Comparative study of degassing membrane modules for the removal of
dissolved methane from EGSB anaerobic reactor effluent

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Abstract

The feasibility of an emergent technology for in situ removal/recovery of methane from
the effluent of anExpanded Granular Sludge Bed (EGSB) anaerobic reactor has been
studied. For this purpose, the performances of two commercial hollow fibre degassing
contactors with different membrane materials – microporous (polypropylene, PP) and
non-porous (polydimethylsiloxane, PDMS) – were compared. The influence of water
fluxes ($Q_l/A_{membrane}$ ranging from 22.6 to 377.4 L h$^{-1}$ m$^{-2}$), vacuum pressure (140 to 800
mbar), sweep gas fluxes ($Q_{N2}/A_{membrane}$ ranging from 0.14 to 4.44 m$^3$ h$^{-1}$ m$^{-2}$), and mode
of operation (liquid flowing in the lumen side or the shell side) was studied. Both
materials showed different behaviours with the variations in operational conditions. In
liquid flowing in the lumen mode operation, PP microporous membrane was slightly
more efficient under soft or mild operational conditions (low liquid flow and/or vacuum
pressure) but showed a wetting phenomenon when operational conditions were harder.
In shell side mode, PDMS was more efficient and no wetting phenomenon was
observed with this contactor. The differences have been explained, taking into account
the material properties (porosity, material resistance ...) of the membrane and structure (packing density, fibre diameter ...) of the modules. Methane removal efficiencies of up to 98% could be achieved, showing the viability of methane removal/recovery using this technology. Simultaneous degassing of CO₂ was also monitored in both modules, showing that the removal efficiency of this gas was considerably lower than for methane. In general terms, the removal of dissolved CO₂ followed a quite similar behaviour from that described for methane. Experimental overall mass transfer coefficients were also obtained.

**Keywords**

Anaerobic reactor; degassing; greenhouse gas emissions; membrane contactors;

methane recovery
1. Introduction

Anaerobic wastewater treatment is a widely used technology for industrial wastewaters. One of the advantages of the anaerobic treatment, compared to aerobic systems, is that the process produces methane, which can be used as fuel for the generation of electricity or heat for domestic and industrial use. In addition, anaerobic treatment presents important benefits such as lower production of solids, lower requirements for nutrients, lower energy requirements, and a smaller required volume (higher organic loads) than most conventional biological treatments [1].

Domestic and various industrial wastewaters, such as those from the malting industry, bottling processes, drink manufacturing plants, and breweries, are conventionally discharged at moderate to low temperature. The conventional mesophilic anaerobic treatment of such wastewaters (35 to 40 ºC) implies the heating of the reactor content in a more complex system with extra energy consumption from the biogas produced. In some industrial applications, these drawbacks limited the application of this treatment. In this context, some investigations have focused on the study of anaerobic treatment at low temperatures (psychrophilic conditions) for different industrial wastewaters [2–6]. The feasibility of this technology is nowadays proven, and in some cases it can be considered as a convenient option. Nevertheless, low wastewater temperature processes involve a significant quantity of residual dissolved methane (D-CH₄) present in the water effluent of the reactor, as methane solubility rises with the decrease of temperature. The recovery of the residual D-CH₄ in the anaerobic effluent is important for several reasons. Firstly, D-CH₄ discharge of these kinds of effluents represents a loss of a potential energy source. In addition, emissions with D-CH₄ can also generate explosive atmospheres when the effluent is discharged to drain or into other closed containers, so it is important to adhere to the safety requirement of keeping the methane
concentration in air below the Lower Explosive Limit (5% v/v). Finally, D-CH₄ discharge causes an important carbon footprint to the environment due to fugitive emissions of CH₄ [7,8], as the global warming potential of methane is 28 times higher than that of carbon dioxide [9].

The removal of dissolved gases from liquids is conventionally achieved with vacuum packed towers. These columns are filled with packing that creates a large surface area for the contact of liquid and gas phases. Nevertheless, in this system, the direct contact of liquid and gas phases can frequently lead to problems such as foaming, flooding, and emulsions. Among the alternative technologies under investigation for the removal of dissolved gas from anaerobic effluents, one can find methods such as micro-aeration using biogas containing air or biological oxidation. Nevertheless, these methods also present drawbacks such as low concentration in the removed gas and/or low recovery efficiency [10–12]. It seems that improvement of the existing process, development of new processes, or both are needed in order to minimize the discharge of D-CH₄.

In this context, degassing membrane (DM) contactors have appeared as an emergent technology that is being used to remove dissolved gases in several processes. The main advantage of this technology is related to the fact that a gas and a liquid phase come into contact in the pore of the membrane, without the need for dispersion of one phase into another, allowing previously mentioned problems to be avoided [13]. DM contactors present other advantages over conventional dispersed phase contactors, such as availability at high and low flow rates as they are modular, ease of scaling up, a wide range of capacities by adding or removing membrane modules, a high interfacial area per volume unit, and high efficiency. Nevertheless, DM contactors can also have some disadvantages such as membrane resistance to mass transfer, bypassing in the shell side,
fouling problems, and limitations with regard to pressure drop [14], so investigations like the one presented in this work are still necessary.

A hollow fibre module is the most common configuration used in DM contactors in order to remove gases such as CO₂ and O₂ from a liquid phase, so a considerable number of studies related to the removal or recovery of these gases can be found [15–21]. This technology seems especially interesting in some industrial processes where the removal of dissolved gases is crucial, such as in the process of production of ultrapure water, in which one of the major contaminants is the dissolved oxygen, whose removal is essential [15,19]. Unfortunately, studies on the removal of D-CH₄ from anaerobic effluents are still very scarce. Bandara et al. studied D-CH₄ recovery by degasification from the effluent of a bench-scale upflow anaerobic sludge blanket (UASB) reactor treating synthetic wastewater [22]. They used a multi-layered composite hollow fibre degassing module made of polyethylene and polyurethane under vacuum pressure. Cookney et al. studied the recovery of D-CH₄ from a low-temperature (16 ºC) anaerobic process treating domestic wastewater with a polydimethylsiloxane membrane contactor using nitrogen as sweep gas [23]. Recently, Cookney et al. studied the desorption of D-CH₄ from both synthetic and real anaerobic effluents using different membrane hollow fibres [24]. Further research in this field is needed to improve and deepen the knowledge and performance of this technology.

The selection of a suitable membrane is a crucial factor for optimal contactor performance, since membrane material properties can significantly affect the overall mass transfer. In this sense, the porosity of the polymeric material for contactor devices applied to water treatment can have a positive influence on the permeability of dissolved gas but a negative effect on the flooding prevention of the membrane material [25].
The main objective of this work was to investigate the performance of two DM 111
contactors in the recovery of D-CH₄ from a recirculating stream of a lab-scale Expanded 112
Granular Sludge Bed (EGSB) anaerobic reactor. Two different materials for the 113
membrane of the hollow fibre membrane modules are compared: polypropylene (PP, 114
microporous) and polydimethylsiloxane (PDMS, non-porous). The effects of liquid 115
flux, vacuum pressure, sweep gas flow rate, and operating mode (lumen and shell sides) 116
were investigated. The removal of dissolved carbon dioxide (D-CO₂) was also 117
monitored to study the simultaneous removal of both gases.

2. Experimental

2.1. Degassing membrane modules

This study employed two types of hollow fibre membrane contactors, which were 121
selected as representative of two different and efficient types of commercial modules for 122
industrial applications with different porosity properties. The first module was 123
PDMSXA-250, a membrane contactor with fibres of polydimethylsiloxane (PDMS, 124
non-porous) with an internal surface area (Aᵢ) of 0.0159 m², supplied by PermSelect, 125
MedArray Inc. (USA). The second module was the 1 × 5.5 MiniModule supplied by 126
Liqui-Cel, Membrana GmbH (Germany). This contactor was made of polypropylene 127
(PP, microporous) fibres with an Aᵢ of 0.18 m². The main characteristics of both 128
modules are summarized in Table 1. 129

Since both modules have different physical properties, including different sizes, in order 130
to compare behaviours and performances between the two contactors, the characteristic 131
parameter defined as the water flux rate (Qᵢ/Aᵢ,e, liquid flow rate per the membrane 132
surface, L h⁻¹ m⁻²) has been widely used.
### Table 1. Characteristics of PDMS and PP modules

<table>
<thead>
<tr>
<th></th>
<th>PDMS</th>
<th>PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of fibres</td>
<td>320</td>
<td>2300</td>
</tr>
<tr>
<td>Effective length, m</td>
<td>0.083</td>
<td>0.1397</td>
</tr>
<tr>
<td>Inner diameter, μm</td>
<td>190</td>
<td>220</td>
</tr>
<tr>
<td>Outer diameter, μm</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Pore diameter, μm</td>
<td>Non-porous</td>
<td>0.04</td>
</tr>
<tr>
<td>Internal area (A_i), m^2</td>
<td>0.0159</td>
<td>0.180</td>
</tr>
<tr>
<td>External area (A_o), m^2</td>
<td>0.0250</td>
<td>0.303</td>
</tr>
<tr>
<td>Shell tube inner diameter, m</td>
<td>0.016</td>
<td>0.025</td>
</tr>
<tr>
<td>Packing fraction</td>
<td>0.113</td>
<td>0.33</td>
</tr>
<tr>
<td>Maximum flow rate (Q_L), L h^-1</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>N_2 flow rate, L h^-1</td>
<td>26.0–800</td>
<td>2.7–27.0</td>
</tr>
</tbody>
</table>

### 2.2. Experimental setup and procedure

A laboratory-scale EGSB anaerobic reactor was operated at 25 °C for more than 24 months. The EGSB reactor was initially inoculated with 4 L of granular anaerobic sludge from the wastewater treatment plant of a local brewery. The reactor treated 8 L d^-1 of synthetic wastewater polluted with ethanol with an organic load rate of 32 kg chemical oxygen demand (COD) m^-3 d^-1. A high recirculation flow was kept to expand the sludge bed with an upflow velocity of 10.7 m h^-1. Similar work conditions were used in the study of Lafita et al. [26]. A liquid–gas separator device was placed at the top of the reactor, and the biogas was collected through a sodium hydroxide solution. The methane flow rate was periodically monitored with a biogas flow meter (MGC-10 PMMA, Ritter, Germany) and the pH and conductivity with a multi parameter sensor (pH/Cond 340i WTW, Germany). Alkalinity, volatile fatty acids (VFA), COD, and nutrient concentration in the inlet and outlet of the reactor were analysed according to standard methods [27]. A scheme of the EGSB reactor and the DM contactor is shown...
in Fig. 1. A detailed description of the system and procedure can be found elsewhere [6].

Fig. 1. Scheme of the setup of the EGSB reactor and degassing membrane modules

Membrane modules were coupled to the EGSB reactor and feed with a fraction of the flow from the recirculation stream, in which the concentration of the D-CH₄ was similar to that in the effluent stream. The stream flowed through a 40 μm filter to minimize membrane fouling, and then through the contactors, using a peristaltic pump (Watson-Marlow, USA), resulting in flow rates ranging from 0.36 to 10.80 L h⁻¹ for the PDMS module and from 4.1 to 27.2 L h⁻¹ for the PP module. For vacuum pressure experiments, a vacuum pump N026.3.AT.18 (KNF Neuberger, Germany) was used for the vacuum operation, giving vacuum pressures (Pᵥₐₑ) of 140, 500, and 800 mbar. For countercurrent sweep gas experiments, nitrogen gas with a high purity (> 99.8%) supplied by Carburos Metálicos S.A. (Spain) was introduced into the contactors in a range of flow rates between 2.7 and 27.0 L h⁻¹ (STP) for the PDMS module and between 26.0 and 800 L h⁻¹ (STP) for the PP module, using a mass flow controller (Bronkhorst Hi-Tec, The
Netherlands). The liquid pressures at the inlet and outlet of the membrane were measured using an MP 112 portable manometer (Kimo, Spain).

DM contactors were operated in two modes. Initially, experiments with the liquid flowing in the lumen side and vacuum pressure or sweep gas applied in the shell side (lumen side mode) were carried out. Afterwards, the opposite operation mode was studied (shell side mode).

**2.3. Evaluation of membrane contactor performance**

The determination of dissolved CH₄ and CO₂ was carried out with a headspace method. Liquid samples of 50 mL were collected at the inlet and outlet of membranes and were injected in sealed vials of 125 mL prefilled with helium. The vials were shaken vigorously for 30 seconds and left at 25 ºC for 3 hours in an orbital shaker to allow the gases to equilibrate. After equilibration, 0.5 mL of the headspace gas was injected into a gas chromatograph (Agilent GC 7820A, Spain) equipped with Agilent HP-PLOT/Q and Agilent HP-MOLESIEVE columns. The concentration of D-CH₄ and D-CO₂ in liquid phase was calculated as:

\[
C_L = \frac{C_G (V_G + H V_L)}{V_L} \tag{1}
\]

where \(C_L\) is the concentration of D-CH₄ or D-CO₂ in liquid phase (mg L⁻¹), \(C_G\) is the concentration of CH₄ or CO₂ in the headspace after equilibration (mg L⁻¹), \(V_L\) and \(V_G\) are the volumes of liquid and gas space in the vial, respectively (mL), and \(H\) is the dimensionless Henry’s law constant for methane (29.55) and carbon dioxide (1.20) at 25 ºC [28].

The performance of the degassing module was evaluated with the removal efficiency (RE, %) of the membrane, defined as:

\[
\text{RE} = \frac{C_{L_{in}} - C_{L_{out}}}{C_{L_{in}}} \times 100\%
\]
where $C_{L1}$ and $C_{L2}$ are the concentrations of D-CH$_4$ or D-CO$_2$ in liquid phase (mg L$^{-1}$) at the inlet and outlet of the membrane module, respectively. Samples from the inlet and outlet were taken in duplicate and analysed in triplicate. The average values of the measures and standard deviation are presented in the figures and tables.

Cleaning of the DM module with deionized water in countercurrent flow was done after every experiment. A control experiment was repeated every month to ensure that the DM module was operating without fouling and the RE was maintained at the same value.

Analysis of mass transfer is important to evaluate the performance of membrane contactor operations. Assuming negligible mass transfer resistance into gas phase, the experimental overall mass transfer coefficient ($K_{exp}$, m s$^{-1}$) can be determined from the liquid phase mass balance in the contactor by the following differential expression:

$$Q_L \frac{dC}{dA} = - K_{exp} (C_L - C_L^*)$$

(3)

where $Q_L$ is the liquid flow rate (m$^3$ s$^{-1}$), $A$ is the interfacial area (m$^2$), $C_L$ is the concentration of CH$_4$ or CO$_2$ in the liquid phase (mg L$^{-1}$), and $C_L^*$ is the equilibrium concentration of these species in the liquid phase (mg L$^{-1}$), resulting in:

$$C_L^* = H \cdot C_G$$

(4)

Integrating the above equation between inlet and outlet concentrations ($C_{L1}$ and $C_{L2}$) and assuming negligible variation of concentration in the gas phase,

$$K_{exp} = - \frac{Q_L}{A} \ln \left( \frac{C_{L2} - C_L^*}{C_{L1} - C_L^*} \right)$$

(5)
When it can be assumed that the concentration of each actively transferring specie in the gas phase is very low, the equilibrium concentration in liquid phase is negligible compared to the actual concentration in the liquid phase \((C_L \gg C_L^*; C_L - C_L^* \approx C_L)\), and Eq. (5) can be simplified to:

\[
K_{\text{exp}} = -\frac{Q_L}{A} \ln \frac{C_{L2}}{C_{L1}}
\]  

3. Results and discussion

3.1. Anaerobic reactor performance

During start-up of the EGSB anaerobic reactor, the organic load rate of ethanol was increased gradually for two weeks from 5 to 32 kg COD m\(^{-3}\) d\(^{-1}\) and the EGSB reactor was operated during two years at the maximum organic load rate. After the shutdown of the reactor during the vacation period, the system was restarted with new sludge.

The EGSB reactor achieved a removal rate of around 31.4 kg COD m\(^{-3}\) d\(^{-1}\), resulting in a COD removal efficiency of 98%. The biogas composition was 77% (v/v) CH\(_4\) and 23% (v/v) CO\(_2\) and the methane flow rate was 1.65 L h\(^{-1}\). The VFA concentration was kept lower than 5 mg CH\(_3\)COOH L\(^{-1}\). These results are in agreement with those obtained previously in the same reactor under similar operational conditions [26]. The average D-CH\(_4\) concentration measured in the water effluent of the reactor was around 30 mg L\(^{-1}\). This indicates an oversaturation of the anaerobic effluent by a factor of 2 with respect to the equilibrium D-CH\(_4\) of 15 mg L\(^{-1}\) (estimated from a composition of 77% CH\(_4\) and the Henry’s constant at 25 °C) under experimental conditions. D-CH\(_4\) oversaturation is commonly observed in UASB reactors with oversaturation factors ranging from 1.6 to 6.9 [10, 23, 29]. The average measured D-CO\(_2\) concentration was
around 250 mg L$^{-1}$ and no oversaturation was observed with respect to the equilibrium (345 mg L$^{-1}$).

No significant effect on the EGSB performance was observed when the degassing operation was carried out on the recirculation stream in discontinuous mode; COD removal, biogas production and composition, and effluent quality were not affected. These results are in agreement with those of Luo et al. [30], who stated that COD removal efficiency and CH$_4$ yield were not affected in a UASB when a DM was coupled to the recirculation stream of a reactor. Bandara et al. [31] reported that no significant differences were observed in total methane production when a degassing membrane was submerged in the bulk liquid of a UASB reactor.

3.2. Effect of time on-stream

A fast approach to the stationary state was observed when the D-CH$_4$ concentration at the outlet ($C_{L2}$) of both membrane modules was monitored over time. In Fig. 2 and Fig. 3, the results of two representative experiments under different operational conditions are shown with PDMS and PP modules, respectively. As expected, $C_{L2}$ initially decreased with the time of operation and was almost constant after 60 min. Thus, in this study, the membrane performance results were those obtained after a minimum of 60 minutes of operation, considering the stationary state values.
3.3. Effect of vacuum pressure and sweep gas flow rate

In order to evaluate the influence of $P_{\text{vac}}$ on the methane RE, both DM contactors were operated in lumen side mode under $P_{\text{vac}}$ conditions ranging from 140 to 800 mbar while maintaining a constant water flux rate ($Q_{L}/A_{i}$). The results at a $Q_{L}/A_{i}$ of 22.64 L h$^{-1}$ m$^{-2}$ can be seen in Fig. 4. An increase of RE with the rise of $P_{\text{vac}}$ was observed as the concentration gradient increased with the $P_{\text{vac}}$, and therefore degassing of D-CH$_4$ from the liquid phase is favoured. In both contactors, a practically linear increase of the RE was observed under the operational conditions studied, with values between 60 and 77% for PDMS membrane and between 69 and 93% for PP membrane. These values are similar to those described in previous degassing of O$_2$ and CH$_4$ studies under similar vacuum conditions [16,23,32]. Like this work (Fig. 4), these studies showed an increase in the RE with the rise of vacuum pressure. Cookney et al. [23] studied CH$_4$ removal from an anaerobic effluent using values of $P_{\text{vac}}$ from 0.5 to 380 mbar and obtained a maximum RE of around 80%. Ito et al. [16] and Tan et al. [32] evaluated O$_2$ removal from water under varying vacuum conditions from 500 to 960 mbar and from 200 to
960 mbar, respectively, with a maximum RE of 80% in both cases. The variations of RE with P\textsubscript{vac} seem to indicate that the equilibrium concentration in liquid phase (C\textsubscript{L}*) was not negligible compared with the concentration in liquid phase (C\textsubscript{L}). This fact was corroborated experimentally with C\textsubscript{L}* values not much lower than concentrations in liquid phase. Moreover, an increasing vacuum results in decreasing C\textsubscript{L}*. As can be observed in Fig. 4, the PP module showed a higher RE than the PDMS one, at least under the tested operational conditions (relatively low Q\textsubscript{L}/A\textsubscript{i}). The better performance of porous membranes can be related to their lower resistance to the mass transfer through the polymer. The different behaviours of porous and non-porous membranes have also been pointed out by Ozturk and Hughes [21], who evaluated the performance of both modules for the removal of CO\textsubscript{2} using absorbent solvents, and found a better performance of the porous membrane module.

![Graph showing the effect of P\textsubscript{vac} on RE at Q\textsubscript{L}/A\textsubscript{i} of 22.64 L h\textsuperscript{-1} m\textsuperscript{-2} in lumen side operation.](image)

The effect of flux of sweep gas (Q\textsubscript{N2}/A\textsubscript{i}) on methane RE was also studied. For this purpose, DM contactors were operated in the lumen side mode at a fixed Q\textsubscript{L}/A\textsubscript{i} of 113.21 L h\textsuperscript{-1} m\textsuperscript{-2} while varying Q\textsubscript{N2}/A\textsubscript{i} from 0.17 to 1.70 m\textsuperscript{3} h\textsuperscript{-1} m\textsuperscript{-2} for PDMS contactor and from 0.14 to 4.44 m\textsuperscript{3} h\textsuperscript{-1} m\textsuperscript{-2} for PP contactor. As can be observed in Fig. 5, at low...
values of $Q_{N2}/A_i$, an increase in the RE was achieved with an increase of $Q_{N2}/A_i$.

Nevertheless, at higher values of $Q_{N2}/A_i$, no improvement in the RE was observed. The limit value of $Q_{N2}/A_i$ from which the RE was constant also depends on the $Q_L/A_i$, as can be seen in Fig. 6, where an increase in the RE was observed with the increase of $Q_{N2}/A_i$ for high values of $Q_L/A_i$ (377.4 L h$^{-1}$ m$^{-2}$). A constant RE with an increase of gas side hydrodynamics has also been reported by Cookney et al. [23,24]. Facts such as the almost negligible gas phase mass transfer resistance and the low partial pressure of methane in the sweep gas can explain this behaviour [32]. In these experiments, the PP module again presented higher RE than the PDMS module, although RE was quite similar at this intermediate $Q_L/A_i$.

![Graph](image)

**Fig. 5.** Effect of $Q_{N2}/A_i$ on the RE at $Q_L/A_i$ of 113.21 L h$^{-1}$ m$^{-2}$ in lumen side operation.

The decision to operate in vacuum or sweep gas modes for the removal of D-CH$_4$ depends on different factors that should be taken into account, such as the D-CH$_4$ RE, reuse of the recovered compound, and energy consumption. Regarding the performance of the D-CH$_4$ removal, in the PDMS module (Fig. 6), a higher RE was achieved under vacuum operation than under sweep gas operation, although at low values of $Q_L/A_i$, values of RE were very similar in both modes of operation. On the contrary, in the PP
module (Fig. 7), RE values were slightly higher in sweep gas operation. Considering the energy consumption, Vallieres and Favre [33] highlighted that at industrial scale, sweep gas operation consumed less raw energy than vacuum operation, except when a low vacuum pressure can be practicable. Nevertheless, vacuum operation is preferred when it is desired to recover pure or high-purity components to reuse them as a source of energy. In this case, sweep gas operation would involve a subsequent purification step that would increase the overall energy consumption, so vacuum operation can be considered as the most feasible solution for reusing the recovered gas.

![Fig. 6. PDMS module performance in the lumen side mode and different operating conditions.](image)

![Fig. 7. PP module performance in the lumen side mode and different operating conditions.](image)

3.4. Effect of liquid flux rate

To evaluate the effect of liquid flux rate on the methane RE, a set of experiments was carried out in a range of values of $Q_L/A_i$ from 22.6 to 377.4 L h$^{-1}$ m$^{-2}$ with the water flowing through the lumens. The results obtained at $P_{vac}$ of 500 mbar are presented in Fig. 8. As was expected for both modules, the D-CH$_4$ RE decreased when the $Q_L/A_i$ was increased, a behaviour commonly observed in degassing operations with hollow fibre membranes for both porous and non-porous materials [20,24,34].
As can be seen in Fig. 8, DM modules showed a different behaviour, with a more pronounced decrease of RE in the PP module at intermediate values of $Q_L/A_i$, changing from being more efficient than the PDMS module at low water fluxes ($< 90 \text{ L h}^{-1} \text{ m}^{-2}$) to less efficient in the removal of D-CH$_4$ at the highest water fluxes ($> 90 \text{ L h}^{-1} \text{ m}^{-2}$). This phenomenon can be associated with the wetting of hydrophobic microporous membranes, in which the pores of the microporous membrane can be totally or partially filled with the liquid phase. This behaviour was corroborated by the estimation of the experimental mass transfer coefficient (Eq. 5). In Fig. 9, the effect of $Q_L/A_i$ on experimental mass transfer coefficients ($K_{exp}$) at a vacuum pressure of 500 mbar is shown. The obtained values of overall mass transfer coefficients were comparable to that previously reported by Sinha and Li for O$_2$ removal from water with a PP microporous membrane [17], those reported by Cookney et al. [24] for D-CH$_4$ removal with PP and PDMS, and overall mass transfer values obtained by Bhaumik et al. [15] for CO$_2$ and O$_2$ removal from deionized water. The value of $K_{exp}$ increased with the rise of $Q_L/A_i$ for the PDMS module, with values between $1.65 \times 10^{-5}$ and $8.75 \times 10^{-5}$ m s$^{-1}$. Nevertheless, for the PP module, $K_{exp}$ increased from $1.08 \times 10^{-5}$ to $2.94 \times 10^{-5}$ m s$^{-1}$ at low values of $Q_L/A_i$ but a decrease to $1.80 \times 10^{-5}$ m s$^{-1}$ was observed at values of $Q_L/A_i$ higher than 90 L h$^{-1}$m$^{-2}$. An analogous behaviour of $K_{exp}$ was observed in experiments carried out under lumen side operation.
out at 180 and 500 mbar of vacuum pressure. During the wetted operation, the
membrane resistance to mass transfer increased, so the $K_{\text{exp}}$ value for the PP module
decreased, which affected the efficiency of the membrane. This phenomenon has been
reported in similar applications with porous membranes [17,35]. Pore wetting
essentially depends on the operating pressure [36,37], although other factors such as
characteristics of the material, the nature of liquid in contact with the membrane, and
membrane fouling are also important [38,39]. The entry pressure was evaluated for the
PP module between water flux values of 22.6 and 151.0 L h$^{-1}$ m$^{-2}$, resulting in pressure
values from 1080 to 1247 mbar. A sharp increase of the entry pressure was noted at
water fluxes higher than 90 L h$^{-1}$ m$^{-2}$, which is probably the cause of the wetting
phenomenon mentioned previously.

![Graph](image)

**Fig. 9** Effect of $Q_L/A_i$ on $K_{\text{exp}}$ at a $P_{\text{vac}}$ of 500 mbar in lumen side operation.

This higher stability of dense composite fibres compared with microporous materials
has been shown in other applications of absorption/desorption [40], where the PP
module shows a high sensitivity toward wetting conditions. Keeping the operational
conditions below the critical pressure in which wetting occurs would be the key
parameter for stable and high-efficiency operation of the PP module at industrial scale.
The selection of suitable operational conditions and type of membrane for this
application seems crucial. While the microporous module provides greater efficiency at lower flow rates (pressure), when the operation requires higher liquid flow rates the non-porous membrane shows better performance.

### 3.5. Effect of mode of operation: lumen and shell side operation

In Table 2, experiments on both DM modules operating in the lumen side and shell side modes are shown in order to compare D-CH₄ RE. Experiments were carried out at a constant Qᵢ/Aᵢ, where the wetting phenomenon was not observed. As can be seen, higher RE values were achieved in lumen side operation for both DM modules, independently of the operating conditions. As the Reynolds numbers (Re) were quite similar in both modes of operation for each module, the worst performance in the shell side mode can be attributed to the channelling phenomenon that can occur when liquid passes through the shell of the module and not all fibres of the module properly contribute to D-CH₄ RE. The channelling phenomenon was also observed in the removal of dissolved oxygen from water by DM contactors [20,41]. No significant effect of QN₂/Aᵢ on the performance of both modules was observed for shell and lumen side operations.

<table>
<thead>
<tr>
<th>DM module</th>
<th>Pᵥac, mbar</th>
<th>QN₂/Aᵢ, m³ h⁻¹ m⁻²</th>
<th>RE₈₇⁴ CH₄, %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lumen side</td>
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<tr>
<td>PDMS</td>
<td>800</td>
<td>0.17</td>
<td>77.2 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.70</td>
<td>74.0 ± 4.1</td>
</tr>
<tr>
<td>PP</td>
<td>800</td>
<td>–</td>
<td>93.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.44</td>
<td>98.5 ± 0.9</td>
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<tr>
<td></td>
<td>800</td>
<td>4.44</td>
<td>97.2 ± 0.7</td>
</tr>
</tbody>
</table>

Comparing the performance of the two DM contactors (Table 2), as previously described for lumen side operation, the PP module showed higher removal efficiency.
than the PDMS module, but the opposite was observed in shell side operation. This difference in the behaviour of the DM contactors could be related to the different packing densities of the two modules, since a lower packing density could promote a higher mass transfer coefficient in shell side operation [42,43]. As can be observed in Table 1, the PDMS module showed a lower packing density, and therefore a higher mass transfer rate should be achieved with this contactor, assuming that the main mass transfer resistance is associated with liquid flow mass transfer. In the shell side mode and at a \( Q_l/A_i \) value of 22.6 L h\(^{-1}\) m\(^{-2}\), the calculated \( K_{exp} \) resulted in 0.87 and 0.19 m s\(^{-1}\) for the PDMS and PP modules, respectively.

The pressure at the inlet and outlet of the DM modules was measured in lumen and shell side operation and the liquid pressure drop (\( \Delta P \)) was calculated (Fig. 10 and Fig. 11). In both modules, the \( \Delta P \) at the lumen side is higher than the \( \Delta P \) at the shell side. This fact indicates why the shell side mode is the preferred one in real industrial operations or treatments since it minimizes problems such as high pressure drops and fouling, which can limit the flow capacity of the modules. Thus, some design modifications to improve the RE in shell side operation have been studied, such as the use of a transverse-flow design of the contactor in industrial modules to enhance the flow hydrodynamics [34]. Comparable results and analogous behaviour have been found in previous studies for different hollow fibre membrane contactors [18,20].

The pressure drop is higher for the PP module than for the PDMS module for a similar liquid velocity. In lumen side operation, a greater length and porosity of the PP module involve a higher pressure drop. In shell side operation, similar values for pressure drop were obtained for both modules.
3.6. Degassing of CO$_2$

A summary of the most representative results of CO$_2$ degassing of the samples can be found in Table 3. The wetting phenomenon was not observed for PP in the operating conditions described in this table. In general, lower D-CO$_2$ RE is achieved compared with D-CH$_4$ removal under the same conditions, especially for experiments carried out under vacuum pressure conditions. Nevertheless, the behaviour of both modules in the case of CO$_2$ removal was quite similar to that observed for CH$_4$ removal. As for D-CH$_4$ removal, both modules showed higher RE in lumen side operation than in shell side operation.

In lumen side operation, the PP module is more efficient that the PDMS module at low water flux rates. The contrary behaviour is observed in shell side operation, in which the PDMS contactor gives a higher RE, possibly related to its lower packing density value, as has been mentioned previously.
The most significant differences were observed under vacuum pressure conditions, in which notably lower performances were achieved for D-CO$_2$ removal than in sweep gas operation.

Table 3. Effect of operating mode, $P_{\text{vac}}$ and $Q_{\text{N2}}/A_i$ on the D-CO$_2$ RE. $Q_L/A_i = 22.64$ L h$^{-1}$ m$^{-2}$.

<table>
<thead>
<tr>
<th>DM module</th>
<th>$P_{\text{vac}}$, mbar</th>
<th>$Q_{\text{N2}}/A_i$, m$^3$ h$^{-1}$ m$^{-2}$</th>
<th>RE$_{\text{CO2}}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lumen side</td>
<td>Shell side</td>
<td></td>
</tr>
<tr>
<td>PDMS</td>
<td>800</td>
<td>28.7 ± 3.1</td>
<td>25.8 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>58.0 ± 2.3</td>
<td>33.1 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>– 0.17</td>
<td>57.4 ± 3.2</td>
<td>37.1 ± 4.1</td>
</tr>
<tr>
<td></td>
<td>– 1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>800</td>
<td>31.1 ± 3.6</td>
<td>15.3 ± 4.7</td>
</tr>
<tr>
<td></td>
<td>– 0.44</td>
<td>77.1 ± 1.9</td>
<td>19.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>– 4.44</td>
<td>80.3 ± 1.5</td>
<td>29.0 ± 0.2</td>
</tr>
</tbody>
</table>

4. Conclusions

The methane degassing capabilities over an EGSB effluent reactor of two commercially available small DM contactors with different membrane materials – microporous (polypropylene, PP) and non-porous (polydimethylsiloxane, PDMS) – have been tested and compared. Not very large differences in performance of the two modules were observed. In lumen mode operation, the PP contactor showed better performance under soft or mild operational conditions (e.g. low liquid flow and/or vacuum pressure), but the wetting phenomenon occurred when the liquid flow rate was increased. In shell side mode, PDMS was more efficient and no wetting phenomenon was observed with this contactor.

For both membranes, the results obtained in vacuum pressure experiments showed that the concentration of methane specie in the gas phase was not low enough to consider that equilibrium concentration in liquid phase was negligible compared to the actual concentration in the liquid phase ($C_L >> C_L^*$; $C_L - C_L^* \approx C_L$). The opposite was observed in sweep gas operation, where the influence of the nitrogen flow rate was
negligible, from relatively low nitrogen fluxes, showing that the gas phase mass transfer resistance was almost negligible.

Lumen mode operation was more efficient, but the pressure drop was considerably higher than in shell mode operation, especially for the highest water flow rates.

Methane removal efficiencies ranging from 25 to 98% under experimental conditions can be achieved, showing the viability of methane removal/recovery using this technology.

Simultaneous degassing of CO₂ was considerably less efficient than that observed for CH₄, and the general behaviour of the DM contactors was quite similar to that obtained for CH₄.

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References


