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# 1 Influence of particle size distribution on carbon- 2 based flowable electrode viscosity and 3 desalination efficiency in flow electrode 4 capacitive deionization.

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14

## 15 Abstract

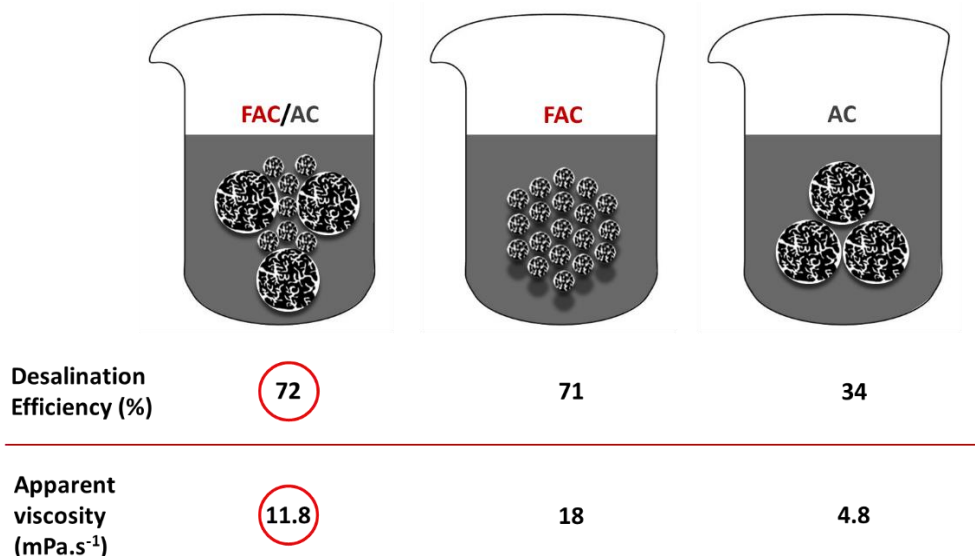
16 Flow-electrode capacitive deionization (FCDI) is a potential energy-efficient electrochemical  
17 water desalination technology that combines ion-exchange membranes and flowable  
18 electrodes (FE). The performance of activated carbon (AC)-based FEs in FCDI systems is  
19 influenced by various factors, including particle size. Here, particle size commercial AC was  
20 reduced by dry ball milling to produce FEs for FCDI. Physical analysis by scanning electron  
21 microscopy and particle size analyzer confirmed the particle size reduction after dry ball milling.  
22 Then, the effect of particle size distribution on the rheological behavior and desalination  
23 performances of AC-based FEs was investigated by desalination performance indicators, such  
24 as desalination efficiency, average salt adsorption rate and charge efficiency. FE samples  
25 were prepared using different mixtures of fine-size range (0.65-0.92  $\mu\text{m}$ ; fine AC, FAC) and  
26 large-size range (1.5-2.3  $\mu\text{m}$ ; AC) particles. The AC to FAC particle ratio influenced the  
27 rheological properties of AC-based FEs in FCDI. Bimodal mixtures with 75% of FAC and 25%  
28 of AC (0.75:0.25 FAC:AC) particles displayed the highest desalination efficiency compared  
29 with pure AC and pure FAC FEs (72% *versus* 34% and 71%, respectively). Moreover, in our  
30 FCDI set-up, 0.75:0.25 FAC:AC bimodal mixtures showed better flowing properties than the  
31 pure FAC FEs, characterized by high viscosity.

32

33 **Keywords:** Flow electrode capacitive deionization, activated carbon flow electrode, particle size  
34 distributions, rheology, stability and desalination.

35

36 **Graphical abstract**



37

38

39 **1. Introduction**

40 Capacitive deionization (CDI) is used to eliminate charged species from water with various  
 41 applications, such as brackish and sea water desalination,<sup>1,2</sup> water softening,<sup>3</sup> and wastewater  
 42 remediation.<sup>4</sup> CDI is an energy-efficient, cost-effective, and ecofriendly technology.<sup>5</sup> The first  
 43 and most widely-used CDI set-up requires two porous carbon electrodes separated by a  
 44 spacer through which water flows perpendicularly to the applied electric field.<sup>5</sup> In membrane  
 45 CDI (MCDI), a key variation of the basic CDI set-up<sup>6</sup>, the feed water flows between an anion  
 46 exchange membrane at the anode and a cation exchange membrane at the cathode.<sup>7</sup> The  
 47 membrane main role is to reduce co-ion adsorption. This improves the charge efficiency and  
 48 can increase the charge storage in the electrode porous structure.<sup>8</sup> In the last decade, a new  
 49 MCDI-based approach was developed to introduce carbon-based flowable electrodes.<sup>9</sup> The  
 50 basis of this technology, called flow-electrode CDI (FCDI), is similar to that of electrochemical  
 51 flow capacitors<sup>10</sup>. The process is based on electrical double layers that are formed on  
 52 interfaces between porous activated carbon (AC)-based electrodes and an electrolyte (e.g.  
 53 NaCl solution).<sup>11</sup> Ions are adsorbed and stored in the electrical double layers when a cell  
 54 voltage in the range of 1–1.2 V is applied to the cell<sup>12</sup>. FCDI has three major advantages  
 55 compared with other CDI systems. First, the continuous desalination of the feed water flowing  
 56 through a single cell does not require an in situ discharge step for regenerating the ion-  
 57 saturated AC-based electrodes, which is done in a separate process. This allows the easy  
 58 scaling-up of FCDI<sup>13</sup>. Second, the continuous inflow of uncharged carbon particles into the  
 59 charging cell increases the capacitance, which is needed for desalination, above that of static-  
 60 electrode CDI systems.<sup>14</sup> This offers more flexibility because the desalination rate and kinetics  
 61 can be easily controlled by adjusting the saline solution, flow electrode retention time, and the  
 62 applied current charge. Third, in AC-based flowable electrodes, pores are more exposed and  
 63 easily accessible for ion adsorption.

64 The choice of electrode material is a crucial factor in CDI system performance. The ideal CDI  
 65 electrode material should meet the following criteria: 1) large specific surface area, high ion

66 adsorption sites; 2) high conductivity and ion mobility; 3) hydrophilicity to ensure full contact  
67 between the electrode porous structure and water; 4) electrochemical stability at different pH  
68 and voltages to ensure the system reliability and sustainability; 5) easily shapeable in function  
69 of the design requirements and economically feasible (i.e. availability, cost, and recyclability)  
70 for industrial development. Carbon-based materials are mostly used in this field because they  
71 meet these requirements. Moreover, to improve the properties of the carbon-based materials  
72 used as CDI electrodes, many methods have been tested and many carbon forms have been  
73 exploited, for instance AC, AC fibers, carbon aerogels, AC cloths,<sup>15,16</sup> carbon nanotubes,<sup>17</sup>  
74 graphene,<sup>18</sup> carbon nanofibers,<sup>19</sup> carbon sheet<sup>20</sup>.

75 Porous AC, a cheap, easily available and reusable material, is widely used to prepare flowable  
76 electrodes for FCDI.<sup>21</sup> The electrochemical performance of AC-based flowable electrodes is  
77 influenced by several parameters, including mass loading, particle size and morphology,  
78 specific surface area, surface charge, viscosity, and hydrophilicity.<sup>22</sup> However, they display low  
79 wettability, pore inaccessibility for ions, and low conductivity. Therefore, to improve its features  
80 and overcome some of its limitations, AC can undergo physical or chemical treatments. For  
81 instance, pores can be expanded using physical treatments, such as thermal modification  
82 using inert gases (e.g. N<sub>2</sub>, Ar, CO<sub>2</sub>).<sup>23</sup> Surface area can be improved by exposure to KOH or  
83 NaOH followed by thermal treatment.<sup>24</sup> Much research has been done on hierarchical porous  
84 carbons with interconnected micro-mesopores for increasing ion adsorption.<sup>25</sup> Recent studies  
85 have investigated the particle size effect on the desalination performance of AC-based  
86 electrodes in CDI.<sup>26</sup> Cohen *et al.* combined dilute slurry electrodes and dense fluidized bed  
87 electrodes for better electric conductivity and lower resistance.<sup>27</sup> Zhang *et al.* found that AC-  
88 based electrodes with different particle sizes provide different CDI performances. Particularly,  
89 a mixture of large and small particles gave the best desalination performance in CDI.<sup>26</sup>  
90 However, the effect of particle size distribution on the viscosity and desalination performance  
91 of carbon slurry electrodes in FCDI has not been investigated yet. In a previous study, we  
92 found that reducing AC particle size in flowable electrodes can double the desalination rate in  
93 FCDI.<sup>28</sup> This was attributed to the enhanced connectivity between particles that increases  
94 charge transport and storage, thus improving conductivity through the AC percolating network.  
95 Moreover, in AC-based electrodes with finer particles, obtained by grinding, pores were more  
96 exposed, leading to faster ionic diffusion.<sup>28</sup> However, viscosity was increased upon particle  
97 size reduction. As the flowable electrode must flow along a narrow channel in the FCDI set-  
98 up, its rheological features are a crucial factor for limiting pressure drops and ensuring the  
99 absence of clogging. Indeed, the higher viscosity of the flowable electrode with fine AC  
100 particles, compared with normal AC particles, led to pumping and flowing difficulties inside the  
101 FCDI system. Therefore, in the present study, we wanted to decrease the viscosity of AC-  
102 based flowable electrodes, while maintaining the good desalination performance obtained with  
103 fine AC particles. To this aim, we mixed two AC particle size ranges to produce flowable  
104 electrodes for FCDI. We prepared bimodal slurries with different ratios of fine AC (FAC) to AC  
105 particles with the same carbon loading (10%) and characterized their rheological properties  
106 and desalination performance to find the best compromise between these parameters.

107 Our AC modification strategy for desalination improvement in FCDI is very simple, compared  
108 with the complex physical and chemical AC modifications that have been recently used in CDI.  
109 This is important, especially due to the major improvements in FCDI desalination efficiency

110 and viscosity reduction observed with these bimodal flowable electrodes compared with pure  
111 AC and FAC flowable electrodes.

112

## 113 2. Experimental

### 114 2.1. Material preparation

115 Commercial AC (Darco; CAS no: 7440-44-0) and sodium chloride (NaCl, CAS no: 7647-14-5,  
116 MW 58.44 g mol<sup>-1</sup>, 99%) were purchased from Sigma Aldrich. Cationic and anionic exchange  
117 membranes were purchased from Membranes International Inc. (Ringwood, New Jersey,  
118 USA). Deionized water (18 MΩ cm<sup>-2</sup>) was prepared using a purification system.

119 AC powder was dry ball-milled using 50-mm diameter balls (350 rpm rotation speed) at room  
120 temperature for 90 minutes to obtain finer particles (

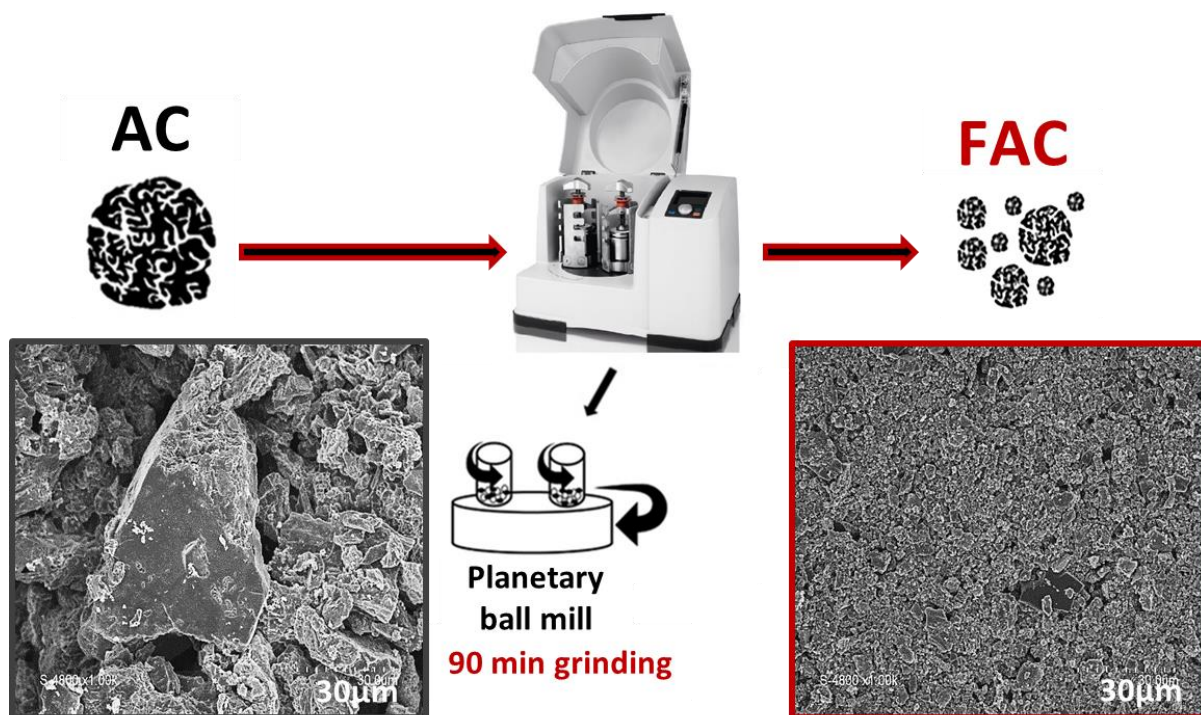
FE (10 % wt)	AC (% wt)	FAC (% wt)	[NaCl] (g/L) (V=70 mL)	
FE1	10	0	1	124
FE2	8	2	1	125
FE3	5	5	1	126
FE4	2.5	7.5	1	127
FE5	0	10	1	128

)**Erreur ! Source du renvoi introuvable.**<sup>28</sup> Ball-milled AC, called fine particle AC (FAC), and pristine AC with different particle size ranges (0.3-0.6 μm and 0.8-1.6 μm, respectively) were used for this study.

129 AC suspensions, used as flowable  
130 electrodes, were prepared by mixing the desired amounts of AC and FAC (10% wt as total  
131 weight percentage in each electrode) in 1 g/L NaCl solution (**Erreur ! Source du renvoi  
132 introuvable.**). Two different packing characteristics were chosen; i) monomodal distribution,  
133 where slurry electrodes contained only one particle size range (AC or FAC), and ii) bimodal  
134 distribution where slurry electrodes were mixtures of AC and FAC at different ratios. Then, the  
135 mixtures were sonicated for 2 h and stirred for 1 h to obtain a uniform particle distribution in  
136 suspension. The slurry electrode in a beaker was continuously stirred and was fed into the cell  
throughout the FCDI experiments (repeated three times for each sample).

137

138



139

140 **Figure 1:** Planetary dry ball milling of activated carbon (AC) into fine activated carbon (FAC).

141 **Table 1:** Composition of the flowable electrodes (FE) used in this study

FE (10 % wt)	AC (% wt)	FAC (% wt)	[NaCl] (g/L) (V=70 ml)
FE1	10	0	1
FE2	8	2	1
FE3	5	5	1
FE4	2.5	7.5	1
FE5	0	10	1

148

## 149 2.2. AC Material Characterization

150 For all sample characterizations, carbon suspensions prepared in 1 g/L NaCl solution  
 151 (experimental conditions) were used. Our previous study included a detailed physical  
 152 characterization of AC and FAC (after grinding) samples<sup>28</sup>. AC and FAC particle size  
 153 distribution and their zeta potentials were measured by dynamic light scattering using a  
 154 Litesizer 500 particle size analyzer (Anton Paar, France). The particle structure was analyzed  
 155 by scanning electron microscopy (SEM) (SEM, Hitachi S4800, Tokyo, Japan), and the atomic  
 156 composition (chemical moieties) of the material was studied before and after ball milling  
 157 (analyzed surface area = 300 x 700 µm) by X-ray photoelectron spectroscopy (XPS)  
 158 (Spectrometre XPS/UPS KRATOS AXIS Ultra DLD). The surface area was measured using  
 159 N<sub>2</sub> adsorption/desorption at 77 K. The specific surface area was calculated using the Brunauer-  
 160 Emmett-Teller method (Micromeritics 2020 ASAP, Merignac France). The total pore volume  
 161 (V<sub>t</sub>) was calculated from the amount of N<sub>2</sub> adsorbed at 0.99 relative pressure (P/P<sub>0</sub>). The

162 mesopore volume ( $V_{\text{meso}}$ ) was calculated with the Barrett-Joyner-Halenda model. The dynamic  
163 viscosity of the different carbon suspensions (flow electrodes) was measured using a Paar  
164 Physica UDS 200 Rheometer, a concentric cylinder adapted for heterogeneous solutions or  
165 water suspensions, as a function of the shear rate at 25 °C. Dynamic viscosity describes the  
166 resistance of a liquid solution to flow, whereas the shear rate is the deformation speed of the  
167 suspension under an applied force. The physical stability or sedimentation rate of the different  
168 AC slurries over time was measured with a Formulaction TURBISCAN® in which static multiple  
169 light scattering is used to monitor particle migration in liquids. A measurement head with two  
170 detectors moves along the cell height to measure the transmission (T) and backscattering (BS)  
171 signals that are related to particle size and concentration in the sample. The changes over time  
172 are a sign of destabilization that is quantified using the TURBISCAN® stability index (TSI).  
173 Each experiment was repeated three times for each electrode type. The electrochemical  
174 properties of AC and FAC were tested by cyclic voltammetry (CV) method. CV tests were  
175 performed using OrigaLys OrigaStat OGS080 potentiostat and 3 electrodes system with a 5  
176 mm carbon glass rotating disk electrode (RDE) as working electrode while a platinum mesh  
177 and a saturated 3 M KCl, Ag/AgCl electrode served as counter and reference electrodes  
178 respectively. 10% wt. activated carbon suspensions were prepared, 100  $\mu\text{l}$  were deposited on  
179 the surface of the RDE then dried at 80°C before adding one drop of nafion ink to hold the  
180 material on the electrode. Voltammetry measurements were performed at a -0.2 V-0.4 V vs ref  
181 operating potential window in 5 g/L NaCl solution as electrolyte. The electrical double layer  
182 capacitance (EDLC) was determined using cyclic voltammetry cycles at 0.02 V.  $\text{s}^{-1}$  scan rate.

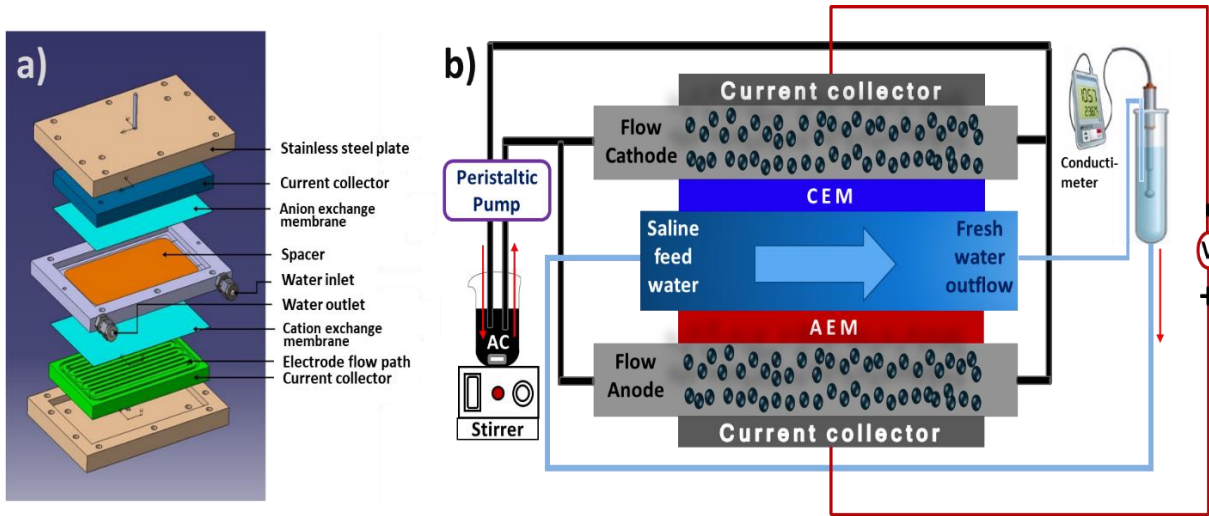
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### 184 2.3. FCDI experiments

185 Figure 2 shows the FCDI experimental set-up and its operating principle. The system was  
186 composed of a homemade FCDI cell, a potentiostat (OrigaLys Electrochem, OrigaFlex), a  
187 conducti-meter (HANNA Instruments) to monitor the saline solution conductivity during the  
188 desalination experiment, and two beakers (one for the flowable electrode and the other for the  
189 saline solution) with two peristaltic pumps to recirculate both solutions through the  
190 electrochemical cell. Experiments were performed in a closed loop reactor at 1V constant  
191 voltage, using 5g/L NaCl as feed solution (FS), and lasted 30 min. The FCDI cell (**Erreur !  
192 Source du renvoi introuvable.**(a)), specifically designed for these experiments, was  
193 composed of two current collectors (0.9mm depth, 8.5 cm width, and 14.5 cm length) with two  
194 channels each as flow electrode inflow and outflow of 7.8 cm depth, two ion exchange  
195 membranes (IEM) of 142  $\text{cm}^2$  effective area, a spacer (0.9 mm thick), two stainless steel plates,  
196 and nails to hold all parts together.

197 The electrical field created inside the FCDI cell drives ions present in the FS (5 g/L NaCl)  
198 through a spacer, sandwiched between two IEM, to be electrostatically attracted to the charged  
199 flowable electrodes that circulate through the flow paths carved on the current collectors, as  
200 shown in **Erreur ! Source du renvoi introuvable.**(a). When the flowable electrodes exit the  
201 channels, they are fed back into the reservoir, stirred, and then re-circulated inside the cell.  
202 The resulting current at the electrodes was monitored throughout the experiment by  
203 chronoamperometry. The FS and flowable electrodes were flowing at a constant flow rate of 3  
204  $\text{ml}\cdot\text{min}^{-1}$  and 40  $\text{ml}\cdot\text{min}^{-1}$  respectively. Throughout the process, the conductivity of the FS that  
205 was recirculated in a closed loop system was monitored at room temperature with a

206 conductimeter (Hannah Instrument), as depicted in **Erreur! Source du renvoi**  
 207 **introuvable.**(b). To mention that no significant water transmembrane migration was observed  
 208 during the desalination experiments.



209  
 210 **Figure 2:** (a) FCDI cell. (b) Experimental set-up and operating principle. CEM: cationic exchange  
 211 membrane; AEM: anionic exchange membrane

212  
 213 FCDI desalinating performance indicators were calculated for each experiment.

214 Salt adsorption capacity (SAC) indicating the mass of adsorbed salt as function of the  
 215 adsorbent electrode weight is calculated according to equation (1) and expressed in mg of salt  
 216 adsorbed per g of electrode material:

$$217 \quad SAC = \frac{(C_0 - C_f) V}{m_{electrode}} \quad (1)$$

218 Where  $C_0$  is the initial solute concentration of the feed solution,  $C_f$  the final solute concentration,  
 219  $V$  is the volume of the feed solution and  $m_{electrode}$  is the mass of the electrode material.<sup>29</sup>

220  
 221 The salt removal efficiency or desalination efficiency (DE) was calculated using equation (2):

$$223 \quad DE = \frac{(C_0 - C_f)}{C_0} \quad (2)$$

224  
 225 where  $C_0$  and  $C_f$  are the initial and final concentrations (mol. L<sup>-1</sup>) of the FS.<sup>1</sup>

226 The salt adsorption rate (SAR), which represents the amount of salt adsorbed (μg) per  
 227 electrode surface (cm<sup>2</sup>) per unit of time (min), was calculated using equation (3):



228  $SAR (\mu\text{g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}) = \frac{(C_0 - C_f) V}{A t}$  (3)

229

230 where  $V$  is the volume of the feed solution (L),  $A$  is the contact area between the feed electrode  
231 and the current collector, and  $t$  is the charging time.<sup>30</sup>

232 The charge efficiency (CE) or faradaic efficiency is the ratio of the electrical charges related  
233 specifically to ion removal over the total electrical charge applied by the potentiostat. It  
234 represents the energy efficiency of the system and was calculated using equation (4):

235

236  $CE = \frac{z (C_0 - C_f) V F}{\int I dt}$  (4)

237

238 where  $z$  is the equivalent charge of ions,  $V$  is the FS volume,  $F$  is the Faradaic constant, and  
239  $\int I dt$  is the integrated quantity of charge passed to the system over time.<sup>31</sup>

240 The Reynolds number shows the electrode flowing nature in the channel and was calculated  
241 with equation (5):

242  $Re = \frac{\rho v D}{\eta}$  (5)

243 where  $\rho$  and  $v$  are the flowable electrode density and velocity, respectively, in the flow channel  
244 calculated from the flow rate of the flowable electrode ( $0.0024 \text{ m}^3 \text{ h}^{-1}$ ) to the area of the flow  
245 cell ( $5.4 \times 10^{-6} \text{ m}^2$ ),  $D$  is the hydraulic diameter of the flow channel (6 mm), and  $\eta$  is the mean  
246 coefficient of dynamic viscosity of the flowable electrode in function of the shear rate at  $25^\circ \text{C}$ .

247 Stokes's law of sedimentation shows the drag force resisting the fall of small particles through  
248 a fluid medium under the influence of gravity, and is described by equation (6):

249  $V = \frac{2 (\rho_p - \rho_f)}{9 \eta} g R^2$  (6)

250 where  $\rho_p$  is the particle density,  $\rho_f$  is the fluid density,  $g$  is the acceleration of gravity,  $R$  is the  
251 particle radius, and  $\eta$  is the viscosity.<sup>32</sup>

252 The linear pressure drop is the loss of mechanical energy caused by friction on the common  
253 walls of the network. It is directly affected by the fluid viscosity, and is described by equation  
254 (7):

255 
$$\Delta P = \mu \frac{L}{D} \frac{1}{2} \rho v^2 \quad (7)$$

256 where  $\mu$  is the friction coefficient with  $\mu = 64/Re$ , L and D are the canal length and diameter,  
 257  $\rho$  is the fluid apparent density, and  $v$  its velocity.<sup>33</sup>

258 The electrical double-layer capacitance (EDLC) was calculated according to equation (8):

259 
$$C_{EDL} = \frac{\int I dV}{2 u A \Delta V} \quad (8)$$

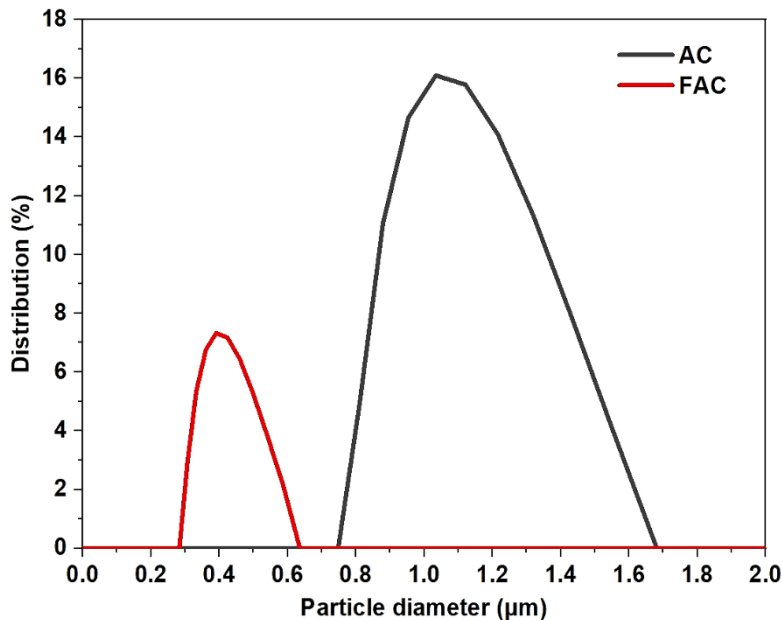
260 where  $C_{EDL}$  is the double layer capacitance,  $I$  is the current response,  $\Delta V$  is the potential  
 261 window,  $A$  is the effective area, and  $u$  is the scan rate.<sup>34</sup>

262

### 263 3. Results and discussion

#### 264 3.1. Particle size reduction

265 AC and FAC morphological and structural properties were investigated in our previous study.<sup>28</sup>  
 266 The dynamic light scattering (DLS) data (**Erreur ! Source du renvoi introuvable.** (a)) showed  
 267 the difference in particle size distribution between pristine AC and FAC samples: 0.8-1.6  $\mu\text{m}$   
 268 versus 0.3 to 0.6  $\mu\text{m}$  respectively.



269 **Figure 3:** particle size distribution of AC and FAC after ball-milling measured by DLS method  
 270

271

#### 272 3.2. Structural and textural characteristics

273 The structural and textural characteristics as well as the chemical moieties and composition of  
 274 AC and FAC samples were described in our previous study and are summarized in Figure S1,

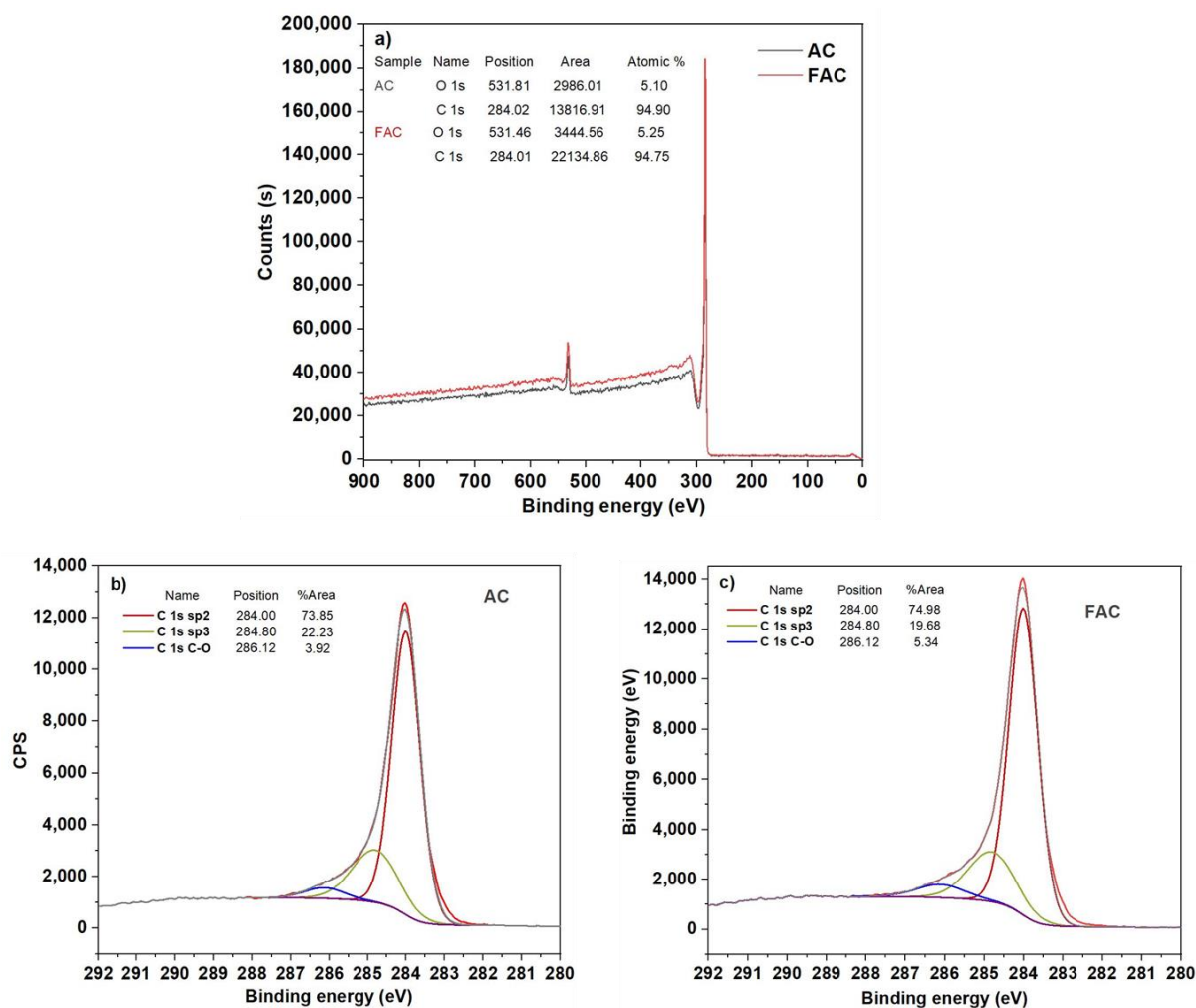
275 Table S1 and Figure S2 in supplementary information. Briefly, all AC characteristics were  
276 maintained in FAC after dry ball grinding, without any significant difference in texture (pores  
277 structure and surface area).<sup>28</sup>

278

### 279 **3.3. Physical and chemical properties**

#### 280 **3.3.1. Atomic composition**

281 The atomic composition of the carbon material before and after ball milling was investigated  
282 using XPS. No band reduction was observed after ball milling. However, according to XPS  
283 analysis, the O1s atomic percentage of the carbon material slightly increased after ball milling  
284 from 5.10 % (AC) to 5.25 % (FAC), which can be due to the generation of new oxygenated  
285 surface functional groups after ball milling. Figure 4 a shows the complete spectra of both AC  
286 and FAC, while c and d present the resolved C 1s spectrum of AC and FAC respectively into  
287 their individual peaks. 284.00, 284.80 and 286.10 eV binding energies correspond to C 1s sp<sup>2</sup>,  
288 C 1s sp<sup>3</sup> and C 1s C-O respectively.<sup>35</sup> As well Figure 4 b and c show a slight increase in the  
289 C 1s C-O band area from 3.92% to 5.34% after ball milling (FAC) proving the formation of new  
290 C-O functional groups on the surface of the activated carbon material.



291

292 **Figure 4:** XPS complete survey of AC and FAC (a), deconvoluted XPS C 1s spectra of AC (b) and  
 293 FAC (c)

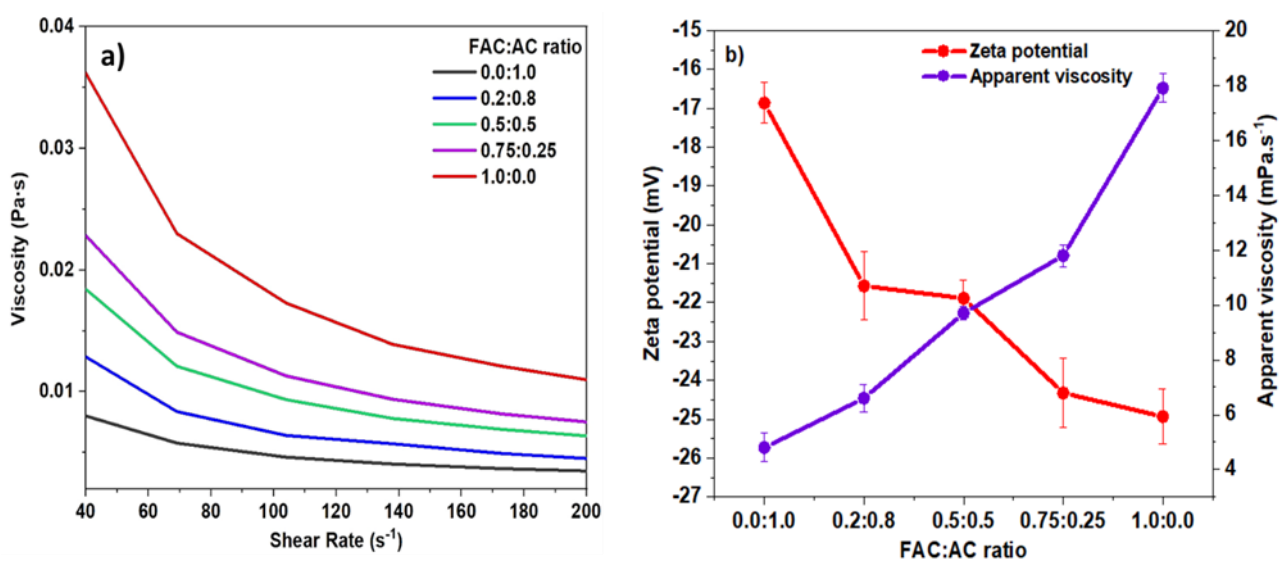
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295 **3.3.2. Rheological properties and zeta potential: effect of particle distribution**

296 To improve the flowing properties of carbon-based flowable electrodes in FCDI systems,  
 297 bimodal distributions were used by mixing (different ratios) of FAC (size range: 0.3-0.6  $\mu\text{m}$ )  
 298 and AC (size range: 0.8-1.6  $\mu\text{m}$ ). This was based on the hypothesis that fine particles can fill  
 299 the gaps between larger particles (packing effect), increasing the connectivity within the carbon  
 300 network, while keeping enough free spaces for water to flow through (i.e. acceptable viscosity).  
 301 The packing effect on the dynamic viscosity and surface charge (zeta potential) was studied  
 302 first by measuring the viscosity in function of the shear rate and zeta potential of carbon  
 303 suspensions with monomodal and bimodal distributions (different FAC to AC ratios) (Figure ).  
 304 The apparent viscosities of all carbon suspensions decreased when the applied shear rate  
 305 was increased, showing a flow behavior typical of a pseudo-plastic fluid, this phenomenon is  
 306 typical of non-Newtonian fluids.<sup>36</sup> Moreover, their viscosity (Figure 5(a)) increased  
 307 proportionally with the FAC percentage. Upon dry ball grinding of AC, each particle is divided  
 308 into many particles, thus increasing the particle number for the same weight percentage and  
 309 flowable electrode volume. Consequently, the higher specific surface area of particles  
 310 increases interactions with water, and dissipates more energy due to friction. This also

311 promotes particle-particle interactions, notably repulsion forces, leading to higher resistance to  
 312 flow or higher viscosity. This is observed particularly at low shear rates.<sup>37</sup> This effect becomes  
 313 less significant at higher shear rates because the interactive forces between particles are less  
 314 effective. Moreover, wide and narrow particle size ranges are associated with low and high  
 315 viscosity, respectively.<sup>38</sup> This explains the lower viscosity of AC samples because their particle  
 316 size range was wider than that of FAC samples. Suspensions with wide particle size  
 317 distribution (large polydispersity) aggregate more easily than suspensions with narrow  
 318 polydispersity. This gives more of free space that facilitates the movement (flow) of individual  
 319 particles, and thus lower viscosity. These results are in agreement with those by Harmadi *et*  
 320 *al.*<sup>39</sup> and Buranasrisak *et al.*<sup>40</sup> who studied the particle size effect on the rheology and stability  
 321 of carbon-water mixtures.

322 Zeta potentials represent the surface charge of particles in suspension. The particle size  
 323 effects on zeta potential and apparent viscosity was studied. The electrostatic repulsive forces  
 324 of particles in suspension under an applied voltage depend on their surface charge. It was  
 325 found that zeta potential increases after ball-milling, which can be attributed to the increase in  
 326 oxygenated functional groups on the surface of the material as shown previously in the XPS  
 327 study. The addition of large particles with low zeta potential to the flow electrodes leads to  
 328 decreased repulsive behavior, and decrease the suspension viscosity because the smaller  
 329 specific surface area leads to less friction, as explained previously. However, suspensions of  
 330 finer particles, which have strong surface charge (high zeta potential) increase particle-particle  
 331 repulsion and the resistance to flow or viscosity. Similarly, zeta potential measurements  
 332 (Figure (b)) showed the interdependence between viscosity, surface charge, and FAC  
 333 percentage. As finer particles in suspension have stronger surface charge (higher zeta  
 334 potential), particle-particle repulsion is promoted, decreasing aggregation. Consequently, the  
 335 whole space is occupied by well-dispersed particles, and less space is available for free water  
 336 flow, leading to higher viscosity. Upon reducing FAC percentage in the suspension, repulsion  
 337 forces between particles were decreased as well as resistance to flow, and therefore, flowing  
 338 behavior in the FCDI system was improved. These results are fully in line with those by  
 339 Buranasrisak *et al.*<sup>40</sup>.



340  
 341 **Figure 5:** (a) Viscosity of carbon suspensions with different FAC to AC ratios at different shear rates.  
 342 (b) Dependence of the apparent viscosity on zeta potential and fine particle (FAC) fraction (100rps

343 shear rate). All experiments were carried out with carbon suspensions with 10 % wt carbon loading,  
344 fine particle size range of 0.3-0.6  $\mu\text{m}$ , and large particle size range of 0.8-1.6  $\mu\text{m}$ .

### 345 **3.3.3. Reynolds number**

346 Reynolds number (i.e. the inertial forces to viscous forces ratio) is used to categorize the fluid  
347 systems where viscosity has an important effect in controlling the fluid velocity or flow pattern,  
348 a critical parameter in our study. For all mixtures, the Reynolds number (calculated using  
349 equation (5)) was <2100, indicating a laminar flow (i.e. the flow type needed for flowable  
350 electrodes in FCDI systems) (Table 2). As flow velocity is directly proportional to the Reynolds  
351 number, this explains the decrease of the Reynolds number in carbon suspensions with higher  
352 FAC percentages because they decrease the flow velocity. Consequently, when the viscosity  
353 increased with higher FAC: AC ratios, the Reynolds number decreased.

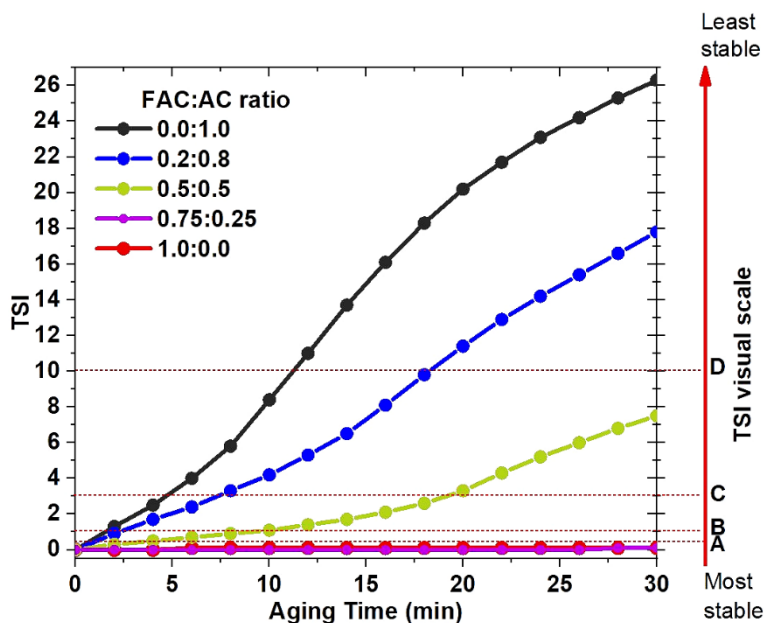
354 **Table 2:** Reynolds number of the indicated carbon suspensions

FAC : AC ratio	Reynolds n°
0.0 : 1.0	57.787 $\pm$ 0.006
0.2 : 0.8	45.033 $\pm$ 0.006
0.5 : 0.5	30.620 $\pm$ 0.001
0.75 : 0.25	21.808 $\pm$ 0.008
1.0 : 0.0	13.106 $\pm$ 0.030

355

### 356 **3.3.4. Physical stability**

357 AC particles suspended in water tend to settle due to gravitational force. In FCDI systems, this  
358 can cause clogging inside the channels, thus reducing the particle availability for ion adsorption  
359 during the process. The destabilization kinetics of suspensions with different fine to large  
360 particle ratios (at 10% wt) were evaluated by measuring the TSI (TURBISCAN<sup>®</sup> technology)  
361 over 30 minutes (**Erreur ! Source du renvoi introuvable.**). The TSI (i.e. destabilization)  
362 progressively increased for samples with lower FAC percentages. This indicates that the  
363 stability of the carbon suspensions increased with higher FAC percentages, although no  
364 difference was observed for samples with fine particles to large particle ratios of 0.75:0.25 and  
365 1.0:0.0. Particle size reduction is associated with slower sedimentation rates. This is explained  
366 by the sedimentation velocity law shown in equation (6). Indeed, the particle size has an effect  
367 on the sedimentation velocity. According to Stokes' law, the particle sedimentation velocity is  
368 proportional to the density difference between the solid and liquid phase, inversely proportional  
369 to the fluid viscosity, and proportional to the particle diameter square. This explains the  
370 important decrease in sedimentation velocity with FAC percentage increase in the  
371 suspensions: smaller particle size is associated with higher viscosity. FAC particles remained  
372 in suspension and well dispersed for a longer period of time, thus increasing the intra-particle  
373 interactions in solution. These results are in agreement with the rheology and zeta potential  
374 data, and explain the behavior of the different carbon particle size suspensions as flowable  
375 electrodes.

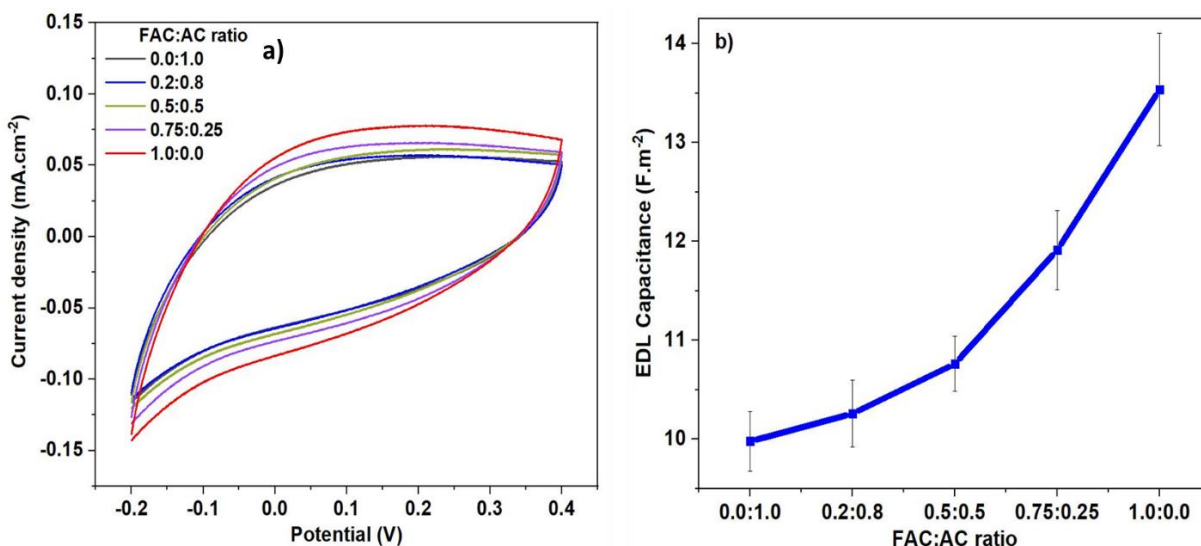


376

377 **Figure 6:** TURBISCAN® stability index (TSI) of the carbon suspensions at different ratios of fine particles  
 378 to large particles. Below level A (lowest TSI dash line) on the TSI visual scale, no destabilization is  
 379 observed. Level A marks the beginning of the very early destabilization stage. Level B indicates the  
 380 beginning of destabilization, and levels C and D describe high sedimentation stages.

### 381 3.4. Electrochemical properties

382 To evaluate the electrochemical behavior of activated carbon electrodes with different  
 383 FAC:AC ratios, cyclic voltammetry (CV) measurements were carried out using a 1 g/L NaCl  
 384 electrolyte solution at 2 mV. s<sup>-1</sup> scan rate with a -0.2 – 0.4 V voltage window. The CV results  
 385 are shown in Figure 7 (a). All the electrodes displayed a symmetrical box-like shape, which  
 386 reflects good capacitor characteristic. The larger area obtained under the CV curves implies  
 387 the higher specific capacitance of the materials. The 1.0: 0.0 FAC: AC ratio (pure FAC)  
 388 electrode showed the highest area obtained under the CV curves, indicating the highest  
 389 specific capacitance compared to the pure AC electrode. As well, based on the cyclic  
 390 voltammetry cycles, the EDL capacitance of the different electrodes of different FAC: AC  
 391 ratios was calculated according to equation 8 and presented in figure 7 (b).<sup>41</sup> Thus, in all  
 392 cases, the addition of FAC to the AC electrodes enhances their double layer capacitance due  
 393 to the increased conductivity of the flow electrodes caused by the improved interconnectivity  
 394 between the carbon particles in the case of FAC as explained in details before. Thus pure  
 395 FAC electrode showed the highest specific capacitance of 35 F.cm<sup>-2</sup> compared to 25.5 F.cm<sup>-2</sup>  
 396 in the case of pure AC marking a higher conductivity of FAC compared to AC.



397

398 **Figure 7:** Cyclic voltammety cycles (a) and electrical double layer capacitance (b) for activated  
399 carbon electrodes with different FAC:AC ratios.

### 400 3.5. Desalination performance

401 The electrosorption characteristics of the different carbon suspensions (10% wt carbon  
402 loading) as flow electrodes were investigated without clogging in our FCDI set-up. FCDI  
403 performance indicators (DE, SAC, SAR and CE) were calculated for the different mixtures  
404 (Table 3 and Figure (b and c)). In all cases, FAC addition strongly improved their salt adsorption  
405 capacity and desalination performance in FCDI. The higher specific surface area, more  
406 accessible pores, better conductivity observed upon particle size reduction explain the  
407 improved DE, SAC, and SAR values (Table 3, Figure 8 (b)). Higher surface area promotes  
408 mass transfer (ion adsorption), which is the limiting mass transfer phenomenon in FCDI. This  
409 strongly influences the SAR values, as seen after FAC addition in the flowable electrodes.

410 Sharper drop in ionic conductivity of the FS when using bimodal mixtures or pure FAC  
411 compared with pure AC was observed (Figure 7 (a)). Flowable electrodes with 0.75:0.25 and  
412 1.0:0.0 FAC:AC ratios exhibited the best DE, the highest SAC and SAR among all samples  
413 (Table 3 Figure 8 (b and c)). DE was 72%, SAC was 32.3 mg.g<sup>-1</sup>, and SAR was 1772 μg.cm<sup>-2</sup>.min<sup>-1</sup>  
414 for the 0.75:0.25 sample compared with 34%, 15.3 mg.g<sup>-1</sup> and 839 μg.cm<sup>-2</sup>.min<sup>-1</sup> for the  
415 pure AC flow electrode respectively. This can be due to the improved ion diffusion pathways  
416 within the carbon network because fine particles filled the void between larger particles, thus  
417 increasing contact areas within the carbon network, and consequently conductivity in the  
418 flowable electrode. The lower desalination performance of the flowable electrode with AC  
419 particles might be due to the lower repulsion forces between particles that aggregate to each  
420 other, thus masking the pores that become less accessible to ions. Furthermore, the higher  
421 resistance and lower conductivity caused by water occupying the large gaps between large  
422 AC particles create long ion diffusion pathways. These parameters explain the lower  
423 performance metrics of these flowable electrodes. The chronoamperometry curves (Figure S3  
424 in SI) for the different carbon slurries showed the current density in function of time at a  
425 constant applied voltage (1V). Current density was lower for pure AC suspensions than for the  
426 samples with different FAC percentages. Therefore, the total charge transferred (which is the  
427 integration of the chronoamperometry curves) was lower for large AC particles, resulting in  
428 lower DE. The current density progressively increased with the percentage of FAC added, and

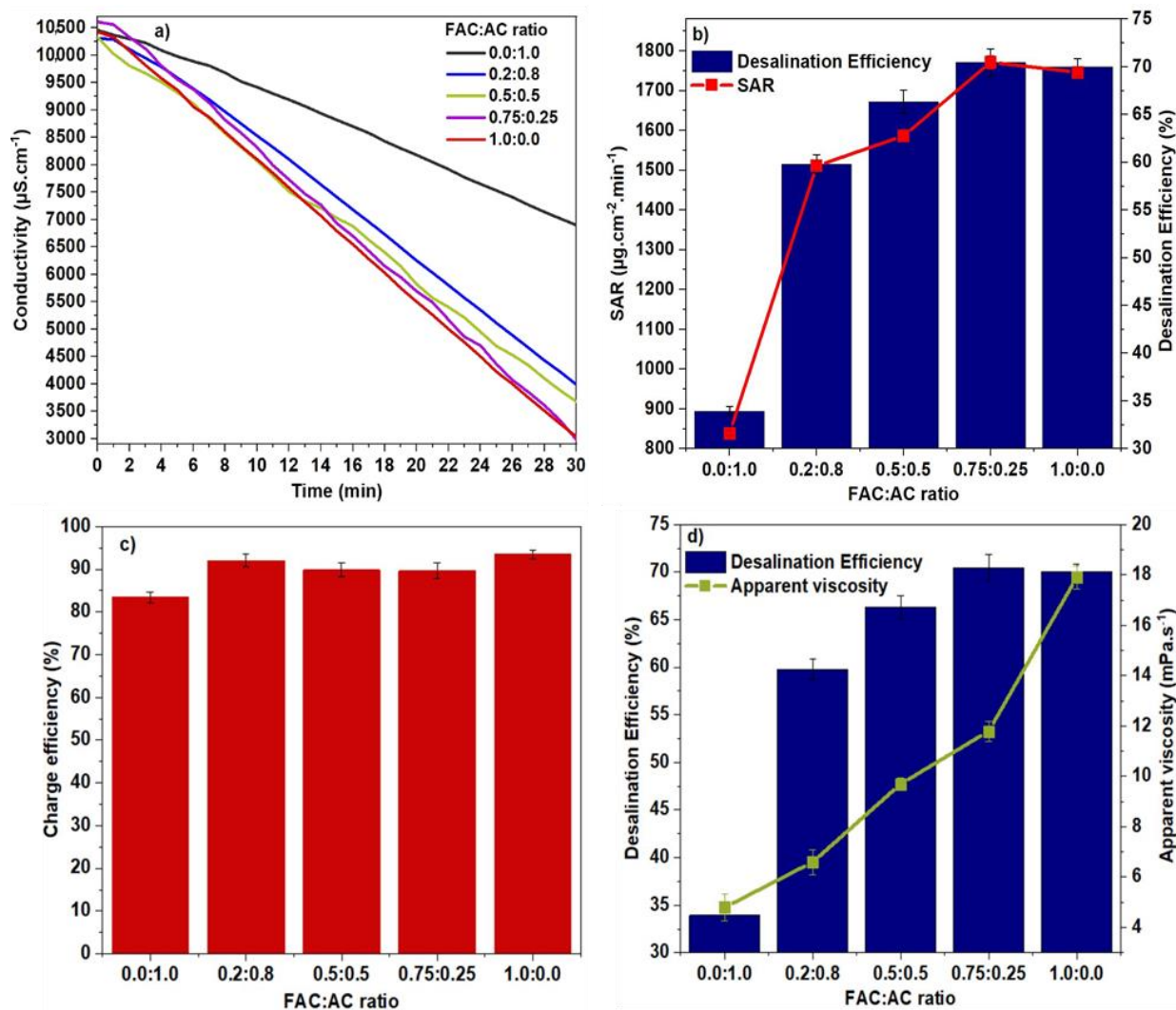


429 DE improved. Conversely, CE was comparable among samples (Figure 8 (c)), likely because  
 430 this parameter is mostly influenced by the ion transfer through the selective IEM. For all  
 431 samples, the same FCDI system with the same IEM was used, the conductivity of the saline  
 432 solution passing between the electrodes was the same (5 g/L NaCl), and the quantity of carbon  
 433 in the electrode compartments was largely enough to receive ions from the central  
 434 compartment. The high selectivity of cationic and anionic membranes in such conditions  
 435 explains the comparable CE values among samples.<sup>42</sup> Analysis of the relationship between  
 436 the apparent viscosity and DE of the different flowable electrodes (Figure 8 (d)) showed that  
 437 with the 0.75:0.25 FAC:AC ratio bimodal mixture, viscosity decreased by 30%, overcoming the  
 438 major limitation of FAC-based flowable electrodes in FCDI (i.e. high viscosity). The challenge  
 439 is always to find a compromise between these parameters to improve desalination  
 440 performance in FCDI, while maintaining good flowing properties of the electrodes inside the  
 441 system. In this study a good compromise between these parameters was achieved with the  
 442 0.75:0.25 FAC:AC ratio bimodal mixture.

443 **Table 3:** salt adsorption capacity (SAC) and average salt adsorption rate (SAR) of carbon flow  
 444 electrodes with different FAC : AC ratio

<b>FAC : AC ratio</b>	<b>SAC (mg.g<sup>-1</sup>)</b>	<b>SAR (µg.cm<sup>-2</sup>.min<sup>-1</sup>)</b>
<b>0.0 : 1.0</b>	15.3	0.51
<b>0.2 : 0.8</b>	27.6	0.92
<b>0.5 : 0.5</b>	28.9	0.96
<b>0.75 : 0.25</b>	32.3	1.08
<b>1.0 : 0.0</b>	31.9	1.06

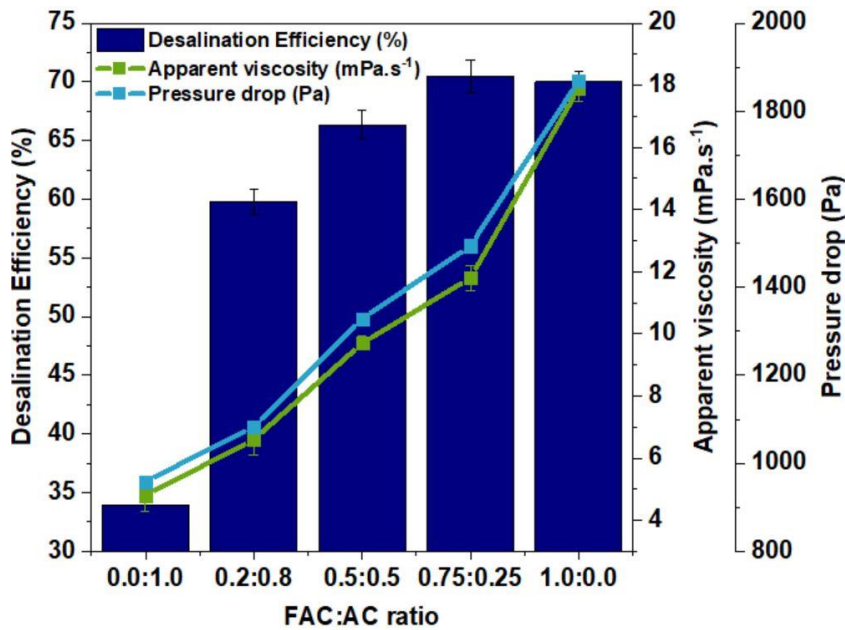
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446

447 **Figure 8:** Feed solution conductivity (a), desalination efficiency and salt adsorption rate (SAR) (b), and  
 448 charge efficiency (c) of carbon-based flowable electrodes with different FAC: AC ratios, during 30 min of  
 FCDI experiment time. Relationship between desalination efficiency and apparent viscosity (d).

449 The rheological characteristics of the carbon slurries were studied to optimize their flowability  
 450 inside the FCDI system because this has a direct effect on the pumping energy and cost. To  
 451 this aim, viscosity effect on the pressure drop was assessed when comparing the desalination  
 452 performances of the different flowable electrodes. In every FCDI process, there is always a  
 453 compromise between particle size and viscosity. Smaller carbon particles increase  
 454 conductivity, and consequently the process efficiency, for instance in terms of charge transfer,  
 455 maximum salt capacity, mass transfer. However, adding small particles to the carbon slurry  
 456 increases viscosity and also pumping costs due to the pressure drop increase. In our set-up,  
 457 pressure drop (calculated with equation (7)) increased with the viscosity increase (Figure 9).  
 458 With higher FAC percentages in the slurry, DE improved but viscosity increased, and also the  
 459 pressure drop, leading to higher pumping energy and costs. Therefore, it is important to find  
 460 the best compromise between particle size distribution and viscosity in order to obtain an  
 461 energy-efficient process with good performance without clogging problems inside the FCDI  
 462 system.



463

464 **Figure 9:** Relationship between desalination efficiency, apparent viscosity, and pressure drop increase  
 465 of carbon-based flowable electrodes with the indicated FAC: AC ratios, during 30 min of FCDI  
 466 experiment time.

467

#### 468 **4. Conclusion**

469 This work investigated the effect of particle size distribution on the viscosity and desalination  
 470 performance of AC-based flowable electrodes in FCDI. Mixtures of two different AC particle  
 471 sizes were used: commercial AC and FAC obtained after ball-milling commercial AC. This  
 472 experimental work shows that particle size distribution has a considerable effect on ion  
 473 diffusion length and on the ion transport pathway that is determined by the packing density of  
 474 flowable electrodes. Particularly, with pure AC suspensions, intraparticle and interparticle ion  
 475 diffusion limited the desalination capacity (34% of DE). By mixing two different particle sizes,  
 476 particle size distribution became broader, leading to better desalination performance, as  
 477 indicated by the 72% of DE and improved flowing properties of the flowable electrode in FCDI  
 478 (decrease by 33% of viscosity compared with the pure FAC suspension that achieved 70% of  
 479 DE) in FCDI. These results highlighted the importance of particle size distribution and packing  
 480 density on the behavior of flowable electrodes optimized for FCDI-based desalination. Fine  
 481 particles and combined (0.75: 0.25 FAC: AC ratio) slurries showed better desalination  
 482 performance compared to large particle slurries. However, large particle slurries showed better  
 483 fluidity and easier flow in our water desalination system leading to lower pressure drop. Thus,  
 484 good compromise must be done between high desalination capacity and acceptable pressure  
 485 drop (viscosity) to have an optimal electrochemical desalination process. To find the best  
 486 balance, more research is needed, including molecular dynamic simulations that can improve  
 487 experimental procedures and save time.

488

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 490 analysis: M.T. S.L. and M.B. Investigation: M.T.; Resources: F.Z., M.B., P.S. and M.C.; Data

491 curation: M.T.; Original draft preparation: M.T.; Writing, review and editing: M.T., F.Z., M.B.  
492 and M.C.; Visualization: F.Z., M.T., M.B. and M.C.; Supervision: F.Z., M.B., P.S. and M.C.;  
493 Project administration: M.B., F.Z., P.S. and M.C. All authors have read and agreed to the  
494 published version of the manuscript.

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498

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