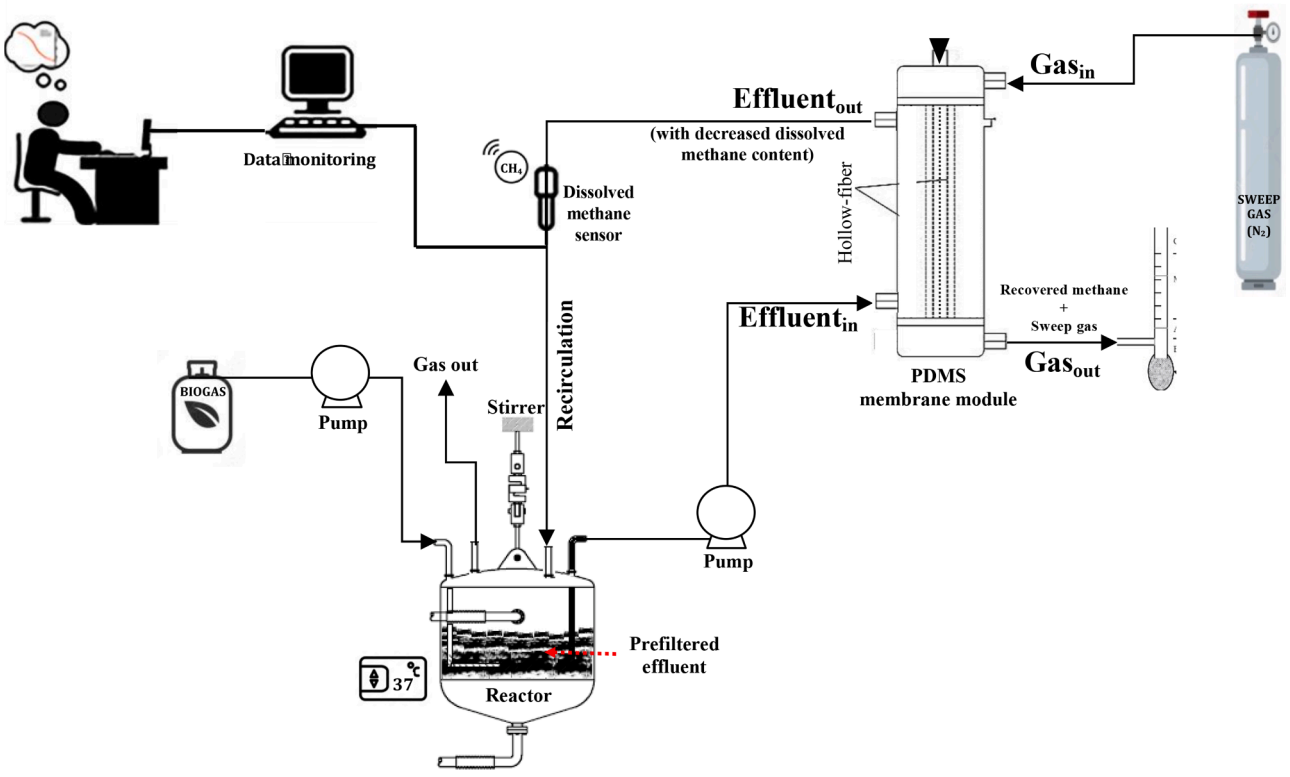

Fig. 1. Experimental setup using membrane contactors to recover CH_4 from the real anaerobic effluent.

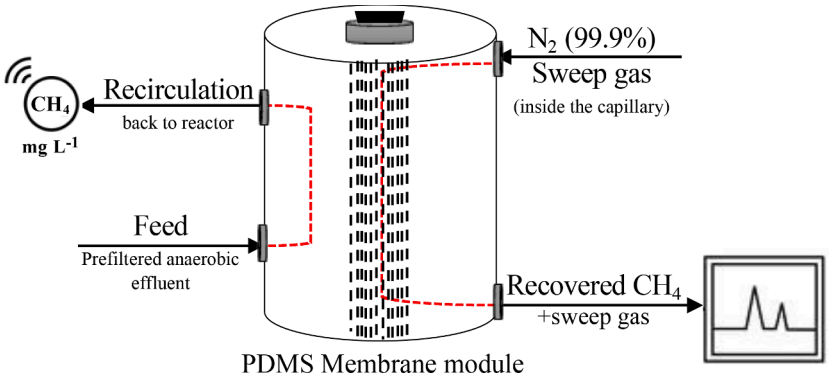

Fig. 2. Flow sheet of methane separation.

was prefiltered to prevent immediate clogging, which could lead to module failure. Recovery experiments for dissolved CH_4 were then initiated using the PDMS hollow fibre membrane module (highlighted in the graphical abstract). The forthcoming discussion will highlight differences and challenges in CH_4 recovery by comparing the data from the current investigation, utilizing real effluent, to previous findings obtained with synthetic effluents, employing an identical membrane module.

3.1. Evaluating the long-term performance of fed-batch biogas fermentation

Laboratory-scale fed-batch anaerobic bioreactor with a total volume of 2 L was inoculated with 1.5 L of sludge from an anaerobic digester treating the secondary sludge of a municipal wastewater treatment plant. The sludge underwent sieving to remove larger particles and the process was facilitated by purging the system with N_2 (99.9 vol%) so that the anaerobic environment was ensured.

3.1.1. Optimizing the glycerol load for enhanced methanogenic activity

During the preliminary experiments, pure glycerol was supplemented to the bioreactor to achieve substrate loading of 6.7–33.3 g L^{-1}. The analysis of fermentation broth showed that organic acids formed by the fermentative acidogenic bacteria were not able to be consumed by

Table 3
Analysis results of the over-produced organic acids (as indicated in Fig. 3, the day #5).

Organic acids	Value, g L^{-1}
Acetic acid	0.6
Propionic acid	1.8
Butyric acid	1.7
Valeric acid	5.8
Caproic acid	11.1

the acetogenic or methanogenic bacteria at the same rate as they are produced (Table 3).

The accumulation of organic acids was the result of an organic (substrate) overload, leading to a drop in the pH from 7.1 ± 0.1 to 5.8 ± 0.1. The dominant VFAs were caproic acid (C6) and valeric acid (C5) but in lower quantities, propionic acid (C3), butyric acid (C4), and acetic acid (C2) were observed. According to Leng et al. [47], caproic acid production can be intensified by the enriched *Eubacterium limosum* with the substrate of glycerol and have a synergistic effect with *Clostridium kluyveri* that uses the charge of the metabolism of acetic acid and ethanol by through chain elongation. Additionally, it can also explain the relatively low acetic acid content. Hydrogen gas concentration was increased due to the acidification of anaerobic digester, forming hydrogen rather than methane [48]. The production of these acids needs to be controlled carefully due to their significant inhibition effect on the methanogenic activity, the accumulation of these metabolites results in a system malfunctioning [43]. Based on the results obtained from these preliminary experiments (3 weeks), one-third of the bioreactor content was drawn and replaced by fresh anaerobic sludge to offset the pH imbalance relying on the alkalinity presented in the bulk inoculum. After the starting period and acclimation, the bioreactor was routinely supplemented with 3.3 g L^{-1} of pure glycerol as a substrate loading in every 4–5 day intervals.

3.1.2. Cumulative biogas production analysis

Fig. 3 illustrates the biogas production rate (mL h^{-1}) and cumulative biogas volume over time, while also emphasizing the timing of substrate addition (SA). At the beginning of the study, low biogas production was observed. This was predicted due to the direct correlation between the rate of biogas production and the specific growth of methanogenic bacteria [49]. The inhibition of this growth was linked to the organic overload of the system, resulting in rather notable hydrogen production than methane in the initial 5 days (as explained in Section 3.1.1). The investigation on anaerobic digestion performance by Abubakar and Ismail [50] resulted in similar findings, indicating a slow initial biogas production primarily due to the lag phase of microbial growth.

When the preliminary experiments were finished, the proper glycerol dose was chosen after 5–6 days of observation; biogas production started to increase substantially due to the exponential growth of methanogens. The performance of the anaerobic digestion process is illustrated in the cumulative biogas production shown in Fig. 4. After 120 days of successful operation of the bioreactor, 120 litres of biogas were produced, giving thus 1 L d^{-1} as averaged biogas production performance. During the experimental period, the pH was stabilized between 6.5 and 7.5 with an average value of 7.1. In stable conditions, the GC results of samples taken from the headspace of bioreactor on a daily basis exhibited a composition of 55–75 %; 25–45 and 0–0.2 % for the gases of CH_4; CO_2 and H_2, respectively. Based on the results, the averaged cumulative biogas composition was CH_4: 67.4 ± 10.3 %; CO_2: 32.5 ± 10.3 %; H_2: 0.1 ± 0.1 %. The theoretical production of CH_4 by anaerobically converting glycerol into biogas was estimated as 605 mL d^{-1} according to the Buswell formula (Eq. (3)) and the ideal gas law [51]:

$$C_3H_5(OH)_3 \rightarrow 1.75CH_4 + 1.25CO_2 + H_2O \quad (3)$$

Based on the experimental results, the methane production was 674 mL d^{-1} which well-approached the estimated theoretical value, even beyond it by ~10 %. This observation was supported by a previous work investigating the effect of glycerol on anaerobic digestion [52]. Overall, this result highlights the complete digestion of glycerol and significant enhancement in the activity and growth of the underlying biomass, facilitating accordingly the methane production in the bioreactor.

3.2. 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 by using a 1 mm sieve to prevent potential membrane clogging caused by suspended solids present in the anaerobic effluent. The main characteristics of the homogenized sludge after filtering were analysed and the results are as follows: TS: 1.0 (w/w%); VS: 0.67 (w/w%); COD: 18.5 ± 1.5 (gO_2/dm^3), resulting VS/TS of 67 % high organic content. It is important to note that the prefiltration removed a notable part of the original (active) biomass which was responsible for the 120 days of biogas production and therefore, the biogas production in the recirculating membrane reactor was reinforced using external "biogas" as the binary mixture of methane/carbon dioxide in different compositions. Firstly, a biogas mixture (70/30 CH_4/CO_2 vol.%) was prepared to match the composition of biogas produced via anaerobic digestion process for 120 days. The sweep gas and the liquid flow rate were varied between 10 and 20 mL min^{-1}. For a comprehensive analysis, additional biogas mixtures (50/50, 30/70 CH_4/CO_2 vol.%) were prepared and the methane recovery experiments were carried out

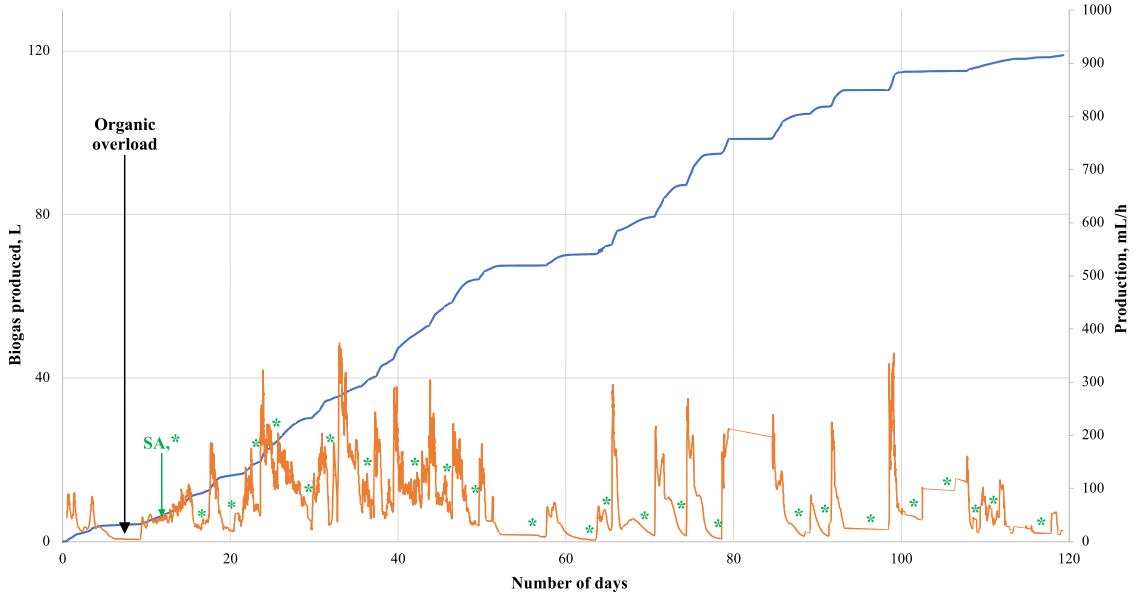

Fig. 3. Production rate and cumulative volume of biogas over time, including the timing of substrate addition (SA).

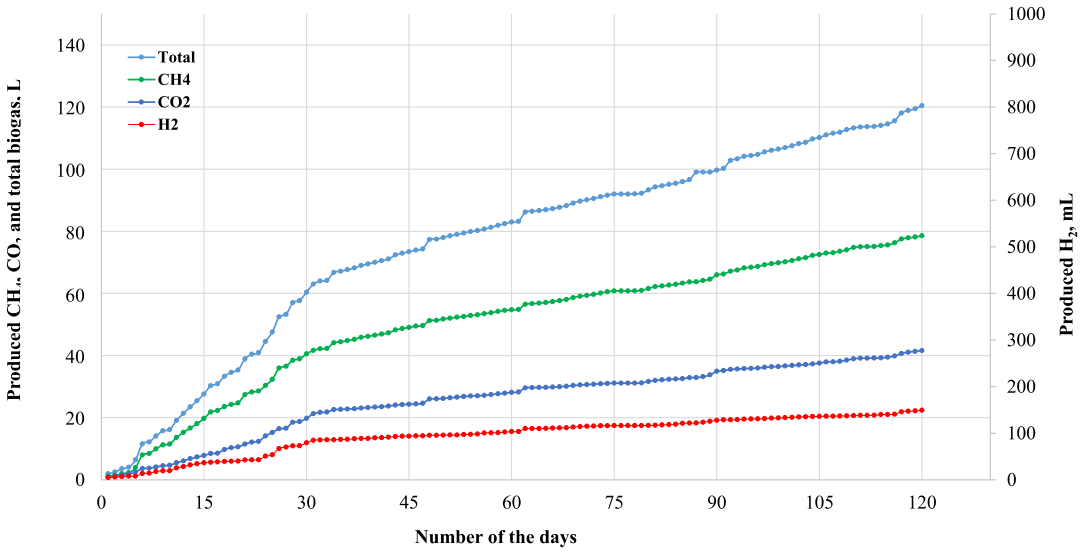

Fig. 4. Cumulative biogas production.

using PDMS hollow-fibre membrane contactor and the results were compared with the previous research work [27].

Fig. 5 demonstrates the methane recovery as a function of gas to liquid flow rate ratio in the case of the different methane/carbon dioxide mixtures supplied thoroughly into the reactor system. The results indicate that the share of methane in the biogas mixture had a small impact on the methane recovery, while the CH_4 recovery was slightly decreased by increasing the G/L ratio. Therefore, the investigation confirmed that the higher G/L ratio had a greater impact on CH_4 transport compared to the composition. It is related to the short residence time of the effluent inside the membrane module at higher liquid flow rates. This behaviour underlines the importance of mass transfer resistance at the liquid boundary layer for the transport of gases in hollow fibre membrane contactors. The permeate flux is reduced due to resistance to gas transfer, however, increasing the liquid flow rate decreases this resistance [17,28,53,54]. Previous studies by different researchers [17,37,55,56] have also presented similar observations.

It was also concluded that the higher CH_4 composition in the biogas mixture corresponded to the slightly higher CH_4 recovery percentages (Fig. 5). This effect was significantly higher in the previous study recorded for the synthetic effluent carried out in similar operating conditions [27].

Fig. 6 presents the comparative analysis of methane degassing experiments using synthetic effluents from previous work [27] and the real effluents in the current study. The results summarized that no significant increase in CH_4 recovery

(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 % 70 %); however, its impact in the case of synthetic effluent (17.8 ± 8.4 %, 47.6 ± 11.4 %, 52.2 ± 7.9 %) was more noticeable. It was also found that there were no significant alterations in the dissolved CH_4 concentration of the prefiltered effluent that was fed to the membrane (5.7 ± 0.8 mg L^{-1}, 4.9 ± 1.8 mg L^{-1}, 4.5 ± 1.1 mg L^{-1}) along with the experimental settings, indicating that the driving force to increase the dissolved CH_4 recovery was not significantly changing between the shell and lumen side of the module. The research findings with the real effluent showed that regardless of the CH_4 content of the biogas mixture, neither the CH_4 recovery nor the dissolved CH_4 concentration in the feed underwent significant changes. The results showed that under all test conditions, the dissolution of methane was observed to be significantly faster than the desorption of methane by the PDMS membrane. In other words, a steady dissolved methane concentration was maintained in the feed stream of the membrane, i.e., the prefiltered effluent purged with the different external binary methane/carbon dioxide mixtures at the flow

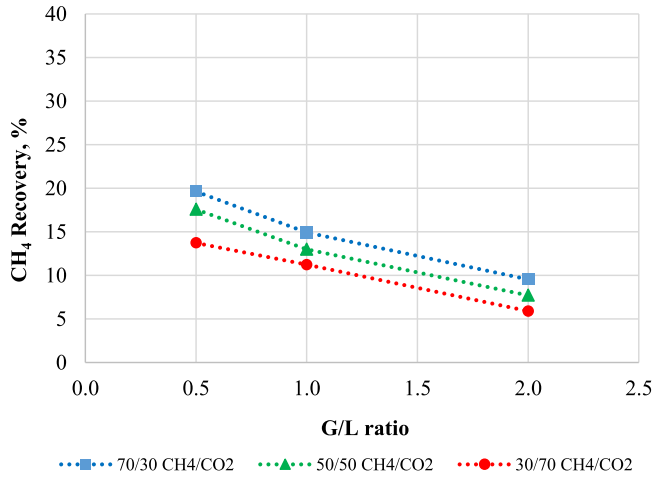

Fig. 5. Methane recovery from different effluents as a function of gas to liquid flow ratio.

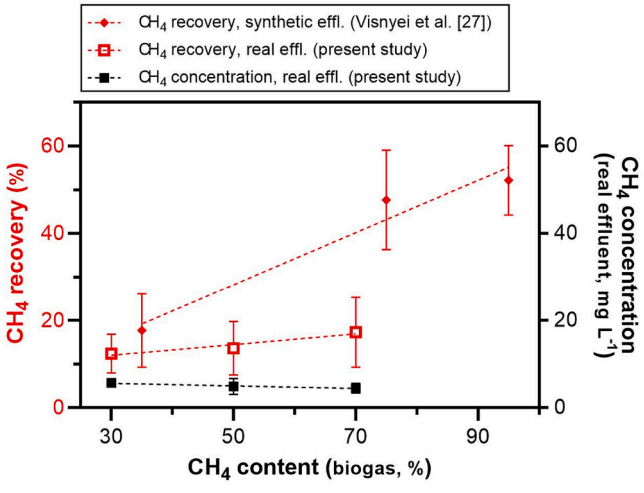

Fig. 6. Comparative data on the CH_4 recovery in real and synthetic effluents (G/L ratio: 1.0).

rate of 1 L d^{-1}. Consequently, any performance the membrane module achieved, it was not influenced by this factor. Moreover, although continuous methane extraction from the effluent by the membrane extraction step was undertaken, it was noted to be slower than the dissolution of methane into the effluent, which obviously compensated for the recovery percentages for CH_4 as 12.4 ± 4.4 %, 13.6 ± 6.1 %, 17.3 ± 8.0 % for the increasing CH_4 concentration in the real effluent as 30 %, 50 % 70 %, respectively.

Overall, the influence of the G/L ratio and CH_4 content in the biogas mixture on CH_4 recovery is shown in the 3D diagrams of Fig. 7. The illustration provides the response surfaces for synthetic effluents from previous work [27] and the real effluents in the current study, assuming linearity between the independent and dependent variables. From the visualised tendencies in Fig. 7a-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.

The methane recovery data observed with the synthetic effluent significantly surpassed that of the real effluent (Fig. 7b vs. Fig. 7a). In our opinion, this difference can be attributed to various effluent-related factors i.e. complexity or composition difference of the synthetic/real effluents. Moreover, flow regime and feeding conditions in the membrane module, such as lumen-to-shell (which was the case with the synthetic effluent in Visnyei et al. [27] as our previous work) vs. shell-to-lumen operation (which was the case with the real effluent in the present study to prevent internal clogging of the capillaries) may have contributed as well.

This observation that higher methane recovery could be attained with synthetic effluent compared to a real one is consistent with the previous works reported by other researchers [27,36,37]. By the end of the actual gas recovery experiments (taking 12 days in total), the membrane fouling effect was also noticed as an emerging phenomenon even though the sludge was pre-filtered, so it seems to be a challenge to pay attention to and a proper cleaning strategy of the module should be considered in the future to restore the performance of the degassing system when running in the longer-term. This limitation was once more emphasized in the comparative analysis between the real and synthetic effluents as feed streams revealing practical challenges. Removing the dissolved methane from the effluent, which was in the scope of this study, would improve the quality of fermentation effluent, however, quantification of standard wastewater quality parameters can give information whether there is a need for additional treatment of the bioreactor content.

4. Conclusions

This study primarily focuses on membrane-based methane recovery from the prefiltered effluent of a fed-batch anaerobic bioreactor. After 120 days of biogas production (120 litres), a PDMS hollow-fibre membrane contactor, together with a dissolved methane sensor was exploited for methane recovery from the prefiltered effluent. Investigation into the impact of sweep gas and liquid flow rates as well as the methane content of the biogas (as operating variables) highlighted the significance of gas to liquid flow ratio on methane transport. The results on methane recovery using the PDMS hollow-fibre membrane module were compared when real and synthetic effluents were utilized as feed streams, revealing differences with the real effluents. Recognizing challenges, such as dealing with fouling effects in real effluents, highlights the importance of investigating sustainable and viable methods for treating anaerobic effluents with membrane technology in order to recover dissolved methane and mitigate the related greenhouse gas emissions. Regarding the popularization of this technology in the future, challenges such as cost, technology readiness, and regulatory frameworks need to be addressed. Overall, the study presents a promising pathway towards sustainable waste management and renewable energy production, while requiring further efforts to overcome existing barriers towards widespread application.

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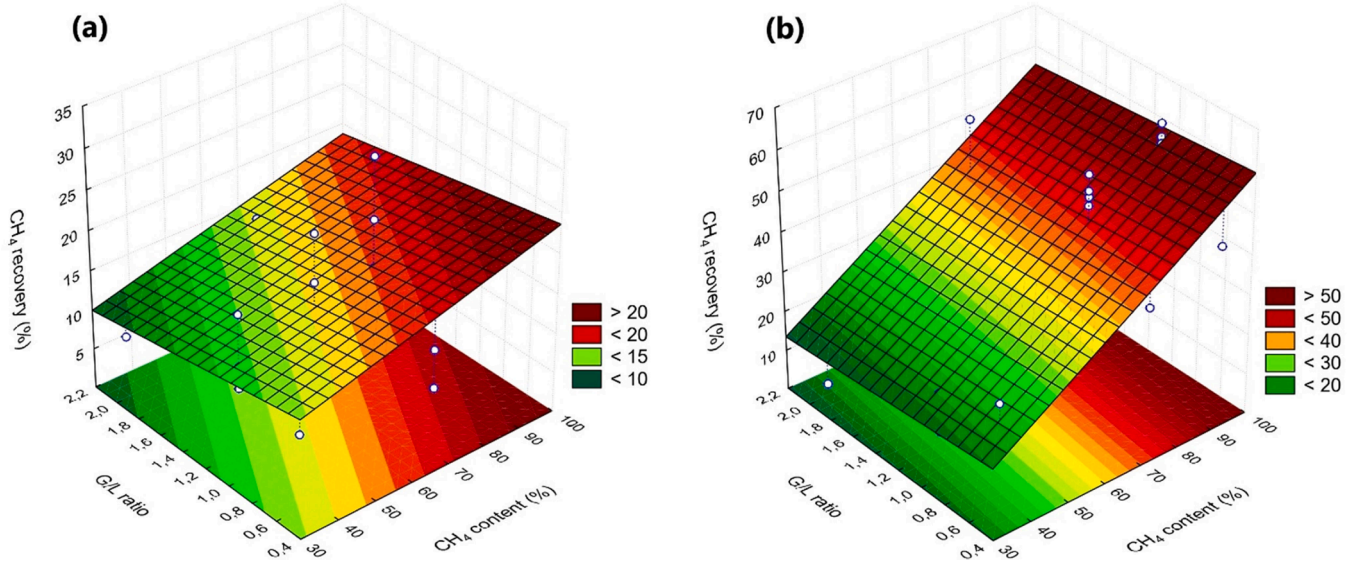

Fig. 7. Response surface for CH_4 recovery as a function of G/L ratio and share of CH_4 content in the gas mixtures produced from real anaerobic effluent (a) and previously done synthetic effluent (b) ($A_{PDMS\ module}$= 1 m^2). The Fig. 7b was taken from our previous paper (Visnyei et al. [27]) White dots: Experimental data. The plain response surfaces were fitted in Statistica 8.

CRediT authorship contribution statement

Merve Visnyei: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Péter Bakonyi:** Writing – review & editing, Visualization, Supervision, Investigation. **Tamás Rózsenberszki:** Writing – original draft, Methodology, Investigation. **László Koók:** Writing – review & editing, Visualization, Formal analysis. **Péter Komáromy:** Writing – review & editing, Investigation. **Katalin Bélafi-Bakó:** Writing – review & editing, Supervision. **Nándor Nemestóthy:** Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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