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CO<sub>2</sub> removal from anaesthesia circuits using gas-ionic liquid membrane contactors

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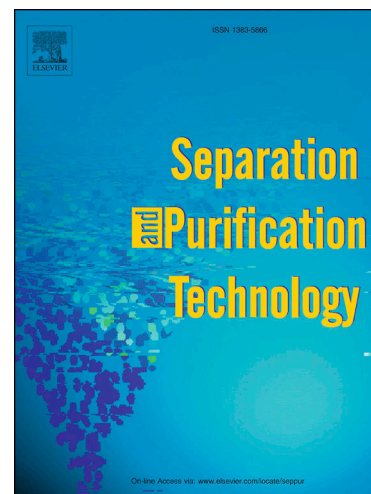
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1 CO<sub>2</sub> removal from anaesthesia circuits using gas-ionic liquid membrane  
2 contactors

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12 **Abstract**

13 Nowadays, the reutilization of anaesthetic gases is accomplished by capturing carbon dioxide  
14 with soda lime, a solid adsorbent mostly composed by calcium and sodium hydroxide. To  
15 overcome the issues regarding the use of soda lime, this work proposes an alternative process to  
16 remove carbon dioxide through the use of a membrane contactor combined with a biocompatible  
17 ionic liquid (IL), cholinium lysinate, with high absorption capacity (5.9 mol<sub>CO<sub>2</sub></sub>/kg<sub>IL</sub>). The carbon  
18 dioxide removal rate and IL solution regeneration, were assessed, varying the feed gas  
19 composition, relative humidity and ionic liquid flow rate conditions. Overall mass transfer  
20 coefficients and separation factors were determined. From the results obtained, the proposed  
21 system is feasible to remove carbon dioxide from anaesthetic gas circuits. Moreover, the system  
22 working operation time obtained was 63 hours, which in a mass basis comparison with soda lime  
23 (current technology), is 3 to 5 times higher.

24 *Keywords:* CO<sub>2</sub> removal, biocompatible ionic liquid, gas-liquid membrane contactor, anaesthetic  
25 gas.

## 26 1. Introduction

27 In the conventional technology to remove carbon dioxide (CO<sub>2</sub>) from inhalation anaesthesia  
28 circuits, a container with soda lime is used to adsorb and degrade the expired gases and  
29 anaesthetics [1]. Soda lime is composed mostly by calcium and sodium hydroxide, which is  
30 proved to remove CO<sub>2</sub> efficiently [2]. Furthermore, it is used in anaesthetic circuits in a closed-  
31 loop operating mode, where the expired CO<sub>2</sub> is removed to allow the recovering and recycling of  
32 the non-absorbed anaesthetics. Typically, the inhaled anaesthetic gas mixture is composed by  
33 70% of the anaesthetic gas and 30% of oxygen, which results in an exhaled gas mixture with 65%  
34 of anaesthetic gas, 27% of oxygen, 5% of carbon dioxide and 3% of nitrogen. The reuse of the  
35 non-absorbed anaesthetics is only possible if the carbon dioxide concentration is lowered down  
36 to 0.5% [3,4].

37 Even though soda lime is used in these circuits, efforts must be done to replace the current  
38 technology, due to existent drawbacks. Several studies show that volatile halogenated  
39 hydrocarbons typically present in anaesthetic streams (e.g. sevoflurane, desflurane and isoflurane)  
40 can react with soda lime with low water content, being chemically degraded to vinyl-ether  
41 molecules known as compounds A–E [1,5]. These compounds along with other toxic compounds,  
42 such as carbon monoxide, may present potential life-threatening complications [6,7].

43 The most used technique for CO<sub>2</sub> capture (from diverse gas streams sources) is absorption  
44 using aqueous amine solutions, specially solutions containing monoethanolamine (MEA) [8].  
45 This technique consists in scrubbing CO<sub>2</sub> from a gas mixture with the aqueous amine solution in  
46 a packed column, followed by a liquid regeneration step with stripping water vapour at  
47 temperatures between 373 and 393 K [9]. However, drawbacks including corrosion, oxidative  
48 degradation, negative environmental impact, high volatility leading to considerable losses of the  
49 absorbent, chemical and thermal instabilities and low energy efficiency, motivate researchers to  
50 seek for more efficient and environment-friendly alternatives [8,10–12].

51 Studies on CO<sub>2</sub> capture using different absorption systems increased progressively over  
52 the last three decades, where ionic liquids (ILs) are emerging as a potential alternative [13]. ILs  
53 are liquid salts with negligible volatility and their potential to capture CO<sub>2</sub> is recognized due to  
54 their unique properties, such as the ability to be tuned for each specific process, excellent thermal  
55 stability, structural functionality, among others. Furthermore, ILs are able to work as solvents and  
56 also for this reason their potential is being explored to replace conventional CO<sub>2</sub> absorbents [14].  
57 CO<sub>2</sub> capture and conversion studies using amino-acid based ILs combined with the cholinium  
58 cation, revealed their strong ability to react with CO<sub>2</sub>, are more resistant to oxidative degradation  
59 and exhibit a higher thermal stability [4,15–19]. Additionally, this group of ILs is even more  
60 interesting due to their low toxicity, biocompatibility and biodegradability. Bhattacharyya *et al.*  
61 [17] synthesized novel ILs containing choline ([Cho]) based on ether functionalized cations with  
62 amino acid ([AA]) anions, aiming an effective CO<sub>2</sub> capture performance and stability in the  
63 presence of oxygen. The synthesized [N<sub>1,1,6,204</sub>][Lys] IL presented a CO<sub>2</sub> capture capacity of 4.31  
64 mol<sub>CO<sub>2</sub></sub>/kg<sub>IL</sub> (at 293 K). Li *et al.* [15] studied the absorption of CO<sub>2</sub> in 30 wt% aqueous solutions  
65 of [Cho][AA]s ILs, obtaining a CO<sub>2</sub> capture capacity of 0.89 mol<sub>CO<sub>2</sub></sub>/kg<sub>IL</sub> for the cholinium  
66 lysinate ([Cho][Lys]) IL, at 303 K and close to the atmospheric pressure. Li *et al.* proposed the  
67 use of aqueous solutions of this family of ILs, in order to reduce the viscosity, the gas-liquid mass  
68 transfer resistance, as well as to turn the ILs more economically viable for the CO<sub>2</sub> capture  
69 application, when compared to less expensive solutions such as aqueous amines.

70 The use of porous membrane contactors for CO<sub>2</sub> capture using ionic liquids or amino acid  
71 salt solutions, as liquid absorbents has also been addressed [20–23]. In this approach, a porous  
72 hydrophobic membrane is used to promote the contact between gas and liquid phases, without  
73 dispersion of one phase into the other. Furthermore, the hydrophobic character of the membrane  
74 prevents the liquid from entering the pores, minimizing the mass transfer resistance of the  
75 membrane. Thus, the membrane acts as a separation barrier providing interfacial area for mass  
76 transfer, while the selectivity is given by affinity to the liquid phase [20, 24]. Portugal *et al.* [4]  
77 proposed this approach for the CO<sub>2</sub> removal from anaesthetic gas circuits, using potassium

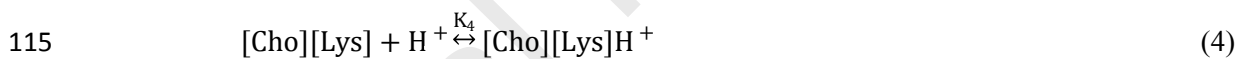
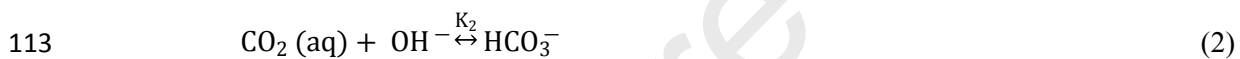
78 glycinate solutions, as the liquid absorbent, and hollow fiber contactors with a composite  
79 membrane made of a porous support of polyethylenimine (PEI) and a polydimethylsiloxane  
80 (PDMS) dense thin layer. For the same purpose, Sirkar *et al.* [25] proposed the use of hydrophilic  
81 porous hollow fiber membrane contactors, with glycinate/glycerol solutions impregnated inside  
82 the pores. Another alternative process was presented by Malankowska *et al.* [26] using a  
83 microfluidic gas-ionic liquid contactor, with a cholinium propionate solution containing the  
84 carbonic anhydrase enzyme, for CO<sub>2</sub> enhanced transport, to remove CO<sub>2</sub> from anaesthetic circuits  
85 with xenon.

86         Following this concept, the present work discusses the removal of CO<sub>2</sub> from a closed-  
87 loop system containing complex gas mixtures with anaesthetic agents, using a membrane  
88 contactor comprised of porous capillaries of polytetrafluoroethylene (PTFE) and a cholinium  
89 lysinate ionic liquid solution as a biocompatible and cost-effective CO<sub>2</sub> absorbent. The IL solution  
90 contains 50 wt% of water, to minimize operation constraints (i.e. overpressure inside the  
91 capillaries due to the high viscosity), as well as to minimize the cost when comparing to the  
92 operation with an IL with higher purity. Regarding the porous membrane selected, it is recognized  
93 that PTFE possesses high chemical resistance and retain their non wetting behaviour even in the  
94 presence of corrosive chemicals [27]. For this reason, Eclipse™ membranes were selected for the  
95 present study. To validate the concept proposed, the following aspects were investigated: 1) Total  
96 CO<sub>2</sub> capture capacity of the system; 2) CO<sub>2</sub> capture capacity, with humidified and dried simulated  
97 exhaled N<sub>2</sub>O streams, with low CO<sub>2</sub> partial pressures; 3) IL solution regeneration efficiency using  
98 a sweep gas. The overall mass transfer coefficient and the CO<sub>2</sub>/N<sub>2</sub>O separation factor (*SF*) were  
99 also evaluated and the proposed technology for CO<sub>2</sub> removal was compared with the present  
100 technology using soda lime.

102 **2. Theory**

103 *2.1. CO<sub>2</sub> absorption with chemical reaction*

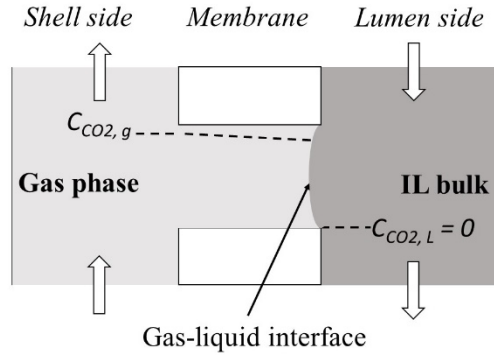
104 [Cho][Lys] is an IL derived from the cholinium family with the amino acid lysine as anion.  
 105 Despite the existence of physical diffusion of CO<sub>2</sub> in this IL, the dominant phenomenon of  
 106 transport is attributed to the chemical reaction between the IL and CO<sub>2</sub> [28]. [Lys] anion is an  
 107 amphoteric species which, combined with the [Cho] cation, acts as a Lewis acid due to the  
 108 presence of the ammonium group in the cation. In the presence of water, the [Lys] anion with its  
 109 two amino groups acts as a strong base and CO<sub>2</sub> absorption occurs *via* bicarbonate and carbonate  
 110 formation [28]. The contact between the amino groups and bicarbonate is extremely reactive. The  
 111 following simplified model describes the CO<sub>2</sub> absorption by chemical reaction in this IL:



117 In the described mechanism, all species are involved in reversible reactions. However, it  
 118 is important to mention that regarding equation (2), CO<sub>2</sub> (aq) concentration is always null, due to  
 119 the fast conversion into bicarbonate, HCO<sub>3</sub><sup>-</sup> and carbonate, CO<sub>3</sub><sup>2-</sup> (depending on the pH).

120 *2.2. CO<sub>2</sub> mass transfer models*

121 In this work, the gas phase flows counter-currently with the liquid phase, promoting a maximum  
 122 driving force between the phases along the membrane contactor. Furthermore, the high  
 123 hydrophobic character of the PTFE membrane allows for operation in a non-wetted pore mode,  
 124 avoiding the resistance promoted in the case of stagnant liquid inside the pores, as it is depicted  
 125 in Figure 1 [24].



126

127

Figure 1. CO<sub>2</sub> mass transfer in a non-wetted pore mode.

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CO<sub>2</sub> mass transfer from the gas to the liquid phase includes diffusion from the gas stream through the membrane pores and diffusion in the liquid phase, which in this work, is accompanied by a fast chemical reaction. The CO<sub>2</sub> flux ( $J_{CO_2}$ , in mol.m<sup>-2</sup>.s<sup>-1</sup>), from the gas to the liquid phase is described by:

132

$$J_{CO_2} = K_{ov} \times (CO_2 - CO_2^*) \quad (6)$$

133

134

135

136

137

where  $(CO_2 - CO_2^*)$  is the concentration driving force (mol.m<sup>-3</sup>), CO<sub>2</sub> is the carbon dioxide concentration in the gas phase, CO<sub>2</sub><sup>\*</sup> is the carbon dioxide concentration in equilibrium with the concentration of CO<sub>2</sub> in the liquid phase, being null in this case, since CO<sub>2 IL</sub> = 0.  $K_{ov}$  is the overall mass transfer coefficient (m.s<sup>-1</sup>), which is obtained by the resistance-in-series approach [29].

138

$$\frac{1}{K_{ov}} = \underbrace{\frac{1}{k_g}}_{\text{gas phase resistance}} + \underbrace{\frac{d_0}{k_m \times d_{lm}}}_{\text{membrane resistance}} + \underbrace{\frac{d_0}{\varphi \times d_i \times k_l}}_{\text{liquid phase resistance}} \quad (7)$$

139

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145

where  $\varphi$  is the product between the gas-liquid partition coefficient  $-m-$  and an enhancement factor  $-E-$  due to the chemical reaction contribution in the CO<sub>2</sub> absorption,  $d_0$ ,  $d_{lm}$  and  $d_i$  are the external, logarithm mean and internal diameters of the capillaries,  $k_g$ ,  $k_m$  and  $k_l$  are the individual mass transfer coefficients in the gas, membrane and liquid. In a non-wetted pore operation mode, mass transfer resistances in the gas phase ( $k_g^{-1}$ ) and membrane ( $d_0.d_{lm}^{-1}.k_m^{-1}$ ) are negligible, and the liquid phase resistance controls the CO<sub>2</sub> mass transfer in the module. In this work, the liquid phase

146 flows in laminar regime inside the capillaries of the Eclipse™ module (Reynolds number,  $\leq 2200$ ).  
 147 Therefore, the liquid mass transfer coefficient ( $k_l$ , in  $\text{m}\cdot\text{s}^{-1}$ ) can be estimated using the following  
 148 equation [29,30]:

$$149 \quad \frac{k_l \times d_i}{D_{\text{CO}_2, l}} = 1.62 \times \left( \frac{d_i^2 \times u_l}{L \times D_{\text{CO}_2, l}} \right)^{0.33} \quad (8)$$

150 where  $d_i$  is the capillaries internal diameter (m),  $D_{\text{CO}_2, l}$  the  $\text{CO}_2$  diffusion coefficient in the liquid  
 151 ( $\text{m}^2\cdot\text{s}^{-1}$ ),  $u_l$  the average liquid velocity ( $\text{m}\cdot\text{s}^{-1}$ ) and  $L$  the capillaries length (m). In a previous work,  
 152 it was reported a predictive correlation between  $\text{CO}_2$  diffusion coefficient and viscosity for  
 153 cholinium-based ILs [19]. To estimate the  $\text{CO}_2$  diffusion coefficient in [Cho][Lys], the following  
 154 assumptions were considered: the absorption capacity of the ionic liquid is dependent on the anion  
 155 nature; the experiments must be performed under isothermal conditions; and the viscosity of the  
 156 ionic liquid does not vary with the absorption of the gas.  $\text{CO}_2$  diffusion coefficient in the IL  
 157 [Cho][Lys] can be obtained through the following equation:

$$158 \quad D_{\text{CO}_2, l} = 6.569 \times 10^{-6} \frac{\mu^{-0.805 \pm 0.087} \times V_{m, \text{IL}}^{0.508 \pm 0.009}}{\rho^{0.507 \pm 0.006}} \quad (9)$$

159 where  $\mu$  is expressed in  $\text{Pa}\cdot\text{s}$ ,  $V_{m, \text{IL}}$  in  $\text{m}^3\cdot\text{mol}^{-1}$  and  $\rho$  in  $\text{kg}\cdot\text{m}^{-3}$  are the ionic liquid viscosity, molar  
 160 volume and density, respectively.

### 161 3. Experimental

#### 162 3.1. Materials

163 The [Cho][Lys] ionic liquid was synthesized from a choline hydroxide solution (45 wt% in  
 164 methanol, Acros Organics, USA) and L(+)-Lysine monohydrate (99%, Acros Organics, USA),  
 165 supplied by Thermofisher Scientific. The gases used in the experiments were carbon dioxide  
 166 ( $\text{CO}_2$ , high-purity grade 99.998%, Praxair, USA), oxygen ( $\text{O}_2$ , purity grade 99.999%, Praxair,  
 167 USA), nitrogen ( $\text{N}_2$ , purity grade 99.998%, Praxair, USA), nitrous oxide ( $\text{N}_2\text{O}$ , purity grade  
 168 99.6%, Air Liquide, France) and helium (He, purity grade 99.998%, Praxair). Two identical gas-  
 169 liquid membrane contactors were used for the  $\text{CO}_2$  capture and IL solution isothermal  
 170 regeneration. Membrane modules are composed by Eclipse™ capillary membranes, supplied by

171 Markel Corporation (USA) and are made of porous polytetrafluoroethylene, assembled in a  
 172 stainless-steel housing. Membrane and module specifications were provided by the supplier and  
 173 are presented in Table 1.

174 *Table 1. Eclipse™ membrane modules specifications.*

<b>Capillaries</b>		<b>Modules</b>	
<i>Inner diameter (mm)</i>	1.5	<i>Number of fibers (N)</i>	537
<i>Outer diameter (mm)</i>	1.9	<i>Active area (m<sup>2</sup>)</i>	1
<i>Porosity (%)</i>	53	<i>Inner diameter (mm)</i>	60
<i>Maximum pore diameter (μm)</i>	0.82	<i>Effective length (mm)</i>	406
<i>Mean pore diameter (μm)</i>	0.65		
<i>Minimum pore diameter (μm)</i>	0.61		

175

### 176 3.2. [Cho][Lys] synthesis and characterization

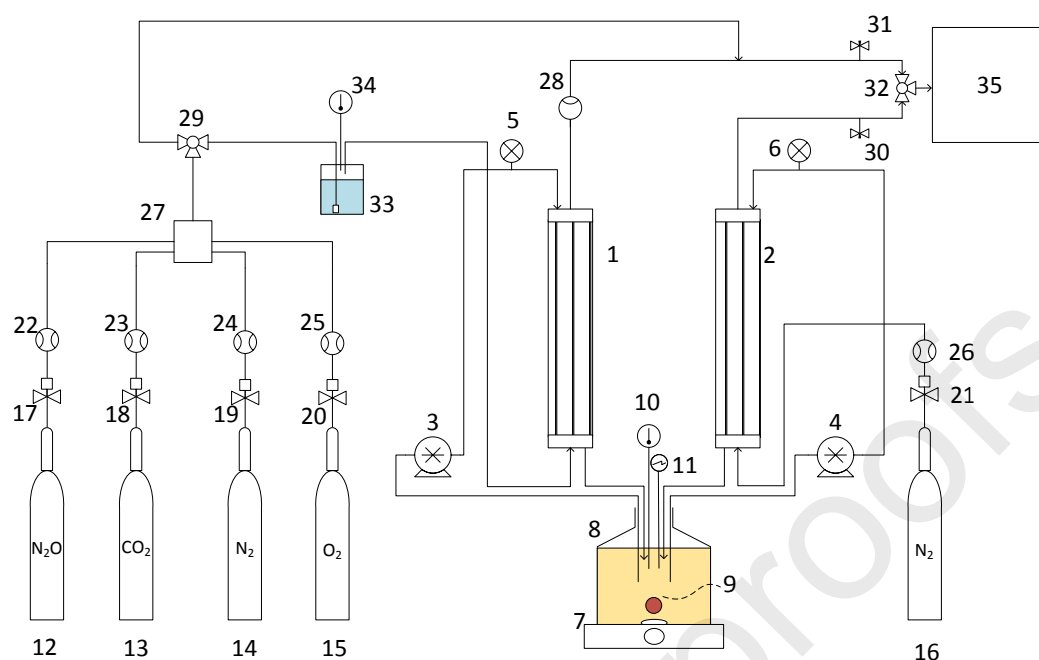
177 L(+)-Lysine monohydrate was dissolved in water and added directly to choline hydroxide *via* a  
 178 neutralization reaction. The final product was an aqueous solution of [Cho][Lys] ionic liquid,  
 179 containing  $50 \pm 2\%$  (w/w) of water. No dehydration step was performed in the IL solution. The  
 180 reaction was followed by pH measurement, using a Mettler Toledo pH probe (model I405-DPAS-  
 181 SC-K8S, USA) connected to an in-line tester (Jenco, model 3621, USA). The water content was  
 182 measured by titration, using a Karl-Fischer coulometer without diaphragm (Metrohm, USA,  
 183 model 831 KF coulometer). The [Cho][Lys] molecular structure was confirmed by proton nuclear  
 184 magnetic resonance (<sup>1</sup>H-NMR) and by attenuated total reflectance Fourier transform infra-red  
 185 (ATR-FTIR) analyses. Both spectra were recorded at room temperature on a Bruker AVANCE  
 186 Digital operating at 400 MHz and a Perkin Elmer Spectrum Two FT-IR Spectrometer,  
 187 respectively. [Cho][Lys] thermal stability was accessed by thermogravimetric analysis (TGA),  
 188 with 10 K per minute up to 873 K under nitrogen environment with a flow rate of 40 mL.min<sup>-1</sup>,  
 189 using a Q50 thermogravimetric analyser from TA Instruments (USA). [Cho][Lys] viscosity and  
 190 density were determined using a Stabinger viscometer™ SVM 3000 from Anton Paar (Austria),

191 in the temperature range between 293 to 308 K. The IL surface tension was also measured using  
192 a KSV sigma 702 tensiometer from KSV Instruments Ltd. (Finland), at 293 K. A goniometer  
193 (KSV Instruments Ltd., Finland) with image analysis software CAM 2008 was used to measure  
194 the contact angle between the IL and the surface of the Eclipse™ membrane. The contact angle  
195 was calculated as the average between the right and left contact angles.

### 196 *3.3. CO<sub>2</sub> absorption and IL solution regeneration experimental procedures*

197 Prior the evaluation of CO<sub>2</sub> absorption in the membrane contactor system, the saturation  
198 absorption capacity of the [Cho][Lys] IL solution was evaluated. Experiments were carried out in  
199 a stainless steel cell, by monitoring the CO<sub>2</sub> pressure decay with time in contact with a small  
200 volume of the IL solution, as described in previous works [19,31]. Different concentrations of  
201 [Cho][Lys] aqueous solutions were tested, and the saturation absorption capacity was determined  
202 for each one.

203 Afterwards, CO<sub>2</sub> absorption and IL solution regeneration were conducted in a gas-liquid  
204 membrane contactor system, as represented in Figure 2, at 295±2 K. Mass flow controllers (Alicat  
205 Scientific Inc., MC-series, USA), solenoid valves (ASCO®, USA) and pressure gauges  
206 (Omega™, USA), controlled the gas flow. Liquid flow was monitored using positive  
207 displacement pumps (Micropump®, GJ series, USA) and digital pressure gauges (WIKA, DG-10  
208 series, Germany). The IL solution was constantly stirred using a magnetic stirrer plate (Velp  
209 Scientifica®, Germany), the pH was measured using a Mettler Toledo pH probe (model I405-  
210 DPAS-SC-K8S, USA) connected to an in-line tester (Jenco, model 3621, USA) and the  
211 temperature measured with a digital thermometer (Huberlab, Switzerland).



213 *Figure 2. Schematic representation of the experimental set-up: 1, 2 - absorption and regeneration membrane modules,*  
 214 *respectively; 3, 4 - positive displacement pumps; 5, 6 - pressure gauges; 7 - stirrer plate; 8 - ionic liquid vessel; 9 -*  
 215 *sampling point; 10 - digital thermometer; 11 - pH meter; 12-16 - gas cylinders; 17-21 - solenoid valves; 22-26 - mass*  
 216 *flow controllers; 27 - gas mixture unit; 28 - mass flow indicator; 29, 32 - 3 way manual valves; 30, 31 - needle valves,*  
 217 *33 - stainless steel boiler with a gas disperser, 34 – thermocouple, 35 – GC on-line.*

218        Inside the CO<sub>2</sub> absorption module (Figure 2, module 1), the gas phase flowed in the shell  
 219 side of the contactor, with a constant flow rate of 250 mL.min<sup>-1</sup>, simulating what is called minimal  
 220 gas flow rate anaesthesia [32,33]. Since the system was operated in open circuit, the gas pressure  
 221 was similar to the atmospheric pressure. The IL solution pressure was maintained higher than the  
 222 gas pressure avoiding bubbling. The [Cho][Lys] solution circulated counter currently, with a  
 223 constant flow rate of 790 mL.min<sup>-1</sup>, in the lumen of the capillaries to promote a high driving force  
 224 between the phases throughout the membrane pores. The regeneration of the IL solution was  
 225 performed in a second module, connected in series with the absorption module. N<sub>2</sub> at atmospheric  
 226 pressure with a flow rate of 30 mL.min<sup>-1</sup> was used as sweep gas. The sweep gas flowed counter  
 227 currently in the shell side. [Cho][Lys] solution circulated with the lowest flow rate possible (570  
 228 mL.min<sup>-1</sup>), assuring a liquid pressure higher than the sweep gas pressure, in order to avoid  
 229 bubbling and allow for a higher residence time in the contactor. All the experimental conditions  
 230 tested are shown in Table 2.

231

Table 2. Experimental conditions in the absorption and regeneration modules.

	Absorption module	Regeneration module
<i>Temperature (K)</i>	295±2	
<i>Gas flow rate (mL.min<sup>-1</sup>)</i>	250	30
<i>IL flow rate (mL.min<sup>-1</sup>)</i>	790	570
<i>Feed gas composition (mol%)</i>	3% N <sub>2</sub> , 5% CO <sub>2</sub> , 27% O <sub>2</sub> , 65% N <sub>2</sub> O	100% N <sub>2</sub>
<i>IL solution inlet pressure (bar)</i>	0.10 - 0.14	0.09
<i>Pressure drop (bar)</i>	0.07	0

232

233 The regeneration efficiency was followed by monitoring the composition of the sweep  
 234 gas stream at the outlet of the module. Aliquots of IL were collected over time and analysed by  
 235 ATR-FTIR, to evaluate the effect of the CO<sub>2</sub> absorption in the molecular structure of the ionic  
 236 liquid. Also, accessing the FITR spectrum over time allowed to monitor the absorption kinetics.  
 237 Gas streams were analysed online using an Agilent gas chromatograph (GC) 7890B, equipped  
 238 with a thermal conductivity detector (TCD). The GC carrier gas was helium and the samples were  
 239 analysed using an isothermal method with a Poraplot U column connected to a Molesieve 5A  
 240 column, at 313 K. The TCD detector temperature was maintained at 473 K. Gas samples were  
 241 introduced into the GC using an automated VICI-Valco gas valve.

242 To evaluate the maximum capacity of the proposed system, the absorption of CO<sub>2</sub> was  
 243 performed with a pure CO<sub>2</sub> feed stream, without regenerating the ionic liquid solution.  
 244 Afterwards, 3 cycles of CO<sub>2</sub> absorption / IL regeneration were conducted aiming to access the  
 245 regeneration efficiency, from the limit situation where the IL solution was fully saturated. Finally,  
 246 aiming real conditions simulation, experiments with a gas mixture of 65 mol% N<sub>2</sub>O, 5% CO<sub>2</sub>,  
 247 27% O<sub>2</sub> and 3% N<sub>2</sub>, either 100% humidified or dried, were performed to evaluate the CO<sub>2</sub> removal  
 248 efficiency, determine the separation factor, as well as determine the effect of water vapour in the  
 249 process efficiency. The absorption flux of CO<sub>2</sub> and the overall mass transfer coefficient were also  
 250 determined.

## 251 3.4. Evaluation of experimental mass transfer coefficients

252 The parameters obtained by running the experimental set-up, allow to calculate the overall mass  
 253 transfer coefficient,  $K_{ov}$ , according to the following equation:

$$254 \quad K_{ov} = \frac{Q_g \times (C_{CO_2,in,g} - C_{CO_2,out,g})}{A \times \Delta C_{CO_2,g,lm}} \quad (10)$$

255 where the  $Q_g$  is the gas flow rate ( $m^3 \cdot s^{-1}$ ) from the gas phase to the liquid phase,  $C_{CO_2,in,g}$  and  
 256  $C_{CO_2,out,g}$  are the gas phase inlet and outlet  $CO_2$  concentrations ( $mol \cdot m^{-3}$ ),  $A$  is the gas-liquid  
 257 contact area ( $m^2$ ) and  $\Delta C_{CO_2,g,lm}$  is the logarithmic mean driving force based on the gas phase  
 258 concentrations ( $mol \cdot m^{-3}$ ), described as:

$$259 \quad \Delta C_{CO_2,lm} = \frac{(C_{CO_2} - C_{CO_2}^*)_{g,in} - (C_{CO_2} - C_{CO_2}^*)_{g,out}}{\ln \left[ \frac{(C_{CO_2} - C_{CO_2}^*)_{g,in}}{(C_{CO_2} - C_{CO_2}^*)_{g,out}} \right]} \quad (11)$$

260  $C_{CO_2,in}^*$  and  $C_{CO_2,out}^*$  are the equilibrium concentrations at the interface between the gas and liquid  
 261 phases. Due to the fast chemical reaction,  $CO_2$  concentration in the liquid phase is equal to 0, and  
 262  $C_{CO_2,g}^*$  is 0. Therefore, the equation is simplified as follows:

$$263 \quad \Delta C_{CO_2,lm} = \frac{C_{CO_2,g,in} - C_{CO_2,g,out}}{\ln \left[ \frac{C_{CO_2,g,in}}{C_{CO_2,g,out}} \right]} \quad (12)$$

264 Moreover, to determine the process efficiency, a separation factor ( $SF$ ) between  $CO_2$  and  
 265  $N_2O$  was determined. Considering the ratio between the permeable species in the feed and the  
 266 permeate side,  $SF$  was determined according to the following equation:

$$267 \quad SF = \frac{n_{i,p}/n_{j,p}}{n_{i,f}/n_{j,f}} \quad (13)$$

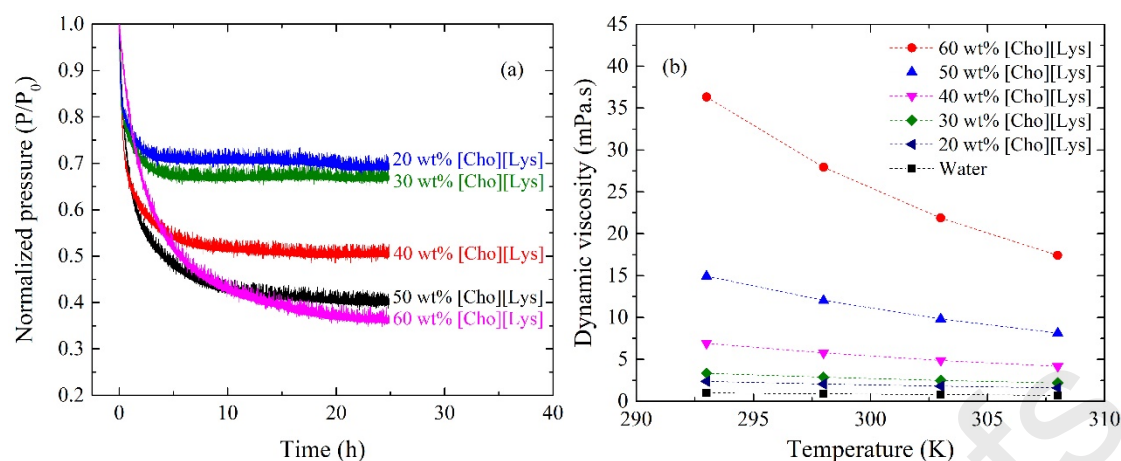
268 where, p and f are the permeate and feed streams and i and j the permeable species, in particular  
 269 i the most permeable one.

270

271

272 **4. Results and discussion**273 *4.1. [Cho][Lys] characterization*

274 In this work, due to the low toxicity and low production cost, when compared to other traditional  
275 ILs, and recognized efficiency to capture CO<sub>2</sub>, [Cho][Lys] was the IL selected to absorb CO<sub>2</sub>  
276 using a membrane contactor system, aiming the operation in a closed-loop anaesthetic circuit. To  
277 increase the cost-effectiveness of this IL, it is proposed the use of an aqueous solution of  
278 [Cho][Lys]. As referred in section 3.3, a pre-screening study of CO<sub>2</sub> absorption with different  
279 [Cho][Lys] IL concentrations was performed. According to the results obtained, the highest CO<sub>2</sub>  
280 absorption was achieved for the IL solution with 60 wt% of [Cho][Lys] (Figure 3a). However,  
281 the solution must possess low viscosity to minimise the gas-liquid mass transfer resistance and  
282 increased pressure in the capillaries. Therefore, dynamic viscosities of the IL solutions were  
283 measured, as shown in Figure 3b. The viscosity obtained for the IL solution with 60 wt% of  
284 [Cho][Lys] was 36 mPa.s, at 293 K, while for the 50 wt% [Cho][Lys] was significantly lower (15  
285 mPa.s). Since a slight difference in the CO<sub>2</sub> absorption between both IL solutions was obtained,  
286 50 wt% [Cho][Lys] was the concentration selected to perform the present study. Additionally, in  
287 the case of the 50 wt% solution, the CO<sub>2</sub> absorption kinetics is faster when compared to the 60  
288 wt% solution, which leads to a faster CO<sub>2</sub> removal rate, as it can be observed in Figure 3a, that  
289 presents the pressure profiles for the first hours of the experiments.

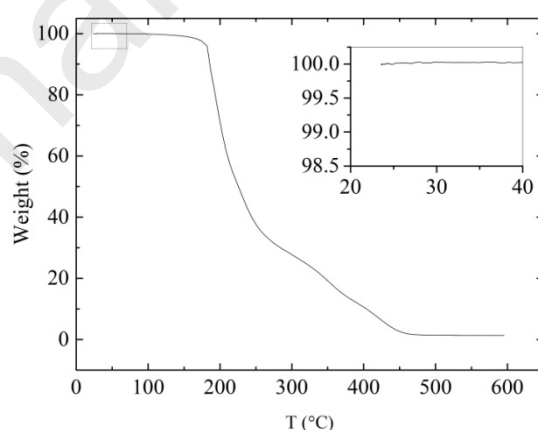


290

291 *Figure 3. (a) Screening of CO<sub>2</sub> absorption in different [Cho][Lys] aqueous solutions; (b) Dynamic viscosity of different*  
 292 *[Cho][Lys] aqueous solutions as a function of temperature.*

293

294 The thermal stability of the CO<sub>2</sub> absorbents is extremely relevant and must be taken into  
 295 account, as it can affect their absorption and desorption behaviour [15]. In a typical hospital  
 296 surgery room temperature ranges between 293 and 297 K [34], and [Cho][Lys] is stable against  
 297 temperature variations, as it is demonstrated in Figure 4. Furthermore, in a perspective of possible  
 298 thermal regeneration, the temperatures should not go higher than 453 K, which corresponds to the  
 299 onset temperature where weight loss was registered due to thermal degradation (Figure 4).



300

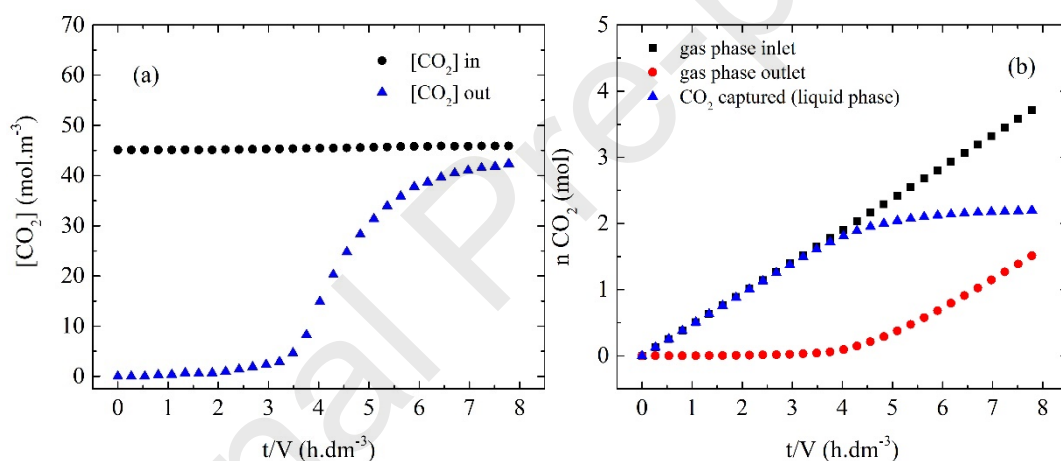
301 *Figure 4. Thermogravimetric curve for [Cho][Lys] as a function of temperature.*

302 The contact angle obtained between the 50 wt% [Cho][Lys] solution and the PTFE membrane  
 303 was 97°, at 295 K. Contact angles higher than 90° are associated to hydrophobic surfaces and  
 304 usually used as a reference to operate membrane modules in a non-wetted pore mode, avoiding

305 liquid penetration and stagnation inside the pores [35]. Therefore, the PTFE modules selected for  
 306 this work assure that the pores of the membrane are not affected by wetting with the liquid phase.  
 307 This is an important feature that allows the operation of the system without resistance to mass  
 308 transfer due to the presence of the membrane.

#### 309 4.2. CO<sub>2</sub> capture maximum absorption capacity

310 The absorption of CO<sub>2</sub> was performed using a pure CO<sub>2</sub> feed stream, to access the maximum  
 311 absorption capacity of the [Cho][Lys] solution (50 wt%). The CO<sub>2</sub> flow rate was adjusted to 250  
 312 mL.min<sup>-1</sup>, which is analogous to the minimal-flow anaesthesia mode [33]. The CO<sub>2</sub> absorption by  
 313 the ionic liquid occurs across the gas-liquid interface, due to the contact between the stabilised  
 314 phases inside the pores of the PTFE capillaries of the membrane contactor.

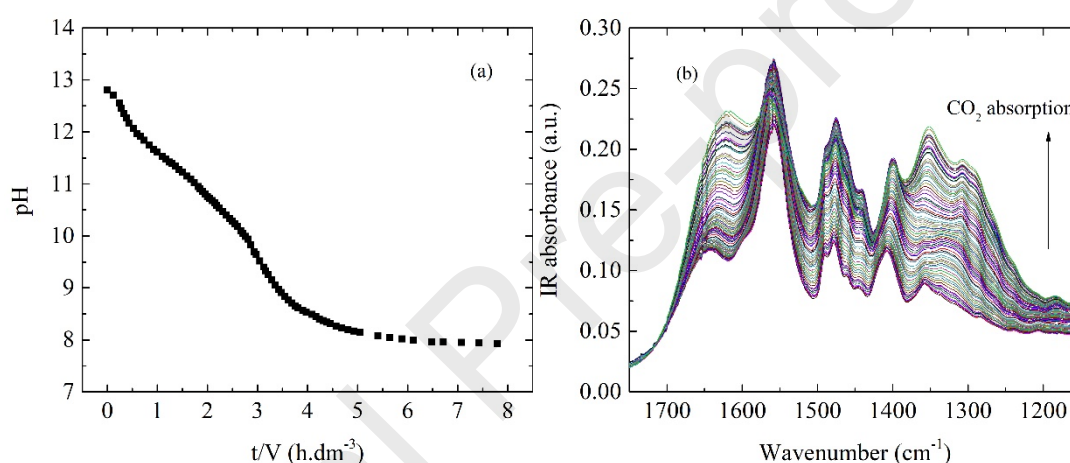


315

316 *Figure 5. Experimental CO<sub>2</sub> absorption curves: (a) inlet and outlet [CO<sub>2</sub>] in the gas phase as a function of time per IL*  
 317 *solution volume; (b) Accumulated [CO<sub>2</sub>] in gas and liquid phases as a function of time per IL solution volume.*

318 In Figure 5a is represented the CO<sub>2</sub> concentration of the inlet and outlet streams in the gas phase  
 319 as a function of time *per* volume of IL. Since the process is completely controlled by the liquid  
 320 phase, the duration of the experiments is dependent of the volume of the IL solution used, thus in  
 321 the present work, the time variable is always shown by the ratio time *per* IL volume used in each  
 322 experiment. The profile obtained for the CO<sub>2</sub> concentration in the gas outlet stream is the result  
 323 of an absorption accompanied by chemical reaction. Once the liquid phase approaches saturation,  
 324 we started to observe the presence and increase of CO<sub>2</sub> concentration in the gas outlet stream. The  
 325 number of CO<sub>2</sub> moles captured by the liquid phase was obtained assuming the difference between

326 the inlet and outlet streams in the gas phase, which is related with the CO<sub>2</sub> absorption by the IL  
 327 (Figure 5b). The absorption of CO<sub>2</sub>, in this case, was performed using 700 mL of 50 wt%  
 328 [Cho][Lys] solution and a liquid flow rate of 524 mL.min<sup>-1</sup>. Saturation was achieved after 5.5  
 329 hours of operation, corresponding to a time *per* IL volume of 7.8 h.dm<sup>-3</sup>. According to equation  
 330 (10), the overall mass transfer coefficient can be calculated through the ratio between the CO<sub>2</sub>  
 331 absorption flux and the mean logarithmic CO<sub>2</sub> concentration in the gas phase (driving force). The  
 332 value obtained for  $K_{ov}$  was  $2.16 \times 10^{-5}$  m.s<sup>-1</sup> with a CO<sub>2</sub> flux of  $1.82 \times 10^{-4}$  mol.m<sup>-2</sup>.s<sup>-1</sup>. The total  
 333 amount of CO<sub>2</sub> captured was 5.9 mol<sub>CO<sub>2</sub></sub>/kg<sub>IL</sub>, which is superior to the maximum absorption  
 334 capacity of soda lime reported in literature (19 wt%, which corresponds to 4.32 mol/kg) [36].



335

336 *Figure 6. CO<sub>2</sub> absorption in [Cho][Lys] IL solution, monitored by pH measurement and ATR-FTIR analysis: (a) pH*  
 337 *variation as a function of time per IL solution volume; (b) IR absorbance as a function of the wavenumber.*

338

339 The absorption of CO<sub>2</sub> by the IL was followed by measuring the pH *in situ* and performing  
 340 an IR spectra analysis of the IL samples. In Figure 6a, the pH variation during the CO<sub>2</sub> absorption  
 341 is represented. [Cho][Lys] solution possess a strong basic character which is confirmed through  
 342 the extremely high initial pH (~13). Due to this strong basicity, the IL is very reactive towards  
 343 CO<sub>2</sub>. The pH decreases over time as a consequence of the neutralization reaction between CO<sub>2</sub>  
 344 and [Cho][Lys] solution due to the formation of the bicarbonate anion. The saturation state of the  
 345 IL solution is represented by the plateau obtained at pH ~8. Figure 6b is a representation of the  
 346 CO<sub>2</sub> absorption impact at a molecular level. Representative differences were obtained in the FTIR

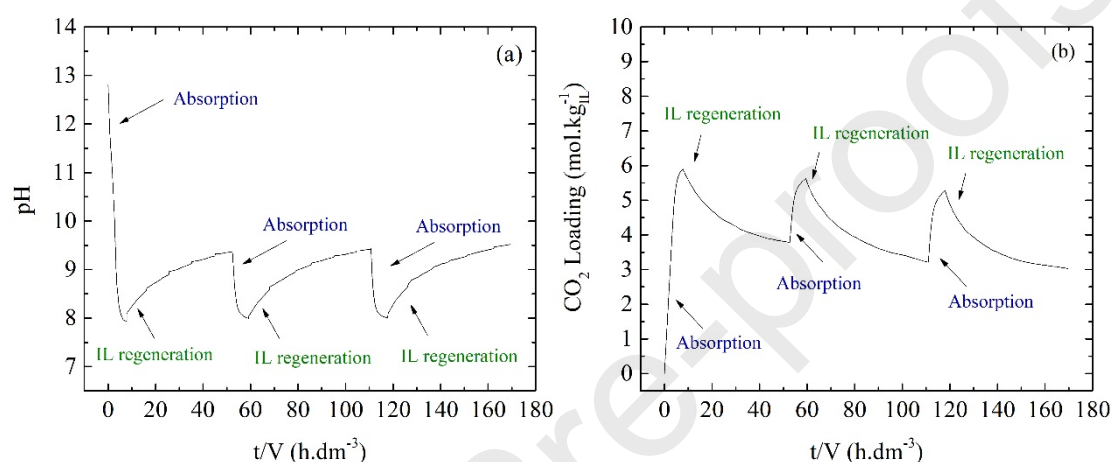
347 spectra of the samples before and after CO<sub>2</sub> absorption, characterized by an increase of the  
348 absorbance bands at 1647 cm<sup>-1</sup>, 1558 cm<sup>-1</sup>, 1478 cm<sup>-1</sup>, 1408 cm<sup>-1</sup> and 1358 cm<sup>-1</sup>. The absorbance  
349 band corresponding to the  $-NH_3^+$  group is observed at the region 1600-1750 cm<sup>-1</sup> [37].  
350 Therefore, the band at 1647 cm<sup>-1</sup> is attributed to the protonated amine groups, which formation  
351 was predicted by the chemical model as described in section 2.1. An absence of a band in the  
352 2500-3000 cm<sup>-1</sup> region after the CO<sub>2</sub> absorption, indicates no formation of carbamic acid.  
353 Generally, the interaction between amine groups and CO<sub>2</sub> can proceed through carbamate or  
354 carbamic acid formation pathways. Hence, the pathway of carbamic acid formation was not  
355 considered in the chemical mechanism described in the present work [28,37]. The two bands at  
356 1558 cm<sup>-1</sup> and 1408 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching vibrations of  
357 COO<sup>-</sup>, respectively. Depending on the molecular constituents, carboxylates bands are generally  
358 present in the 1650-1540 cm<sup>-1</sup> and 1450-1360 cm<sup>-1</sup> regions. Inorganic carbonates do not possess  
359 C-O and C=O stretching vibrations. Thus, the “C-O” bond order of the inorganic carbonates is  
360 between one and two, possessing a stretching vibration band in the region 1410-1510 cm<sup>-1</sup>. The  
361 identified band at 1478 cm<sup>-1</sup> is then attributed to the vibration of the carbonate ion CO<sub>3</sub><sup>2-</sup> [38,39].  
362 Therefore, the FTIR spectra analysis of the IL solution after CO<sub>2</sub> absorption confirmed the  
363 formation of the ionic species bicarbonate ion HCO<sub>3</sub><sup>-</sup>, protonated amine NH<sub>3</sub><sup>+</sup> and carbonate ion  
364 CO<sub>3</sub><sup>2-</sup>, as described by the proposed chemical mechanism (equations (1) to (5) in section 2.1).

365       Regarding to analytical methods, especially in cases of process monitoring, it is important  
366 to mention that both pH measurements and IR spectra analysis are fast techniques, clean and easy  
367 to use, which allow for an efficient monitoring of the CO<sub>2</sub> loading in the ionic liquid solution.

368

369 4.3.  $\text{CO}_2$  maximum absorption capacity and IL solution regeneration cycles

370 Regeneration of the IL solution integrated with the  $\text{CO}_2$  absorption can be a step forward when  
 371 comparing to the current technology, since soda lime is disposed after reaching its saturation,  
 372 adding an extra cost to the hospitals. In Figure 7 are represented the  $\text{CO}_2$  maximum absorption  
 373 and IL regeneration cycles, with the pH evolution as a function of time *per* IL volume (a) and  
 374 the  $\text{CO}_2$  loading as a function of time per IL volume (b).



375

376 *Figure 7.  $\text{CO}_2$  absorption and IL regeneration cycles: (a) pH as a function of time per IL solution volume; (b)  $\text{CO}_2$*   
 377 *loading as a function of time per IL solution volume.*

378 Cycles of  $\text{CO}_2$  absorption/IL regeneration were performed, where the  $\text{CO}_2$  absorption was  
 379 accomplished feeding as gas stream pure  $\text{CO}_2$  and the IL regeneration with  $\text{N}_2$  as the sweep gas.  
 380 In the first cycle, the complete saturation of the IL was achieved, corresponding to a  $\text{CO}_2$  loading  
 381 value of  $5.9 \text{ mol}_{\text{CO}_2}/\text{kg}_{\text{IL}}$ . The IL regeneration efficiency, after the saturation state was 36%, which  
 382 corresponds to the disruption of the weaker chemical bond between the amine in the carboxylic  
 383 acid functional group of the lysinate anion and bicarbonate. In the second cycle, the resulting  $\text{CO}_2$   
 384 absorption capacity corresponded to what was reverted in the first regeneration cycle. In the  
 385 second and third absorption/regeneration cycles, the regeneration was complete, since the amount  
 386 of  $\text{CO}_2$  absorbed in the previous absorption step was totally reverted, as it is demonstrated in  
 387 Figure 7b. Therefore, if a complete regeneration is desired starting from the first cycle, that will  
 388 probably be possible by performing a thermal regeneration step, in order to revert the remaining

389 bond between bicarbonate and the amine group in the alkyl side chain of lysinate anion and, by  
390 this mean, exploit the full potential of the IL solution.

391 *4.4. CO<sub>2</sub> removal from anaesthetic gas mixtures*

392 In a closed-loop operation perspective, the content of CO<sub>2</sub> in the recirculated anaesthetic gas  
393 mixture must be lower than 0.5%, to avoid hypercapnia (high levels of CO<sub>2</sub> in blood), hypoxemia  
394 or hypoxia (low levels of O<sub>2</sub> in blood and tissue). The anaesthetic gas mixture to be recovered  
395 contain around 5% of CO<sub>2</sub>, thus, the following results correspond to experiments aiming an  
396 operation efficiency superior to 90%.

397 To evaluate the CO<sub>2</sub> capture from anaesthetic gas mixtures, experiments considering  
398 nitrous oxide as the anaesthetic gas were conducted, simulating realistic conditions. Therefore, a  
399 gas mixture composition of 65% N<sub>2</sub>O, 5% CO<sub>2</sub>, 27% O<sub>2</sub> and 3% N<sub>2</sub> was used to feed the module,  
400 mimicking the exhalation of a patient. In addition, experiments with 100% humidified feed gas  
401 stream and with simultaneous IL regeneration were also performed. In Table 3 the experimental  
402 and calculated mass transfer parameters obtained are shown.

403

404

405

Table 3. Experimental and calculated mass transfer parameters.

<b>Parameters</b>	<b>5% CO<sub>2</sub></b>	<b>5% CO<sub>2</sub> + 100% RH</b>	<b>5% CO<sub>2</sub> + 100% RH + IL regeneration</b>
$u_l$ ( $m.s^{-1}$ )	1.39		
$k_l \times 10^{-6}$ ( $m.s^{-1}$ )	9.26		
Volume of IL ( $dm^3$ )	0.75	0.80	1.35
Time (h)	36	39	63
Time/IL volume ( $h.dm^{-3}$ )	47.7	48.5	46.9
$J_{CO_2} \times 10^{-6}$ ( $mol.m^{-2}.s^{-1}$ )	8.34	8.55	8.46
$J_{N_2O} \times 10^{-6}$ ( $mol.m^{-2}.s^{-1}$ )	4.43	4.83	5.75
$K_{CO_2, overall} \times 10^{-6}$ ( $m.s^{-1}$ )	9.15	9.36	9.33
$\varphi$	1.25	1.28	1.28
SF	21.4	18.6	14.6
CO <sub>2</sub> Loading ( $mol.kg^{-1}$ )	3.14	2.92	2.86

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The obtained flux of CO<sub>2</sub> was identical for all experiments, using N<sub>2</sub>O in the gas mixture as the anaesthetic gas. Therefore, the presence of water in the gas mixture and the simultaneous IL regeneration do not compromise the CO<sub>2</sub> mass transfer. The regeneration step does not affect the CO<sub>2</sub> transport, since the driving force was already the maximum possible, due to the fast reaction between CO<sub>2</sub> and the liquid phase, resulting in an immediate consumption of CO<sub>2</sub>. The

412 experimental time obtained for all cases, shown in Table 3, correspond to operation efficiency  
413 above 90%, meaning a CO<sub>2</sub> content in the recycled gas mixtures lower than 0.5%, as required.  
414 This experimental condition explains why the values obtained for the CO<sub>2</sub> loadings expressed in  
415 Table 3 are inferior to the reported in section 4.3, since the CO<sub>2</sub> content of 0.5% in the recycled  
416 gas stream is detected before the IL solution reaches its complete saturation.

417 When the feeding gas mixture was humidified, the presence of water vapour leads to an  
418 increase of N<sub>2</sub>O flux. The mass transport in the proposed system is controlled by the chemical  
419 reaction between CO<sub>2</sub> and the IL solution, however the presence of water vapour in the gas phase  
420 may lead to the formation of water microdomains in the ionic liquid phase, offering an additional  
421 path for the transport of solutes through the ionic liquid phase. The increase of N<sub>2</sub>O flux observed  
422 may be justified by the solubility of N<sub>2</sub>O in water and the mobility of these water  
423 microenvironments across the liquid phase. A similar behaviour was already reported in the  
424 literature [40,41].

425 Additionally, when the simultaneous IL solution regeneration step was added, the N<sub>2</sub>O  
426 flux increased. This behaviour results from the removal of N<sub>2</sub>O during regeneration, keeping high  
427 the driving force for transport during the absorption process. This additional transport path has  
428 almost no impact on the transport of CO<sub>2</sub> because, due to its fast reaction at the gas-liquid  
429 interface, its concentration in a free form inside the liquid phase is negligible. Still, the overall  
430 selective removal of CO<sub>2</sub> from the gas phase, when compared with the transport of N<sub>2</sub>O, is rather  
431 impressive if we remember that these molecules possess similar properties, such as molecular  
432 mass, chemical configuration, molecular volume, electronic structure and kinetic diameters  
433 (Table 4), that explain their similar solubility and diffusivity in water.

434

435

436

Table 4. Lennard-Jones and kinetic diameters.

	Lennard-Jones diameter	Kinetic diameter
--	------------------------	------------------

	(Å)	(Å)
CO <sub>2</sub>	3.941 [30]	3.330 [42]
N <sub>2</sub> O	3.828 [30]	3.330 [43]

437

438 Also, it is important to mention the very low partial pressure of CO<sub>2</sub> (5% mol) compared  
439 with the partial pressure of N<sub>2</sub>O (65% mol) in the feed stream, and even though there was a  
440 transport of N<sub>2</sub>O to the liquid phase, the removal of CO<sub>2</sub> was not affected. The separation factors  
441 obtained (*SF*), shown in Table 3, are considerable high for all cases, which is a proof that the  
442 proposed system is very selective towards CO<sub>2</sub>. For the experimental procedure mimicking the  
443 real conditions, *i.e.*, containing 65% of the anaesthetic gas humidified, the system proposed with  
444 simultaneous IL regeneration, was able to operate efficiently during 63 hours.

445 In the current technology, that utilises containers with 1 kg of soda lime for CO<sub>2</sub> capture  
446 in anaesthetic closed circuits, it is recommended to replace the container after 8 to 14 hours of  
447 continuous operation, depending on the supplier recommendations and the usage. Furthermore,  
448 the maximum absorption capacity of soda lime to capture CO<sub>2</sub> is 4.32 mol/kg [36]. Based on the  
449 results obtained in this work, the proposed system was able to operate over 63 hours using 1.44  
450 kg of 50 wt% [Cho][Lys] IL solution with a maximum absorption capacity of 5.9 mol/kg.  
451 Comparing with the use of a container with 1 kg of soda lime, the proposed system possesses a  
452 working operation time 3 to 5 times higher of 1 kg of [Cho][Lys] IL solution is used (~43 hours  
453 of operation).

## 454 5. Conclusions

455 Experiments of CO<sub>2</sub> capture from gas mixture with anaesthetic agents, have been performed,  
456 using a 50 wt% [Cho][Lys] IL solution. The system was composed by polytetrafluoroethylene  
457 porous membrane contactors with the IL solution circulating in counter current with the gas phase  
458 in the lumen of the capillaries. Additionally, a regeneration unit composed by a second membrane  
459 contactor was simultaneously operated. The results obtained revealed a CO<sub>2</sub> capture maximum

460 capacity of the system of 5.9 mol/kg<sub>IL</sub>. In the experiments in which simulated conditions using  
461 65% of nitrous oxide and 5% of carbon dioxide, the results revealed an efficient system able to  
462 operate over 63 hours. However, the regeneration of the IL solution using N<sub>2</sub> as sweep gas, was  
463 not completely efficient for the reversion of the CO<sub>2</sub> absorption. Due to this fact, a thermal  
464 regeneration study is recommended as future work. Additionally, the proposed system should be  
465 tested using a feed stream mimicking real conditions, using the exhaled composition as well as  
466 with pulsed flow, simulating the expiratory frequency.

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473

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