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4 Comparative study of degassing membrane modules for the removal of

5 dissolved methane from EGSB anaerobic reactor effluent

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10 **Abstract**

11 The feasibility of an emergent technology for in situ removal/recovery of methane from

12 the effluent of an Expanded Granular Sludge Bed (EGSB) anaerobic reactor has been

13 studied. For this purpose, the performances of two commercial hollow fibre degassing

14 contactors with different membrane materials – microporous (polypropylene, PP) and

15 non-porous (polydimethylsiloxane, PDMS) – were compared. The influence of water

16 fluxes ($Q_L/A_{membrane}$ ranging from 22.6 to 377.4 L h^{-1} m^{-2}), vacuum pressure (140 to 800

17 mbar), sweep gas fluxes ($Q_{N2}/A_{membrane}$ ranging from 0.14 to 4.44 m^3 h^{-1} m^{-2}), and mode

18 of operation (liquid flowing in the lumen side or the shell side) was studied. Both

19 materials showed different behaviours with the variations in operational conditions. In

20 liquid flowing in the lumen mode operation, PP microporous membrane was slightly

21 more efficient under soft or mild operational conditions (low liquid flow and/or vacuum

22 pressure) but showed a wetting phenomenon when operational conditions were harder.

23 In shell side mode, PDMS was more efficient and no wetting phenomenon was

24 observed with this contactor. The differences have been explained, taking into account

25   the material properties (porosity, material resistance …) of the membrane and structure

26   (packing density, fibre diameter …) of the modules. Methane removal efficiencies of up

27   to 98% could be achieved, showing the viability of methane removal/recovery using this

28   technology. Simultaneous degassing of CO_2 was also monitored in both modules,

29   showing that the removal efficiency of this gas was considerably lower than for

30   methane. In general terms, the removal of dissolved CO_2 followed a quite similar

31   behaviour from that described for methane. Experimental overall mass transfer

32   coefficients were also obtained.

33   **Keywords**

36

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-CH_4) present in the water effluent of the reactor, as methane solubility rises with the decrease of temperature. The recovery of the residual D-CH_4 in the anaerobic effluent is important for several reasons. Firstly, D-CH_4 discharge of these kinds of effluents represents a loss of a potential energy source. In addition, emissions with D-CH_4 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

62   concentration in air below the Lower Explosive Limit (5% v/v). Finally, D-CH_4

63   discharge causes an important carbon footprint to the environment due to fugitive

64   emissions of CH_4 [7,8], as the global warming potential of methane is 28 times higher

65   than that of carbon dioxide [9].

66   The removal of dissolved gases from liquids is conventionally achieved with vacuum

67   packed towers. These columns are filled with packing that creates a large surface area

68   for the contact of liquid and gas phases. Nevertheless, in this system, the direct contact

69   of liquid and gas phases can frequently lead to problems such as foaming, flooding, and

70   emulsions. Among the alternative technologies under investigation for the removal of

71   dissolved gas from anaerobic effluents, one can find methods such as micro-aeration

72   using biogas containing air or biological oxidation. Nevertheless, these methods also

73   present drawbacks such as low concentration in the removed gas and/or low recovery

74   efficiency [10–12]. It seems that improvement of the existing process, development of

75   new processes, or both are needed in order to minimize the discharge of D-CH_4.

76   In this context, degassing membrane (DM) contactors have appeared as an emergent

77   technology that is being used to remove dissolved gases in several processes. The main

78   advantage of this technology is related to the fact that a gas and a liquid phase come into

79   contact in the pore of the membrane, without the need for dispersion of one phase into

80   another, allowing previously mentioned problems to be avoided [13]. DM contactors

81   present other advantages over conventional dispersed phase contactors, such as

82   availability at high and low flow rates as they are modular, ease of scaling up, a wide

83   range of capacities by adding or removing membrane modules, a high interfacial area

84   per volume unit, and high efficiency. Nevertheless, DM contactors can also have some

85   disadvantages such as membrane resistance to mass transfer, bypassing in the shell side,

86   fouling problems, and limitations with regard to pressure drop [14], so investigations

87   like the one presented in this work are still necessary.

88   A hollow fibre module is the most common configuration used in DM contactors in

89   order to remove gases such as CO_2 and O_2 from a liquid phase, so a considerable

90   number of studies related to the removal or recovery of these gases can be found [15–

91   21]. This technology seems especially interesting in some industrial processes where the

92   removal of dissolved gases is crucial, such as in the process of production of ultrapure

93   water, in which one of the major contaminants is the dissolved oxygen, whose removal

94   is essential [15,19]. Unfortunately, studies on the removal of D-CH_4 from anaerobic

95   effluents are still very scarce. Bandara et al. studied D-CH_4 recovery by degasification

96   from the effluent of a bench-scale upflow anaerobic sludge blanket (UASB) reactor

97   treating synthetic wastewater [22]. They used a multi-layered composite hollow fibre

98   degassing module made of polyethylene and polyurethane under vacuum pressure.

99   Cookney et al. studied the recovery of D-CH_4 from a low-temperature (16 ºC) anaerobic

100   process treating domestic wastewater with a polydimethylsiloxane membrane contactor

101   using nitrogen as sweep gas [23]. Recently, Cookney et al. studied the desorption of D-

102   CH_4 from both synthetic and real anaerobic effluents using different membrane hollow

103   fibres [24]. Further research in this field is needed to improve and deepen the

104   knowledge and performance of this technology.

105   The selection of a suitable membrane is a crucial factor for optimal contactor

106   performance, since membrane material properties can significantly affect the overall

107   mass transfer. In this sense, the porosity of the polymeric material for contactor devices

108   applied to water treatment can have a positive influence on the permeability of

109   dissolved gas but a negative effect on the flooding prevention of the membrane material

110   [25].

111   The main objective of this work was to investigate the performance of two DM

112   contactors in the recovery of D-CH_4 from a recirculating stream of a lab-scale Expanded

113   Granular Sludge Bed (EGSB) anaerobic reactor. Two different materials for the

114   membrane of the hollow fibre membrane modules are compared: polypropylene (PP,

115   microporous) and polydimethylsiloxane (PDMS, non-porous). The effects of liquid

116   flux, vacuum pressure, sweep gas flow rate, and operating mode (lumen and shell sides)

117   were investigated. The removal of dissolved carbon dioxide (D-CO_2) was also

118   monitored to study the simultaneous removal of both gases.

119   **2. Experimental**

120   *2.1. Degassing membrane modules*

121   This study employed two types of hollow fibre membrane contactors, which were

122   selected as representative of two different and efficient types of commercial modules for

123   industrial applications with different porosity properties. The first module was

124   PDMSXA-250, a membrane contactor with fibres of polydimethylsiloxane (PDMS,

125   non-porous) with an internal surface area (A_i) of 0.0159 m^2, supplied by PermSelect,

126   MedArray Inc. (USA). The second module was the 1 × 5.5 MiniModule supplied by

127   Liqui-Cel, Membrana GmbH (Germany). This contactor was made of polypropylene

128   (PP, microporous) fibres with an A_i of 0.18 m^2. The main characteristics of both

129   modules are summarized in Table 1.

130   Since both modules have different physical properties, including different sizes, in order

131   to compare behaviours and performances between the two contactors, the characteristic

132   parameter defined as the water flux rate ($Q_L/A_{i,e}$, liquid flow rate per the membrane

133   surface, L h^{-1} m^{-2}) has been widely used.

134

135   **Table 1.** Characteristics of PDMS and PP modules

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

136

137   *2.2. Experimental setup and procedure*

138   A laboratory-scale EGSB anaerobic reactor was operated at 25 ºC for more than 24

139   months. The EGSB reactor was initially inoculated with 4 L of granular anaerobic

140   sludge from the wastewater treatment plant of a local brewery. The reactor treated 8 L d^-

141   ^{1} of synthetic wastewater polluted with ethanol with an organic load rate of 32 kg

142   chemical oxygen demand (COD) $m^{-3}d^{-1}$. A high recirculation flow was kept to expand

143   the sludge bed with an upflow velocity of 10.7 m h^{-1}. Similar work conditions were used

144   in the study of Lafita et al. [26]. A liquid–gas separator device was placed at the top of

145   the reactor, and the biogas was collected through a sodium hydroxide solution. The

146   methane flow rate was periodically monitored with a biogas flow meter (MGC-10

147   PMMA, Ritter, Germany) and the pH and conductivity with a multi parameter sensor

148   (pH/Cond 340i WTW, Germany). Alkalinity, volatile fatty acids (VFA), COD, and

149   nutrient concentration in the inlet and outlet of the reactor were analysed according to

150   standard methods [27]. A scheme of the EGSB reactor and the DM contactor is shown

151   in Fig. 1. A detailed description of the system and procedure can be found elsewhere

152   [6].

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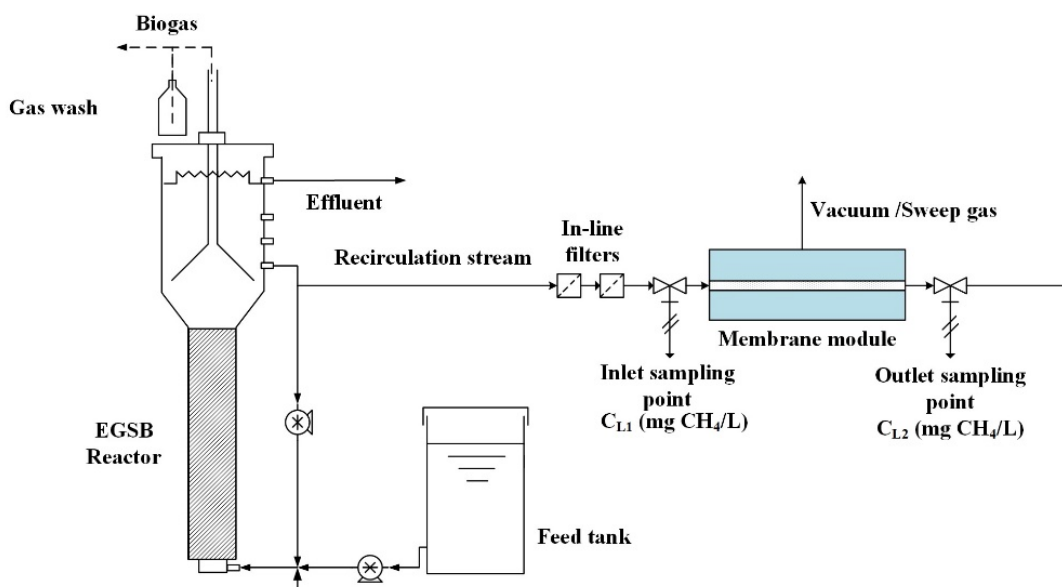
Fig. 1. Scheme of the setup of the EGSB reactor and degassing membrane modules

155   Membrane modules were coupled to the EGSB reactor and feed with a fraction of the

156   flow from the recirculation stream, in which the concentration of the D-CH_4 was similar

157   to that in the effluent stream. The stream flowed through a 40 μm filter to minimize

158   membrane fouling, and then through the contactors, using a peristaltic pump (Watson-

159   Marlow, USA), resulting in flow rates ranging from 0.36 to 10.80 L h^{-1} for the PDMS

160   module and from 4.1 to 27.2 L h^{-1} for the PP module. For vacuum pressure experiments,

161   a vacuum pump N026.3.AT.18 (KNF Neuberger, Germany) was used for the vacuum

162   operation, giving vacuum pressures (P_{vac}) of 140, 500, and 800 mbar. For countercurrent

163   sweep gas experiments, nitrogen gas with a high purity (> 99.8%) supplied by Carburos

164   Metálicos S.A. (Spain) was introduced into the contactors in a range of flow rates

165   between 2.7 and 27.0 L h^{-1} (STP) for the PDMS module and between 26.0 and 800 L h^{-1}

166   (STP) for the PP module, using a mass flow controller (Bronkhorst Hi-Tec, The

167   Netherlands). The liquid pressures at the inlet and outlet of the membrane were

168   measured using an MP 112 portable manometer (Kimo, Spain).

169   DM contactors were operated in two modes. Initially, experiments with the liquid

170   flowing in the lumen side and vacuum pressure or sweep gas applied in the shell side

171   (lumen side mode) were carried out. Afterwards, the opposite operation mode was

172   studied (shell side mode).

173   *2.3. Evaluation of membrane contactor performance*

174   The determination of dissolved CH_4 and CO_2 was carried out with a headspace method.

175   Liquid samples of 50 mL were collected at the inlet and outlet of membranes and were

176   injected in sealed vials of 125 mL prefilled with helium. The vials were shaken

177   vigorously for 30 seconds and left at 25 ºC for 3 hours in an orbital shaker to allow the

178   gases to equilibrate. After equilibration, 0.5 mL of the headspace gas was injected into a

179   gas chromatograph (Agilent GC 7820A, Spain) equipped with Agilent HP-PLOT/Q and

180   Agilent HP-MOLESIEVE columns. The concentration of D-CH_4 and D-CO_2 in liquid

181   phase was calculated as:

$$C_L = \frac{C_G \,(V_G + HV_L)}{V_L} \tag{1}$$

182   where C_L is the concentration of D-CH_4 or D-CO_2 in liquid phase (mg L^{-1}), C_G is the

183   concentration of CH_4 or CO_2 in the headspace after equilibration (mg L^{-1}), V_L and V_G

184   are the volumes of liquid and gas space in the vial, respectively (mL), and H is the

185   dimensionless Henry's law constant for methane (29.55) and carbon dioxide (1.20) at

186   25 ºC [28].

187   The performance of the degassing module was evaluated with the removal efficiency

188   (RE, %) of the membrane, defined as:

9

$$RE = \frac{C_{L1} - C_{L2}}{C_{L1}} \cdot 100 \tag{2}$$

189   where C_{L1} and C_{L2} are the concentrations of D-CH_4 or D-CO_2 in liquid phase (mg L^{-1}) at

190   the inlet and outlet of the membrane module, respectively. Samples from the inlet and

191   outlet were taken in duplicate and analysed in triplicate. The average values of the

192   measures and standard deviation are presented in the figures and tables.

193   Cleaning of the DM module with deionized water in countercurrent flow was done after

194   every experiment. A control experiment was repeated every month to ensure that the

195   DM module was operating without fouling and the RE was maintained at the same

196   value.

197   Analysis of mass transfer is important to evaluate the performance of membrane

198   contactor operations. Assuming negligible mass transfer resistance into gas phase, the

199   experimental overall mass transfer coefficient (K_{exp}, m s^{-1}) can be determined from the

200   liquid phase mass balance in the contactor by the following differential expression:

$$Q_L \frac{dC}{dA} = - K_{exp} (C_L - C_L^*) \tag{3}$$

201   where Q_L is the liquid flow rate (m^3 s^{-1}), A is the interfacial area (m^2), C_L is the

202   concentration of CH_4 or CO_2 in the liquid phase (mg L^{-1}), and C_L^* is the equilibrium

203   concentration of these species in the liquid phase (mg L^{-1}), resulting in:

$$C_L^* = H \cdot C_G \tag{4}$$

204   Integrating the above equation between inlet and outlet concentrations (C_{L1} and C_{L2})

205   and assuming negligible variation of concentration in the gas phase,

$$K_{exp} = - \frac{Q_L}{A} \ln \left(\frac{C_{L2} - C_L^*}{C_{L1} - C_L^*} \right) \tag{5}$$

206 When it can be assumed that the concentration of each actively transferring specie in the

207 gas phase is very low, the equilibrium concentration in liquid phase is negligible

208 compared to the actual concentration in the liquid phase ($C_L \gg C_L^*$; $C_L - C_L^* \approx C_L$),

209 and Eq. (5) can be simplified to:

$$K_{exp} = -\frac{Q_L}{A} \ln \frac{C_{L2}}{C_{L1}} \tag{6}$$

210

211 **3. Results and discussion**

212 *3.1. Anaerobic reactor performance*

213 During start-up of the EGSB anaerobic reactor, the organic load rate of ethanol was

214 increased gradually for two weeks from 5 to 32 kg COD m^{-3} d^{-1} and the EGSB reactor

215 was operated during two years at the maximum organic load rate. After the shutdown of

216 the reactor during the vacation period, the system was restarted with new sludge.

217 The EGSB reactor achieved a removal rate of around 31.4 kg COD m^{-3} d^{-1}, resulting in

218 a COD removal efficiency of 98%. The biogas composition was 77% (v/v) CH_4 and

219 23% (v/v) CO_2 and the methane flow rate was 1.65 L h^{-1}. The VFA concentration was

220 kept lower than 5 mg CH_3COOH L^{-1}. These results are in agreement with those

221 obtained previously in the same reactor under similar operational conditions [26]. The

222 average D-CH_4 concentration measured in the water effluent of the reactor was around

223 30 mg L^{-1}. This indicates an oversaturation of the anaerobic effluent by a factor of 2

224 with respect to the equilibrium D-CH_4 of 15 mg L^{-1} (estimated from a composition of

225 77% CH_4 and the Henry's constant at 25 ºC) under experimental conditions. D-CH_4

226 oversaturation is commonly observed in UASB reactors with oversaturation factors

227 ranging from 1.6 to 6.9 [10,23,29]. The average measured D-CO_2 concentration was

11

228   around 250 mg L^{-1} and no oversaturation was observed with respect to the equilibrium

229   (345 mg L^{-1}).

230   No significant effect on the EGSB performance was observed when the degassing

231   operation was carried out on the recirculation stream in discontinuous mode; COD

232   removal, biogas production and composition, and effluent quality were not affected.

233   These results are in agreement with those of Luo et al. [30], who stated that COD

234   removal efficiency and CH$_4$ yield were not affected in a UASB when a DM was

235   coupled to the recirculation stream of a reactor. Bandara el al. [31] reported that no

236   significant differences were observed in total methane production when a degassing

237   membrane was submerged in the bulk liquid of a UASB reactor.

238   *3.2. Effect of time on-stream*

239   A fast approach to the stationary state was observed when the D-CH$_4$ concentration at

240   the outlet (C$_{L2}$) of both membrane modules was monitored over time. In Fig. 2 and Fig.

241   3, the results of two representative experiments under different operational conditions

242   are shown with PDMS and PP modules, respectively. As expected, C$_{L2}$ initially

243   decreased with the time of operation and was almost constant after 60 min. Thus, in this

244   study, the membrane performance results were those obtained after a minimum of 60

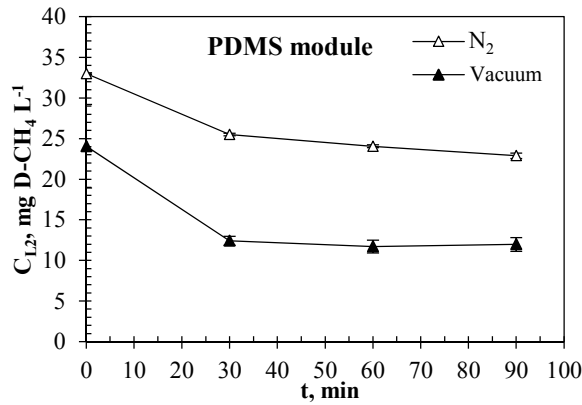245   minutes of operation, considering the stationary state values.

Fig. 2. Variation of C_{L2} with time of operation of PDMS module in shell side operation. Sweep gas: $Q_L/A_i = 377.4$ L h^{-1} m^{-2}; $Q_{N2}/A_i = 1.70$ m^3 h^{-1} m^{-2}. Vacuum: $Q_L/A_i = 75.5$ L h^{-1} m^{-2}; $P_{vac} = 500$ mbar.
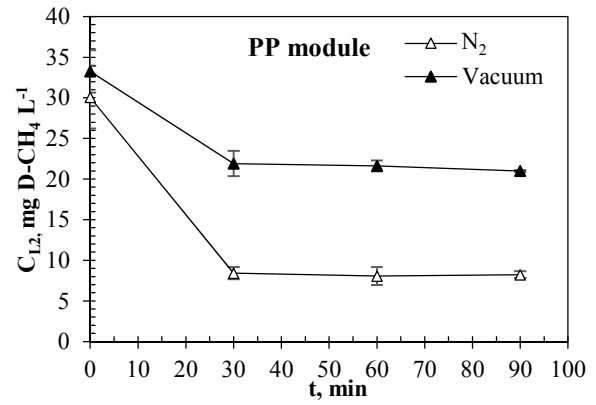
Fig. 3. Variation of C_{L2} with time of operation of PP module in lumen side operation. Sweep gas: $Q_L/A_i = 113.2$ L h^{-1} m^{-2}; $Q_{N2}/A_i = 4.44$ m^3 h^{-1} m^{-2}. Vacuum: $Q_L/A_i = 113.2$ L h^{-1} m^{-2}; $P_{vac} = 140$ mbar.

246

247 *3.3.Effect of vacuum pressure and sweep gas flow rate*

248 In order to evaluate the influence of P_{vac} on the methane RE, both DM contactors were

249 operated in lumen side mode under P_{vac} conditions ranging from 140 to 800 mbar while

250 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}

251 can be seen in Fig. 4. An increase of RE with the rise of P_{vac} was observed as the

252 concentration gradient increased with the P_{vac}, and therefore degassing of D-CH$_4$ from

253 the liquid phase is favoured. In both contactors, a practically linear increase of the RE

254 was observed under the operational conditions studied, with values between 60 and 77%

255 for PDMS membrane and between 69 and 93% for PP membrane. These values are

256 similar to those described in previous degassing of O$_2$ and CH$_4$ studies under similar

257 vacuum conditions [16,23,32]. Like this work (Fig. 4), these studies showed an increase

258 in the RE with the rise of vacuum pressure. Cookney et al. [23] studied CH$_4$ removal

259 from an anaerobic effluent using values of P_{vac} from 0.5 to 380 mbar and obtained a

260 maximum RE of around 80%. Ito et al. [16] and Tan et al. [32] evaluated O$_2$ removal

261 from water under varying vacuum conditions from 500 to 960 mbar and from 200 to

13

262   960 mbar, respectively, with a maximum RE of 80% in both cases. The variations of RE

263   with P_{vac} seem to indicate that the equilibrium concentration in liquid phase (C_L^*) was

264   not negligible compared with the concentration in liquid phase (C_L). This fact was

265   corroborated experimentally with C_L^* values not much lower than concentrations in

266   liquid phase. Moreover, an increasing vacuum results in decreasing C_L^*.

267   As can be observed in Fig. 4, the PP module showed a higher RE than the PDMS one, at

268   least under the tested operational conditions (relatively low Q_L/A_i). The better

269   performance of porous membranes can be related to their lower resistance to the mass

270   transfer through the polymer. The different behaviours of porous and non-porous

271   membranes have also been pointed out by Ozturk and Hughes [21], who evaluated the

272   performance of both modules for the removal of CO_2 using absorbent solvents, and

273   found a better performance of the porous membrane module.
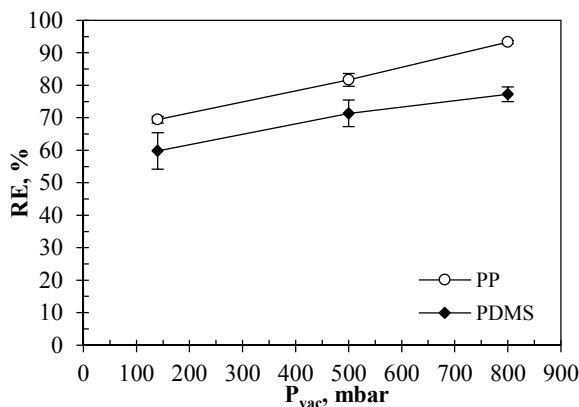
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275   **Fig. 4.** Effect of P_{vac} on the RE at Q_L/A_i of 22.64 L h^{-1}m^{-2} in lumen side operation.

276

277   The effect of flux of sweep gas (Q_{N2}/A_i) on methane RE was also studied. For this

278   purpose, DM contactors were operated in the lumen side mode at a fixed Q_L/A_i of

279   113.21 L h^{-1} m^{-2} while varying Q_{N2}/A_i from 0.17 to 1.70 m^3 h^{-1} m^{-2} for PDMS contactor

280   and from 0.14 to 4.44 m^3 h^{-1} m^{-2} for PP contactor. As can be observed in Fig. 5, at low

14

281   values of Q_{N2}/A_i, an increase in the RE was achieved with an increase of Q_{N2}/A_i.

282   Nevertheless, at higher values of Q_{N2}/A_i, no improvement in the RE was observed. The

283   limit value of Q_{N2}/A_i from which the RE was constant also depends on the Q_L/A_i, as can

284   be seen in Fig. 6, where an increase in the RE was observed with the increase of Q_{N2}/A_i

285   for high values of Q_L/A_i (377.4 L h^{-1} m^{-2}). A constant RE with an increase of gas side

286   hydrodynamics has also been reported by Cookney et al. [23,24]. Facts such as the

287   almost negligible gas phase mass transfer resistance and the low partial pressure of

288   methane in the sweep gas can explain this behaviour [32]. In these experiments, the PP

289   module again presented higher RE than the PDMS module, although RE was quite

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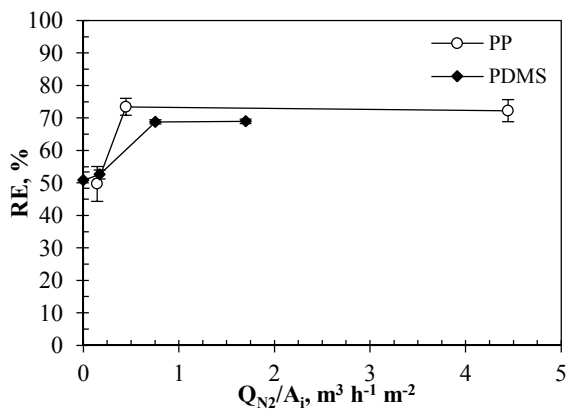
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292   **Fig. 5.** Effect of Q_{N2}/A_i on the RE at Q_L/A_i of 113.21 L h^{-1}m^{-2} in lumen side operation.

293

294   The decision to operate in vacuum or sweep gas modes for the removal of D-CH$_4$

295   depends on different factors that should be taken into account, such as the D-CH$_4$ RE,

296   reuse of the recovered compound, and energy consumption. Regarding the performance

297   of the D-CH$_4$ removal, in the PDMS module (Fig. 6), a higher RE was achieved under

298   vacuum operation than under sweep gas operation, although at low values of Q_L/A_i,

299   values of RE were very similar in both modes of operation. On the contrary, in the PP

300   module (Fig. 7), RE values were slightly higher in sweep gas operation. Considering the

301   energy consumption, Vallieres and Favre [33] highlighted that at industrial scale, sweep

302   gas operation consumed less raw energy than vacuum operation, except when a low

303   vacuum pressure can be practicable. Nevertheless, vacuum operation is preferred when

304   it is desired to recover pure or high-purity components to reuse them as a source of

305   energy. In this case, sweep gas operation would involve a subsequent purification step

306   that would increase the overall energy consumption, so vacuum operation can be

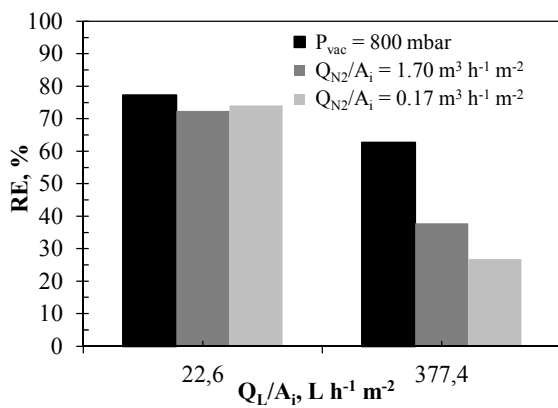307   considered as the most feasible solution for reusing the recovered gas.

Fig. 6. PDMS module performance in the lumen side mode and different operating conditions.
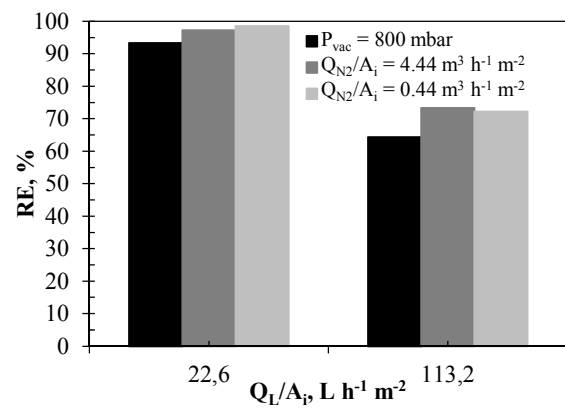
Fig. 7. PP module performance in the lumen side mode and different operating conditions.

308

309   *3.4.Effect of liquid flux rate*

310   To evaluate the effect of liquid flux rate on the methane RE, a set of experiments was

311   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

312   flowing through the lumens. The results obtained at P_{vac} of 500 mbar are presented in

313   Fig. 8. As was expected for both modules, the D-CH_4 RE decreased when the Q_L/A_i was

314   increased, a behaviour commonly observed in degassing operations with hollow fibre

315   membranes for both porous and non-porous materials [20,24,34].
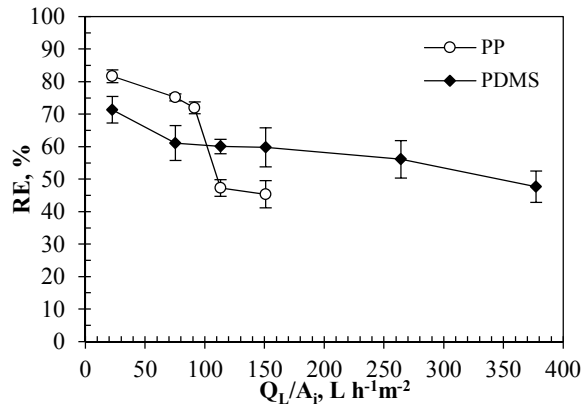
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318 As can be seen in Fig. 8, DM modules showed a different behaviour, with a more

319 pronounced decrease of RE in the PP module at intermediate values of Q_L/A_i, changing

320 from being more efficient than the PDMS module at low water fluxes (< 90 L h^{-1} m^{-2}) to

321 less efficient in the removal of D-CH$_4$ at the highest water fluxes (> 90 L h^{-1} m^{-2}). This

322 phenomenon can be associated with the wetting of hydrophobic microporous

323 membranes, in which the pores of the microporous membrane can be totally or partially

324 filled with the liquid phase. This behaviour was corroborated by the estimation of the

325 experimental mass transfer coefficient (Eq. 5). In Fig. 9, the effect of Q_L/A_i on

326 experimental mass transfer coefficients (K_{exp}) at a vacuum pressure of 500 mbar is

327 shown. The obtained values of overall mass transfer coefficients were comparable to

328 that previously reported by Sinha and Li for O_2 removal from water with a PP

329 microporous membrane [17], those reported by Cookney et al. [24] for D-CH$_4$ removal

330 with PP and PDMS, and overall mass transfer values obtained by Bhaumik et al. [15]

331 for CO_2 and O_2 removal from deionized water. The value of K_{exp} increased with the rise

332 of Q_L/A_i for the PDMS module, with values between 1.65 10^{-5} and 8.75 10^{-5} m s^{-1}.

333 Nevertheless, for the PP module, K_{exp} increased from 1.08 10^{-5} to 2.94 10^{-5} m s^{-1} at low

334 values of Q_L/A_i but a decrease to 1.80·10^{-5} m s^{-1} was observed at values of Q_L/A_i higher

335 than 90 L h^{-1}m^{-2}. An analogous behaviour of K_{exp} was observed in experiments carried

17

336   out at 180 and 500 mbar of vacuum pressure. During the wetted operation, the

337   membrane resistance to mass transfer increased, so the K_{exp} value for the PP module

338   decreased, which affected the efficiency of the membrane. This phenomenon has been

339   reported in similar applications with porous membranes [17,35]. Pore wetting

340   essentially depends on the operating pressure [36,37], although other factors such as

341   characteristics of the material, the nature of liquid in contact with the membrane, and

342   membrane fouling are also important [38,39]. The entry pressure was evaluated for the

343   PP module between water flux values of 22.6 and 151.0 L h^{-1} m^{-2}, resulting in pressure

344   values from 1080 to 1247 mbar. A sharp increase of the entry pressure was noted at

345   water fluxes higher than 90 L h^{-1} m^{-2}, which is probably the cause of the wetting

346   phenomenon mentioned previously.
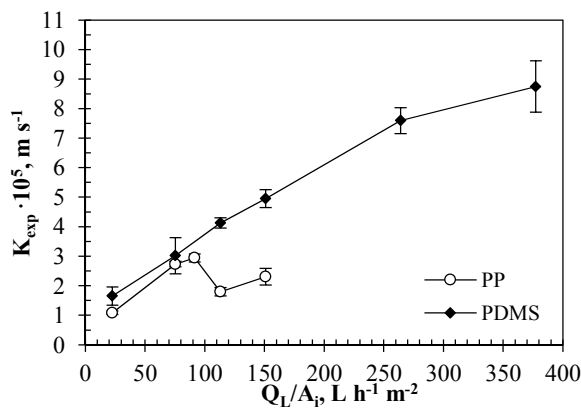
347

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

349   This higher stability of dense composite fibres compared with microporous materials

350   has been shown in other applications of absorption/desorption [40], where the PP

351   module shows a high sensitivity toward wetting conditions. Keeping the operational

352   conditions below the critical pressure in which wetting occurs would be the key

353   parameter for stable and high-efficiency operation of the PP module at industrial scale.

354   The selection of suitable operational conditions and type of membrane for this

18

355 application seems crucial. While the microporous module provides greater efficiency at

356 lower flow rates (pressure), when the operation requires higher liquid flow rates the

357 non-porous membrane shows better performance.

358 *3.5.Effect of mode of operation: lumen and shell side operation*

359 In Table 2, experiments on both DM modules operating in the lumen side and shell side

360 modes are shown in order to compare D-CH$_4$ RE. Experiments were carried out at a

361 constant Q_L/A_i, where the wetting phenomenon was not observed. As can be seen,

362 higher RE values were achieved in lumen side operation for both DM modules,

363 independently of the operating conditions. As the Reynolds numbers (Re) were quite

364 similar in both modes of operation for each module, the worst performance in the shell

365 side mode can be attributed to the channelling phenomenon that can occur when liquid

366 passes through the shell of the module and not all fibres of the module properly

367 contribute to D-CH$_4$ RE. The channelling phenomenon was also observed in the

368 removal of dissolved oxygen from water by DM contactors [20,41]. No significant

369 effect of Q_{N2}/A_i on the performance of both modules was observed for shell and lumen

370 side operations.

371 **Table 2.** Effect of lumen and shell side operating modes on methane RE. Q_L/A_i = 22.64 L h^{-1} m^{-2}. Re at the lumen
372 side: 2.3 (PDMS) and 3.19 m s^{-1} (PP). Re at the shell side: 1.27 (PDMS) and 2.26 (PP).

DM module	P$_{vac}$, mbar	Q_{N2}/A_i, m^3 h^{-1} m^{-2}	RE$_{CH4}$, %	
			Lumen side	Shell side
PDMS	800	–	77.2 ± 2.3	62.0 ± 1.6
	–	0.17	74.0 ± 4.1	35.2 ± 1.7
	–	1.70	72.4 ± 0.8	29.4 ± 2.0
PP	800	–	93.3 ± 0.5	34.5 ± 0.5
	–	0.44	98.5 ± 0.9	26.9 ± 3.4
	–	4.44	97.2 ± 0.7	28.3 ± 1.9

373

374 Comparing the performance of the two DM contactors (Table 2), as previously

375 described for lumen side operation, the PP module showed higher removal efficiency

376 than the PDMS module, but the opposite was observed in shell side operation. This

377 difference in the behaviour of the DM contactors could be related to the different

378 packing densities of the two modules, since a lower packing density could promote a

379 higher mass transfer coefficient in shell side operation [42,43]. As can be observed in

380 Table 1, the PDMS module showed a lower packing density, and therefore a higher

381 mass transfer rate should be achieved with this contactor, assuming that the main mass

382 transfer resistance is associated with liquid flow mass transfer. In the shell side mode

383 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}

384 for the PDMS and PP modules, respectively.

385 The pressure at the inlet and outlet of the DM modules was measured in lumen and shell

386 side operation and the liquid pressure drop (ΔP) was calculated (Fig. 10 and Fig.11). In

387 both modules, the ΔP at the lumen side is higher than the ΔP at the shell side. This fact

388 indicates why the shell side mode is the preferred one in real industrial operations or

389 treatments since it minimizes problems such as high pressure drops and fouling, which

390 can limit the flow capacity of the modules. Thus, some design modifications to improve

391 the RE in shell side operation have been studied, such as the use of a transverse-flow

392 design of the contactor in industrial modules to enhance the flow hydrodynamics [34].

393 Comparable results and analogous behaviour have been found in previous studies for

394 different hollow fibre membrane contactors [18,20].

395 The pressure drop is higher for the PP module than for the PDMS module for a

396 similar liquid velocity. In lumen side operation, a greater length and porosity of the PP

397 module involve a higher pressure drop. In shell side operation, similar values for

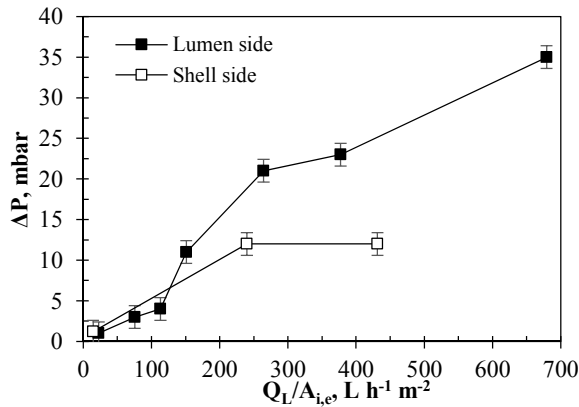398 pressure drop were obtained for both modules.

Fig. 10 Liquid pressure drop of PDMS module in the lumen and shell side modes of operation.
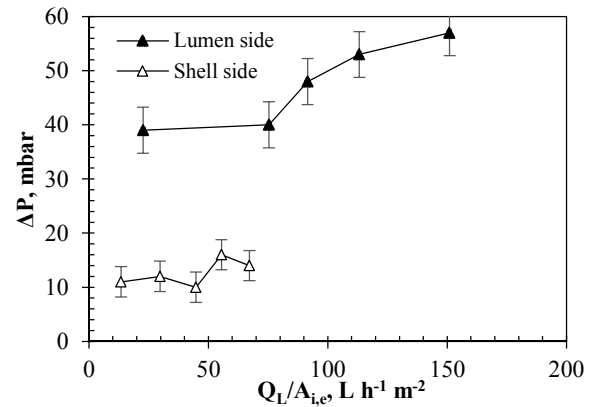
Fig. 11 Liquid pressure drop of PP module in the lumen and shell side modes of operation.

399

400   *3.6.Degassing of CO_2*

401   A summary of the most representative results of CO_2 degassing of the samples can be

402   found in Table 3. The wetting phenomenon was not observed for PP in the operating

403   conditions described in this table. In general, lower D-CO_2 RE is achieved compared

404   with D-CH_4 removal under the same conditions, especially for experiments carried out

405   under vacuum pressure conditions. Nevertheless, the behaviour of both modules in the

406   case of CO_2 removal was quite similar to that observed for CH_4 removal. As for D-CH_4

407   removal, both modules showed higher RE in lumen side operation than in shell side

408   operation.

409   In lumen side operation, the PP module is more efficient that the PDMS module at low

410   water flux rates. The contrary behaviour is observed in shell side operation, in which the

411   PDMS contactor gives a higher RE, possibly related to its lower packing density value,

412   as has been mentioned previously.

21

413 The most significant differences were observed under vacuum pressure conditions, in

414 which notably lower performances were achieved for D-CO_2 removal than in sweep gas

415 operation.

416 **Table 3.** Effect of operating mode, P_{vac}, and Q_{N2}/A_i on the D-CO_2 RE. Q_L/A_i = 22.64 L h^{-1} m^{-2}.

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

417

418 ## 4. Conclusions

419 The methane degassing capabilities over an EGSB effluent reactor of two commercially

420 available small DM contactors with different membrane materials – microporous

421 (polypropylene, PP) and non-porous (polydimethylsiloxane, PDMS) – have been tested

422 and compared. Not very large differences in performance of the two modules were

423 observed. In lumen mode operation, the PP contactor showed better performance under

424 soft or mild operational conditions (e.g. low liquid flow and/or vacuum pressure), but

425 the wetting phenomenon occurred when the liquid flow rate was increased. In shell side

426 mode, PDMS was more efficient and no wetting phenomenon was observed with this

427 contactor.

428 For both membranes, the results obtained in vacuum pressure experiments showed that

429 the concentration of methane specie in the gas phase was not low enough to consider

430 that equilibrium concentration in liquid phase was negligible compared to the actual

431 concentration in the liquid phase (C_L >> C_L^*; $C_L - C_L^* \approx C_L$). The opposite was

432 observed in sweep gas operation, where the influence of the nitrogen flow rate was

22

433   negligible, from relatively low nitrogen fluxes, showing that the gas phase mass transfer

434   resistance was almost negligible.

435   Lumen mode operation was more efficient, but the pressure drop was considerably

436   higher than in shell mode operation, especially for the highest water flow rates.

437   Methane removal efficiencies ranging from 25 to 98% under experimental conditions

438   can be achieved, showing the viability of methane removal/recovery using this

439   technology.

440   Simultaneous degassing of CO_2 was considerably less efficient than that observed for

441   CH_4, and the general behaviour of the DM contactors was quite similar to that obtained

442   for CH_4.

443   **Acknowledgements**

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