

1 **Scale-up of electrolytic and photo-electrolytic processes for**
2 **water reclaiming: A preliminary study**

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8
9 **Abstract**

10 This work focuses on the scale-up of electrochemical and photo-electrochemical oxidation
11 processes with diamond anodes for the removal of organic pollutants and disinfection of
12 treated urban wastewater, two of the most important parameters for the reclaiming of
13 wastewater. The removal of organics was studied with actual biologically-treated urban
14 wastewater intensified with 100 mg dm⁻³ of caffeine, added as a trace organic pollutant.
15 The disinfection was also studied with biologically-treated urban wastewater and *E. coli*
16 was used to monitor the efficiency of the process. Results obtained with a single DiaCell ®
17 101 were compared with those obtained with a single stack DiaCell ® 1001 and with a pilot
18 plant made up of five of these stacks. Results obtained demonstrate that scale-up is not a
19 simple but a very complex process, in which not only the electrode and the irradiation dose
20 are important but also mass transfer conditions. Enhanced mass transport conditions have a
21 determining and very positive effect on the removal of organics and a negative effect on the

22 disinfection. Likewise, UV irradiation affects in a different way in the different setups used,
23 having a great influence on the removal of complex organics and on the speciation of
24 oxidants produced during disinfection. This works helps to understand the key differences
25 observed in the scale-up and it is a first approach for future works focused on the real
26 application of conductive-diamond electrochemical oxidation.

27

28 **Keywords**

29 Electrolysis, photo-electrolysis, scale-up, disinfection, persistent pollutants, diamond.

30 **Highlights**

31 - Scale-up of conductive-diamond electrochemical oxidation is not an easy procedure.

32 - For scaling-up, mass transfer is at least as important as electrode material and UV
33 irradiation dosage.

34 - UV irradiation coupled to electrolysis favors the oxidation of aromatic organics.

35 - Photo-activation of disinfectants improves the disinfection process at pilot plant.

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41 **1. Introduction**

42 Over the last decades, the important population growth and the more intense industrial
43 activities related to this growth have caused an increase in water consumption and,
44 therefore, in the production of a higher volume of wastewater. This fact is leading to an
45 irregular availability of water resources in different regions of the world and, for that
46 reason, the reclamation of wastewater is now starting to be considered as an alternative and
47 very promising water resource (Rodrigo et al. 2010). Many treatment technologies can be
48 used for wastewater reclamation, although the most important are those aiming to deplete
49 refractory pollutants and pathogens in order to attain a healthy reclaimed water, which then
50 can be safely used in different applications. Oxidation technologies are required for both
51 goals and that is why advanced oxidation processes are becoming more and more important
52 every day (Sirés et al. 2014). In this context, conductive-diamond electrochemical oxidation
53 (CDEO) has demonstrated great efficiencies in the disinfection of urban treated wastewater
54 (Cano et al. 2012, Llanos et al. 2015) and in the removal of anthropogenic refractory
55 species. Regarding disinfection, the oxidants electrochemically produced from chlorides,
56 sulfates and other anions contained in wastewater are the main responsible for pathogens
57 inactivation (Bergmann & Koparal 2005, Henquin et al. 2013, Lacasa et al. 2013, Rajab et
58 al. 2015). It has been demonstrated that the application of low current densities helps to
59 attain complete disinfection of wastewater, avoiding the potential formation of undesirable
60 chlorine species (Cano et al. 2011, Cotillas et al. 2015).

61 Regarding the removal of refractory species, the other important factor of reclaiming
62 wastewater, CDEO has proved its efficiency in the removal of persistent organic pollutants
63 (POPs) contained in urban wastewater, such as antibiotics, hormones, stimulants, etc. (El-

64 Shahawi et al. 2010, Indermuhle et al. 2013, Jacob &Cherian 2013, Martín de Vidales et al.
65 2012a, Martín de Vidales et al. 2012b, Martinez-Huitle &Brillas 2009, Oturan &J.J. 2013,
66 Zanin et al. 2013). The production of high concentrations of hydroxyl radicals by water
67 electrolysis and the formation of large amounts of other oxidants such as persulfates,
68 peroxocarbonates and peroxophosphates contributes to the efficient degradation of the
69 different organic pollutants (Marselli et al. 2003). More recently, the coupling of CDEO
70 and ultrasound (US) or ultraviolet (UV) irradiations have been studied in order to evaluate
71 possible improvements in the performance of the electrochemical processes (de Vidales et
72 al. 2015, Goeting et al. 1999, Hurwitz et al. 2014, Khataee et al. 2014, Llanos et al. 2015,
73 Vidales et al. 2014). Specifically, the application of UV irradiation seems to promote the
74 photo-activation of the oxidizing species electrogenerated in the electrochemical cell,
75 favouring the degradation of organic matter (Catanho et al. 2006, de Freitas et al. 2011,
76 Osugi et al. 2005, Socha et al. 2007). Thus, higher efficiencies can be attained for the
77 removal of several pollutants in wastewater using photo-electrolytic processes. US
78 irradiation exhibits a more complex behaviour: it can show this activating effect at high
79 frequencies; however, at low frequencies it only seems to improve mass transfer processes
80 (Souza et al. 2014c).

81 Up to date, most of the studies reported in the literature about electrochemical and photo-
82 electrochemical processes with diamond anodes have been carried out at laboratory or
83 bench scales. However, looking for real implementation, it is necessary to carry out studies
84 at larger scales and, thus, to improve the knowledge of this process for an adequate
85 industrial design. Scaling-up is much more than simply increase the size of the plant; it is a
86 fundamental stage in the assessment of the efficiency, environmental compatibility as well

87 as technical and economic feasibility of a new process (Souza et al. 2015b). Pilot plants, an
88 intermediate stage between laboratory and industrial scale, is a key and often compulsory
89 step to gain technical knowledge for the design, operation and optimization of real plants.

90 In a simplified view, the most important sizing parameters for electrochemical processes
91 are applied electric charge (Ah dm^{-3}) and current density (mA cm^{-2}). Regarding the first, for
92 years electrochemists are confident of this significance and regardless of the scale used, in
93 most of the papers reporting data on electrochemical oxidation, the progress of the reaction
94 is plotted against the electric charge trying to help the reader to extrapolate what it could be
95 obtained when the process would be operated at a larger scale. Regarding the current
96 density, its effect is not as clear in the scientific literature and it is more related to the
97 electrochemical process engineering. Low values lead to large electrodes and, therefore, to
98 high investment costs. Opposite, high current densities decrease the size of electrode but
99 increase the energy consumption, because of the associated cell voltage increase. In
100 addition, the current density influences on the reactions that occur within the
101 electrochemical cell. Therefore, in the case of expensive anodic materials, such as boron-
102 doped diamond (BDD), the current density has to be as high as possible to minimize anodic
103 surface but low enough to avoid undesired side reactions. In a first approach to scaling-up
104 of CDEO, the effect of increasing the numbers of compartment in an electrochemical cell
105 (DiaCell® 1001) has been studied by this research group for the treatment of wastewater
106 polluted with herbicides (Souza et al. 2015a). In that work, no differences were observed in
107 the process efficiency when increasing the number of stacked cells. However, the energy
108 efficiency was improved with the number of cells, due to the reduced cell voltage that result
109 from the application of the same current intensity to the stack. Furthermore, other recent

110 researches have studied the scale-up of CDEO, although most of them reported preliminary
111 results (Tröster et al. 2002, Zhu et al. 2011, Zhu et al. 2010). At this point, the results of the
112 group of Urtiaga are of relevance (Anglada et al. 2010, Urtiaga et al. 2014) because they
113 evaluated very rigorously the treatment of landfill leachate and industrial wastewater
114 polluted with tetrahydrofuran, respectively. The first research describes the electrochemical
115 oxidation using a reactor equipped with a BDD anode area of 1.05 m². COD and
116 ammonium were removed at an applied current density of 450 A m⁻² and operation times
117 lower than 8 hours. The other work shows that it is possible to attain a high removal and
118 mineralization of tetrahydrofuran in wastewater using a pilot plant with a BDD anode area
119 of 0.28 m².

120 With this background, the goal of this work is to evaluate the scale-up of electrochemical
121 and photo-electrochemical oxidation with diamond anodes for the production of reclaimed
122 wastewater, focusing on disinfection and oxidation of refractory organics. Bench scale and
123 pilot plant electrolyses were studied in order to compare the results obtained at both scales.
124 Actual urban wastewater was used for the study of the disinfection process. For the
125 evaluation of the oxidation of organics, it was intensified with caffeine (selected as a model
126 of complex organic pollutant) because it is typically present in domestic wastewater (Lovett
127 2005) and its degradation has been widely studied in the recent years, becoming an
128 interesting trace pollutant.

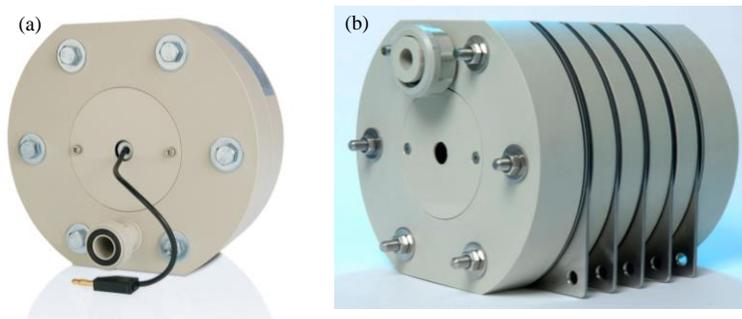
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130 2. Material and Methods

131 2.1. Experimental set-up

132 Bench scale electrolysis and photo-electrolysis were carried out in a single compartment
133 electrochemical cell DiaCell ® type 101 (Figure 1a) equipped with a Boron Doped
134 Diamond (BDD) electrode as anode and a perforated Stainless Steel (SS) plate as cathode
135 (diameter: 100 mm). The electrode gap between both electrodes was 6 mm. Both the
136 electrodes and the DiaCell were provided by Adamant (for information purposes,
137 nowadays, this company does not longer exists and the products are developed,
138 manufactured and marketed by two companies: NeoCoat and WaterDiam). The applied
139 current intensity was provided by a Delta Electronika ES030-10 power supply (0-30 V; 0-
140 10 A). For photo-electrolysis processes, a UV lamp VL-215MC (254 nm) was used to
141 irradiate 4.0 W directly to the quartz cover that substitute one of the plates of the DiaCell ®
142 101. A detail of the electrochemical cell used in this work and of its modification for
143 becoming a photoelectrolytic cell has been described elsewhere (de Vidales et al. 2015,
144 Souza et al. 2014a). Wastewater was stored in a glass tank with a total maximum capacity
145 of 6.0 dm³. The system operates in discontinuous mode with a peristaltic pump (JP Selecta
146 Percom N-M328). Flowrate of the pump was 21.4 or 50 dm³ h⁻¹ (for organic depletion and
147 electrodisinfection, respectively). This means that the total volume stored in the auxiliary
148 tank is completely passed through the cell more than 5 times an hour in the worst case. A
149 heat exchanger with a thermostated bath (Digiterm 100, JP Selecta, Barcelona, Spain)
150 was used to maintain the temperature at the desired set point (25°C). The complete setup is
151 a typical experimental facility for the evaluation of the treatability of organics with CDEO
152 and it has been used in many previous papers of the research group, both in disinfection and

153 depletion of organics studies. For several of the tests carried out in this work, the DiaCell ®
154 Type 101 was replaced by a commercial DiaCell ® Type 1001 (Figure 1b), which is stack
155 of cells typically used in pilot plants. It consists of five cells with 10 BDD electrodes (total
156 effective area: 0.070 m²) as anodes and 5 Stainless Steel (SS) electrodes as cathode (2
157 faces). The electrode gap between each anode and cathode is 1 mm.



158

159 **Figure 1.** DiaCell. (a) Type 101. (b) Type 1001.

160 Pilot plant electrolysis and photo-electrolysis were carried out in a facility equipped with 5
161 electrochemical stacks DiaCells® type 1001 connected in parallel. This plant also operates
162 in discontinuous mode. The total anode and cathode area was 0.35 m² each, distributed in
163 50 anodes (BDD) and 25 cathodes (stainless steel, two faces). This facility was also
164 designed and constructed by Adamant Technologies (Switzerland). A power supply with a
165 maximum voltage of 16 V and 750 A as maximum current intensity was used to provide
166 the current for each experiment. Wastewater was stored in a polypropylene tank (maximum
167 capacity of 750 dm³) and it was continuously recirculated by means of a centrifugal pump.
168 In this case, the flowrate is much higher as compared to the conventional bench scale plant
169 (15,000 dm³ h⁻¹), trying to attain the same range of cell passes per hour. The UV lamp used
170 for the photo-electrolysis at pilot plant was a Bio-UV with a power of 26.0 W (254 nm). In

171 this pilot plant, the UV lamp is placed in the auxiliary tank, allowing the irradiation to the
172 total volume of wastewater.

173 2.2. Experimental procedure

174 Actual wastewater was collected at the secondary clarifiers of the wastewater treatment
175 facilities (WWTF) of Ciudad Real (Spain). The influent of this municipal WWTF is
176 domestic wastewater without a significant industrial contribution. The chemical and
177 microbiological composition characteristics of the samples used in this work are shown in
178 Table 1.

179 **Table 1.** Wastewater composition.

Parameter	Value
Cl ⁻ (mg dm ⁻³)	110-180
NO ₃ ⁻ (mg dm ⁻³)	3-12
SO ₄ ²⁻ (mg dm ⁻³)	120-400
NH ₄ ⁺ (mg dm ⁻³)	10-28
Turbidity (NTU)	10-11
Total suspended solids (mg dm ⁻³)	7-10
Total organic carbon (mg dm ⁻³)	12-14
Chemical oxygen demand (mg O ₂ dm ⁻³)	35-42
<i>E. coli</i> (MPN 100 mL ⁻¹)	5,400-9,100
pH	7.8-8.5

180

181 All the tests were carried out under galvanostatic mode. The current density applied was
182 0.13-300 A m⁻² and 1.14-169 A m⁻² for bench scale and pilot plant electrolysis,
183 respectively. Prior to use in electrochemical assays, the electrode was polarized for 10 min
184 with 5,000 mg dm⁻³ Na₂SO₄ (pH: 2) at 300 A m⁻² to remove any kind of impurity from its
185 surface. Operation conditions of every experiment are clearly described in the R&D
186 section. The sample volume was 100 cm³ and 20 cm³ for the experiments of disinfection
187 and electrochemical oxidation, respectively. The measurement of organics, *E. coli* and
188 disinfectant species (free and combined chlorine compounds) were carried out immediately.

189 2.3. Analytical techniques

190 *E. coli* was determined by most probable number (MPN) technique (APHA-AWWA-
191 WPCF 1998). This method consists of an incubation at 44°C during 24 hours. The samples
192 are diluted 1:10, 1:100 and 1:1000 (multiple tube fermentation: 5 tubes at each dilution).
193 Inorganic ions (Cl⁻, ClO⁻, ClO₃⁻, ClO₄⁻, NO₂⁻, NO₃⁻, NH₄⁺) were measured using ion
194 chromatography (Shimadzu LC-20A). A shodex IC I-524A column was used to determine
195 the anions (eluent: 2.5 mM phthalic acid at pH 4.0; flow rate: 1 cm³ min⁻¹) and a shodex IC
196 YK-421 column was used to analyse the cations (eluent: 5.0 mM tartaric acid, 1.0 mM
197 dipicolinic acid and 24.3 mM boric acid; flow rate: 1 cm³ min⁻¹). The measurement of
198 hypochlorite was carried out by titration because the peak of this compound interferes with
199 that of chloride. A solution of As₂O₃ in 2.0 M NaOH was used to determine the
200 hypochlorite concentration (Freytag 1959, Wilpert 1957). Inorganic chloramines were
201 determined following the DPD standard method described in literature (APHA-AWWA-
202 WPCF 1998). The total organic carbon (TOC) concentration was monitored using a Multi
203 N/C 3100 Analytik Jena analyser. Measurements of pH and conductivity were carried out

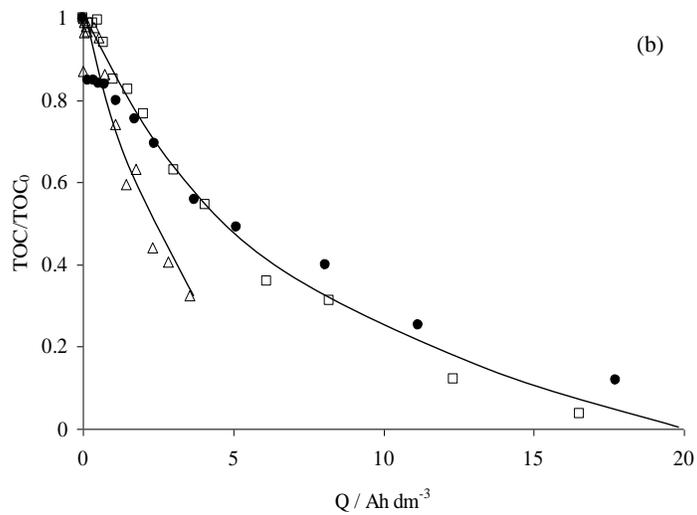
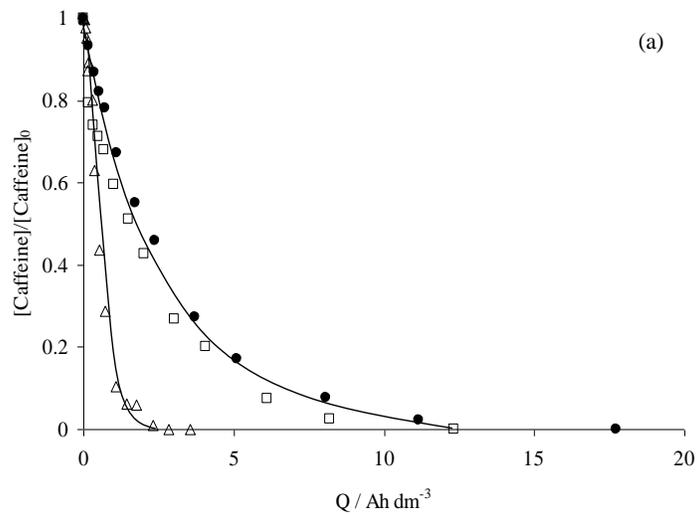
204 with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively. The
205 concentration of caffeine was quantified by HPLC (Agilent 1100 series). The detection
206 wavelength used was 205 nm. For the HPLC measurements, the column temperature was
207 set to 25 °C and the injection volume was set to 50 µL. The analytical column used was a
208 Phenomenex Gemini 5 µm C18 column, and the solvent solution was a mixture of 25 mM
209 of formic acid and acetonitrile (linear gradient chromatographic elution was performed
210 from 10 to 100% acetonitrile in 40 min). Samples extracted from electrolyzed solutions
211 were filtered with 0.20 µm Nylon filters before analysis.

212 **3. Results and Discussion**

213 Figure 2 shows the decay in the concentration of caffeine (Figure 2a) and TOC (Figure 2b)
214 during the electrolyses of actual wastewater taken at the outlet of the secondary treatment
215 of the municipal WWTF of Ciudad Real (Spain). This wastewater was intensified with
216 caffeine, from an initial TOC of around 10 mg dm⁻³ up to values close to 60 mg dm⁻³, in
217 order to monitor the electrolysis of a well-known trace pollutant in a highly complex
218 medium (the actual effluent of a WWTF). The applied current density was kept constant at
219 16.9 mA cm⁻² in the three tests shown in this figure, although the rest of parameters
220 changes importantly. At this point two parameters were specially considered: the volume
221 tank/recirculation flow rate ($V_{\text{tank}}/Q_{\text{recir}}$) ratio, which is directly related to the number of
222 passes of wastewater through the cell and the average velocity of wastewater in the cell,
223 which depends on the flowrate and the cross section. As it is known, one of the major
224 challenges in scale-up is to keep in the same values all parameters. According to the scale-
225 up theory, it is not possible because some of the parameters depend on linear magnitudes;

226 other of surfaces and other are volumetric. In order to deal with that problem, two
227 parameters were kept constant:

- 228 – a comparable value of the $V_{\text{tank}}/Q_{\text{recir}}$ ratio between two tests (comparison of the
229 single cell at bench-scale and pilot plant) and
- 230 – a comparable value of the flowrate in another two tests (comparison of the single
231 cell and stack in the bench-scale plant).



232

233 **Figure 2.** Scale-up of electrolysis of urban treated wastewater polluted with caffeine. (a)
234 Caffeine; (b) TOC. (●) anode area: 70 cm²; V: 0.6 dm³; V_{tank}/Q_{recir}: 0.03 h; (□) anode area:
235 700 cm²; V: 6 dm³; V_{tank}/Q_{recir}: 0.28 h; (Δ) anode area: 3,500 cm²; V: 300 dm³; V_{tank}/Q_{recir}:
236 0.02 h. ([Caffeine]₀: 100 mg dm⁻³; j: 16.9 mA cm⁻²; T: 25°C).

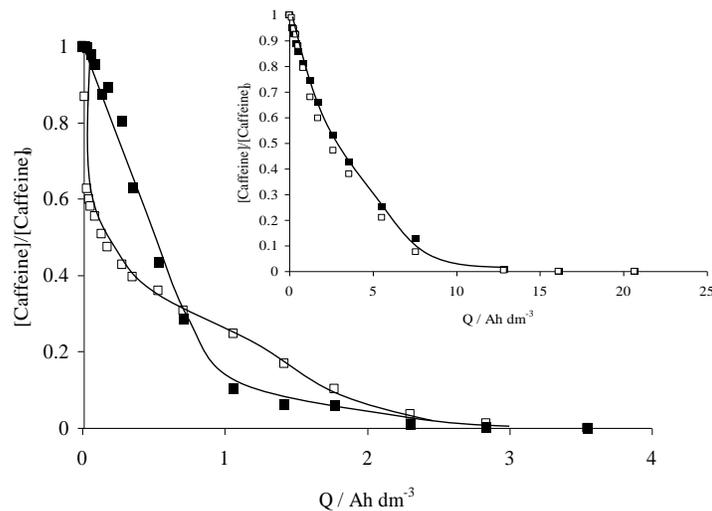
237 As it can be observed in this figure, there are not great differences in comparing the
238 performance of a single commercial cell Diacell ® 101 and the stack of cells Diacell ®
239 1001 (consisting of five cells connected in parallel) in the removal of organics. Just a small
240 improvement in the efficiency is observed with the stack, both in the oxidation of the raw
241 molecule and in the complete mineralization of the TOC, although differences are not very
242 important, at least as compared to the outstanding performance obtained by the pilot plant.
243 It is important to take in mind that flow conditions in both systems were comparable
244 because the same flowrate was fed to both systems (21.4 dm³ h⁻¹) and, hence, initially no
245 great differences in the reactivity associated to mass transfer limitations were expected,
246 despite the huge differences in the V_{tank}/Q_{recir} ratio. However, despite being engineered and
247 manufactured with the same technology, there is an important difference between the
248 DiaCell ® 101 and the Diacell ® 1001, which helps to explain the differences observed: the
249 inter-electrode gap. Thus, the better performance of the stack can be easily explained taking
250 into account the lower cross-section area of the cells of the DiaCell ® 1001, caused by the
251 lower gap between anodes and cathodes. The average velocity of wastewater within the cell
252 is higher in the stack as compared to the cell and this value influences significantly on the
253 mass transfer coefficient. Likewise, the effect of bubbles on the turbulence is higher for
254 lower gaps. Anyhow, although appreciable, changes are not very high as compared to those
255 observed with the same stacks operated in the pilot plant. This observation clearly indicates

256 that increasing electrode size under the same flowrate conditions has not relevant effect
257 when comparing removal results in terms of applied electric charge and that stacking of
258 monopolar-connected cells is a very simple and foreseeable process.

259 Opposite, results obtained in the commercial pilot plant with five parallel Diacell ® 1001
260 were significantly better. Taking into account the small effect observed when the single cell
261 and the stack are compared, this huge difference can only be explained by the much higher
262 flow rate of the pilot plant ($15,000 \text{ dm}^3 \text{ h}^{-1}$), which produces a much higher average
263 velocity of wastewater inside the cell. This explanation points out the well-known
264 importance of mass transfer limitations in the oxidation of organics at very low
265 concentrations reported in the literature (Anglada et al. 2010), that is the case studied in this
266 work. At this point, it is important to take in mind that the $V_{\text{tank}}/Q_{\text{recir}}$ ratio fixed is closer in
267 this case between the experiment carried out in the single cell ($V_{\text{tank}}/Q_{\text{recir}}$: 0.03 h) and in
268 the pilot plant ($V_{\text{tank}}/Q_{\text{recir}}$: 0.02 h), although what it is really different is the flux in contact
269 to the electrode. In the case of the single cell, average velocity is 0.99 cm/s while in the
270 case of the pilot plant the average velocity is 167 cm/s, more than two folds higher. The
271 huge difference clearly suggest improved mass transfer conditions in the pilot plant tests,
272 which helps to understand the better performance. This result also points out the relevance
273 of anodic surface processes on the efficiency of the removal of organics at low
274 concentrations, described in many papers in the literature and explained well by the group
275 of Comninellis many years ago (Panizza & Cerisola 2009, Rodrigo et al. 2001). These
276 anodic processes are not only associated to direct transfer of electrons but also to oxidation
277 mediated by hydroxyl radicals and other very highly reactive reagents. The action of these
278 radicals is directly enhanced in the case of high turbulence conditions because the oxidation

279 process is carried out in the nearness of the electrode surface (due to their very low average
280 lifetime of the radicals formed).

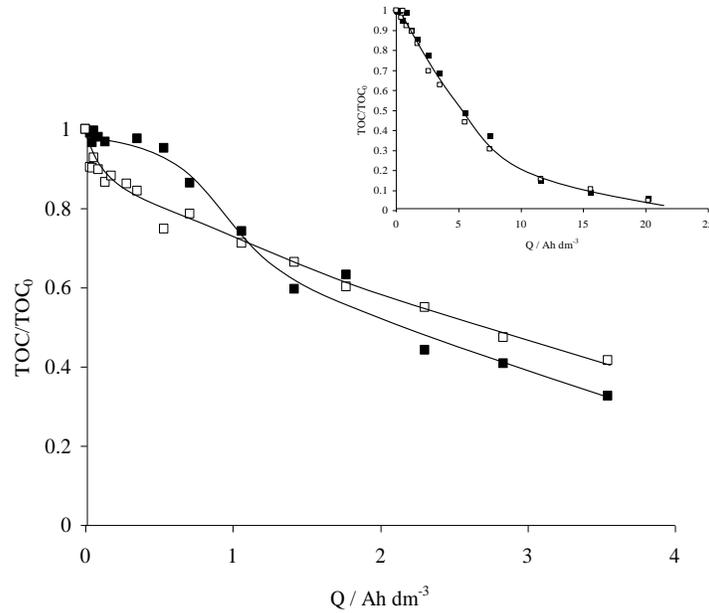
281 Once clarified the role of stacking and flowrate on the electrolysis, Figures 3 and 4 compare
282 the effect of UV irradiation on the electrolyses of the caffeine-intensified wastewater in
283 both plants studied, the bench scale and the pilot plant. As observed, although the removal
284 of the raw caffeine was improved with UV irradiation during the initial stages of the
285 electrolysis, this is not the case of the removal of the oxidation intermediates. This latter
286 statement is supported because the differences observed in TOC-profiles are smaller than in
287 the caffeine-profiles and because there is a clear crossing of the pollutant vs Q depletion
288 plot in the case of electrolysis over the corresponding photo-electrolysis.



289

290 **Figure 3.** Electrolysis (■) and photo-electrolysis (□) of an effluent of the secondary
291 clarifier of a WWTF intensified with caffeine in pilot plant and bench scale (onset).
292 ([Caffeine]₀: 100 mg dm⁻³; j: 16.9 mA cm⁻²; T: 25°C. Pilot plant: V: 300 dm³; UV_{254 nm} = 26
293 W. Bench scale: V: 0.6 dm³; UV_{254 nm} = 4 W).

294 In this context, UV irradiation is known to improve the process efficiency by the generation
295 and/or activation of oxidizing agents in wastewater (Chan et al. 2012, Cotillas et al. 2016,
296 Oliver & Carey 1977). Oxidation by these activated oxidizing agents is very effective with
297 aromatics but not with carboxylic acids, which are the typical intermediates in the
298 electrochemical oxidation of aromatics. The much higher initial rate of the photo-
299 electrolysis can only be explained by the faster and more intense effect of UV irradiation
300 (and consequently of the radicalary oxidants produced) on the oxidation of aromatic
301 compounds, meanwhile the crossing of the plots has to be explained because that effect of
302 these radicals becomes lower with more oxidized organic intermediates (carboxylic acids).
303 In addition, when the organics concentration decreases, the oxidizing agents formed do not
304 find organics to be oxidized and they can be more easily combined among them to form
305 more stable species, resulting in an antagonistic effect of the production of oxidants (Souza
306 et al. 2014b). When results at bench scale and pilot plant are compared, significant
307 differences can be pointed out. The improved mass transfer conditions in the pilot plant
308 made the processes more efficient (much lower required Q for the same removal) and
309 differences caused by irradiating UV light become more relevant. In fact, the UV-activation
310 is more expectable on the bulk in the pilot plant and not only in the nearness of the anode
311 surfaces, according to our previous results.

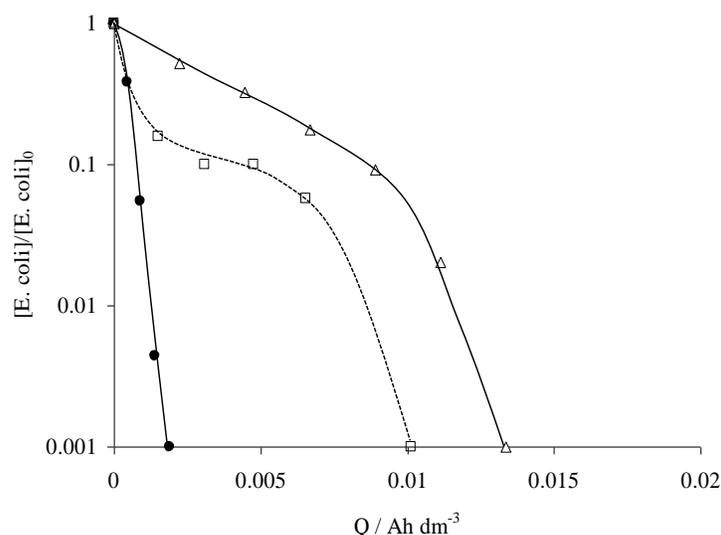


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313 **Figure 4.** Mineralization of organic matter during the electrolysis (■) and photo-
 314 electrolysis (□) of an effluent of the secondary clarifier of a WWTF intensified with
 315 caffeine in pilot plant and bench scale (onset). ([Caffeine]₀: 100 mg dm⁻³; j: 16.9 mA cm⁻²;
 316 T: 25°C. Pilot plant: V: 300 dm³; UV_{254 nm} = 26 W. Bench scale: V: 0.6 dm³; UV_{254 nm} = 4
 317 W).

318 The better performance observed for the removal of caffeine and TOC in pilot plant
 319 reverses with the disinfection process as it is shown in Figure 5. In this case, the efficiency
 320 of the pilot plant is lower. Furthermore, in comparing the single Diacell ® 101 (only one
 321 anode) with the stack Diacell ® 1001 (ten anodes), it can be noticed that the removal of
 322 microorganisms is more efficient when working with only one anode despite of the fact that
 323 the flow rate in both cells were the same (50 dm³ h⁻¹). In this case, in addition to the
 324 opposite change observed, the differences in the performance are even higher than those
 325 observed in the case of the removal of caffeine. Again, the velocity of the fluid and the
 326 turbulence caused by oxygen and hydrogen bubbles is higher in the stack, due to the lower

327 gap. Hence, opposite conclusions of those obtained in the removal of organics can be drawn
 328 in the electrochemical disinfection. Likewise, the results obtained in the pilot plant are
 329 worse than those obtained in the two bench scale plants, despite the flowrate is two folds
 330 higher and hence the turbulence is much greater (linear velocity in the pilot plant cells is
 331 167 cm/s while in the single cell is only 2.3 cm/s).



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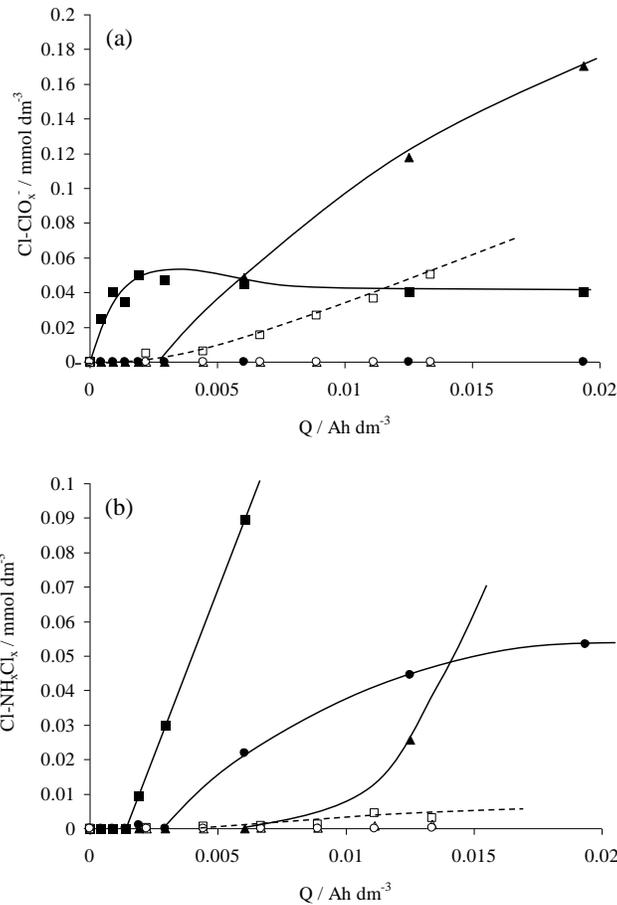
333 **Figure 5.** Scale-up of electrolysis of urban treated wastewater. (●) anode area: 78 cm²; *E.*
 334 *coli*₀: 9,100 CFU 100 ml⁻¹; V: 4 dm³; V_{tank}/Q_{recir}: 0.08 h; (□) anode area: 700 cm²; *E. coli*₀:
 335 9,100 CFU 100 ml⁻¹; V: 4 dm³; V_{tank}/Q_{recir}: 0.08 h; (Δ) anode area: 3,500 cm²; *E. coli*₀:
 336 5,400 CFU 100 ml⁻¹; V: 300 dm³; V_{tank}/Q_{recir}: 0.02 h. (j: 1.20 mA cm⁻²; T: 25°C).

337

338 Again, mass transport gives the explanation to this behaviour. Electrochemically assisted
 339 disinfection is not a surface process but it mainly occurs in the bulk of the electrolyte
 340 (either water or wastewater). Microorganisms are not “electrocuted” on the electrode
 341 surface but the most plausible mechanism is the attacks in the bulk of oxidants to the

342 membrane of pathogens (Bergmann 2010, Cotillas et al. 2013). Hence, the promotion of the
343 anodic surface processes is not good for the performance of disinfection as clearly points
344 out the results shown in Figure 4. Specifically, disinfection is related to the oxidants
345 produced electrochemically on the surface of diamond and transported into the bulk.
346 However, the more efficient transport is not a guarantee of a higher concentration of
347 oxidants in the bulk, but just the opposite. Combination of oxidants such as hydrogen
348 peroxide and peroxosulfates leads to the activation of both reagents to form hydroxyl and
349 sulfate radicals that rapidly react with other species or disappear forming less powerful
350 oxidants. This explains the better performance of the pilot plant with caffeine because of
351 the improved mass transport of this organic to the nearness of the electrode. On the
352 contrary, it leads to a less efficient production of oxidants because of the deactivating
353 mechanisms. This can be clearly seen in Figure 6, where the changes in the concentration
354 of chlorinated species with the applied electric charge is shown during the
355 electrodisinfection process. As it can be observed, concentration of oxochlorinated species
356 and also of chloramines is much higher in the bench scale plant but production of chlorate
357 is prevented in the pilot plant due to the less efficient production of hypochlorite. This fact
358 is of a great importance because it also clearly indicates a promising way to avoid the
359 formation of the non-desired chlorates and perchlorates during disinfection with diamond
360 anodes.

361

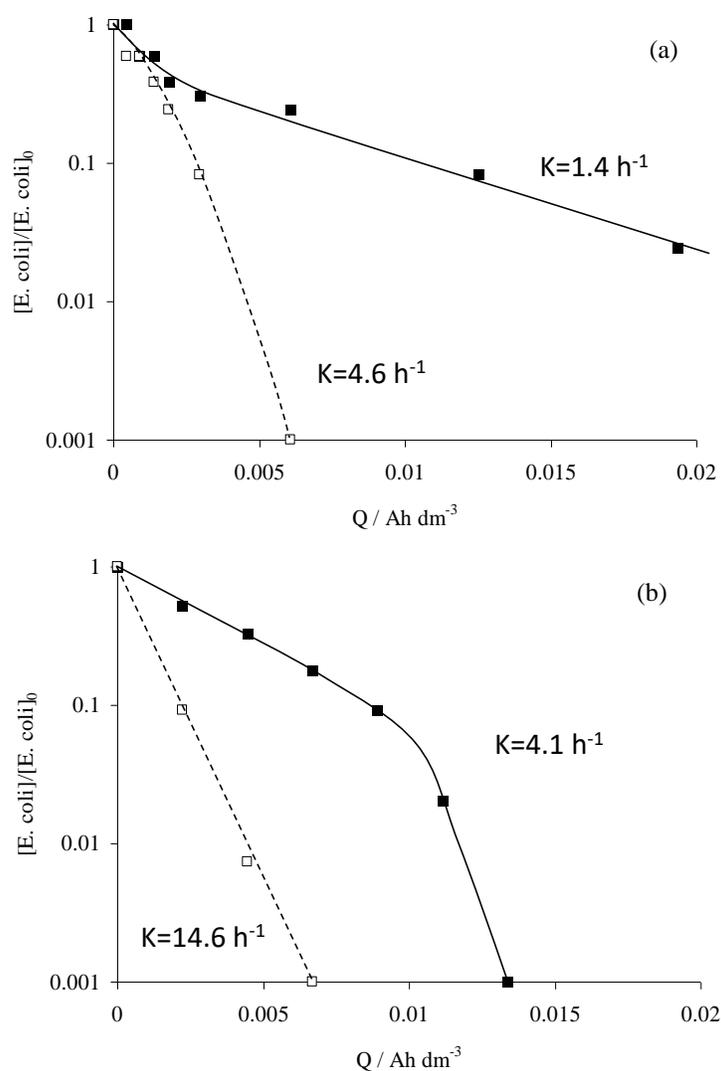


362

363 **Figure 6.** Chlorine speciation during the bench scale (black) and pilot plant (white)
 364 electrolysis of actual treated wastewater (discontinuous process). (a) (■) hypochlorite; (▲)
 365 chlorate; (●) perchlorate. (b) (■) monochloramine; (▲) dichloramine; (●) trichloramine.
 366 Bench scale conditions ($V: 4 \text{ dm}^3$; $j: 1.20 \text{ mA cm}^{-2}$; $T: 25^\circ\text{C}$); pilot plant conditions ($V: 300$
 367 dm^3 ; $j: 1.20 \text{ mA cm}^{-2}$; $T: 25^\circ\text{C}$).

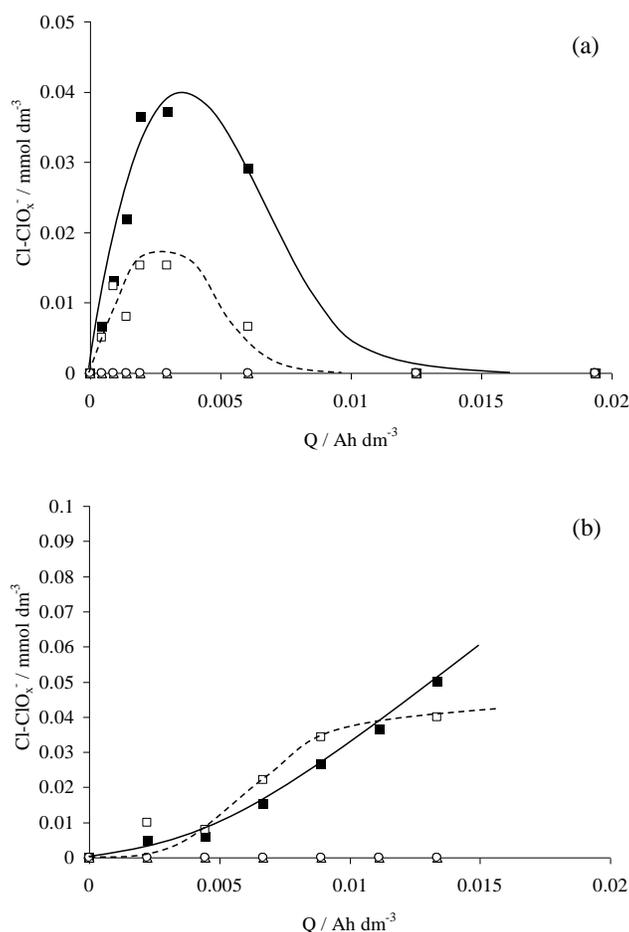
368 Figure 7 compares the effect of UV irradiation in bench scale and pilot plant disinfection.
 369 To prevent the formation of chlorates, and taking into account the results shown in Figure
 370 5, it was decided to operate in the bench scale plant at a much lower current density (0.13
 371 mA cm^{-2} vs. 1.2 mA cm^{-2}). Because of that, the reaction rate was slower as compared to the

372 obtained when working at a current density ten times higher. A clear improvement is
 373 observed in both systems with the irradiation of UV light. This improvement increases four
 374 times the rate in both cases and it is related to the effect of UV irradiation over *E. coli* cells.
 375 At this point, it is important to remember that UV irradiation is a very effective disinfection
 376 treatment and hence the application of the single UV irradiation is expected to have a clear
 377 removal of pathogens.



378

379 **Figure 7.** Electrolysis (■) and photo-electrolysis (□) of urban treated wastewater at pilot
 380 plant scale. (a) bench scale; anode area: 78 cm^2 ; *E. coli*₀: 9,100 CFU 100 ml⁻¹; V: 4 dm³;
 381 $V_{\text{tank}}/Q_{\text{recir}}$: 0.08 h; UV_{254nm}: 4 W; j: 0.13 mA cm⁻². (b) pilot plant; anode area: 3,500 cm²;
 382 *E. coli*₀: 5,400 CFU 100 ml⁻¹; V: 300 dm³; $V_{\text{tank}}/Q_{\text{recir}}$: 0.02 h; UV_{254nm}: 26 W; j: 1.20 mA
 383 cm⁻². (anode: BDD; cathode: SS; T: 25°C).



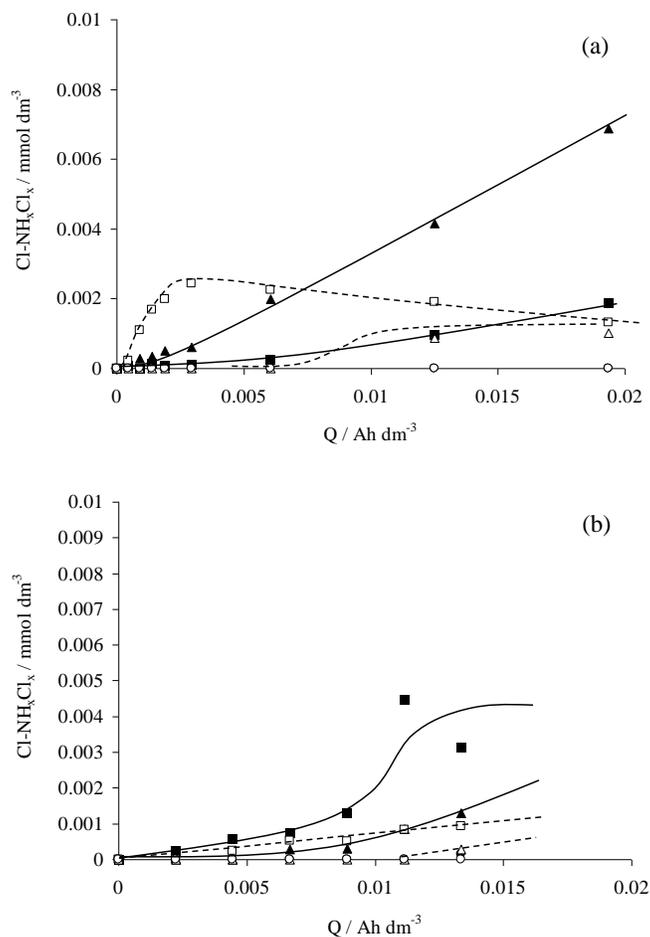
384

385 **Figure 8.** Free chlorine speciation during the electrolysis (black) and photo-electrolysis
 386 (white) of urban treated wastewater (discontinuous process). (a) Bench scale; anode area:
 387 78 cm^2 ; V: 4 dm³; $V_{\text{tank}}/Q_{\text{recir}}$: 0.08 h; UV_{254nm}: 4 W; j: 0.13 mA cm⁻². (b) Pilot plant; anode

388 area: 3,500 cm²; V: 300 dm³; V_{tank}/Q_{recir}: 0.02 h; UV_{254nm}: 26 W; j: 1.20 mA cm⁻². (■)
389 hypochlorite; (▲) chlorate; (●) perchlorate (anode: BDD; cathode: SS; T: 25°C).

390

391 In comparing the chlorine speciation (Figures 8 and 9) it can be seen that despite being
392 more efficient, photo-electrodisinfection produces a significantly lower concentration of
393 chlorine species. Furthermore, softer operation conditions used in the bench scale are
394 shown to be enough to produce hypochlorite and chloramines but not as hard as to
395 produce chlorine compounds in high oxidation state (chlorates and perchlorates). Regarding
396 the pilot plant experiment, despite using a one fold higher current density, no chlorate or
397 perchlorate is produced.



398

399 **Figure 9.** Combined chlorine speciation during the electrolysis (black) and photo-
 400 electrolysis (white) of urban treated wastewater (discontinuous process). (a) bench scale;
 401 anode area: 78 cm²; V: 4 dm³; V_{tank}/Q_{recir}: 0.08 h; UV_{254nm}: 4 W; j: 0.13 mA cm⁻². (b) pilot
 402 plant; anode area: 3,500 cm²; V: 300 dm³; V_{tank}/Q_{recir}: 0.02 h; UV_{254nm}: 26 W; j: 1.20 mA
 403 cm⁻². (■) hypochlorite; (▲) chlorate; (●) perchlorate (anode: BDD; cathode: SS; T: 25°C).

404 Hence, performance of photo-electrolytic processes in wastewater reclamation mainly
 405 depends on hydrodynamic conditions and not on the size of the system. The improvement
 406 of the transport processes caused by the higher pumping enhances the production of oxidant
 407 and thus oxidation of pollutants. This effect goes in a different direction in the depletion of

408 organics and in the disinfection and hence the design of real applications has to take into
409 account these important observations.

410

411 **Conclusions**

412 From this work, the following conclusions can be drawn:

- 413 – Electrolysis at pilot plant scale improves the efficiencies in caffeine removal
414 contained in urban treated wastewater due to the higher flow rate, which decreases
415 the mass transfer limitations.
- 416 – Photo-electrolysis promotes the breaking of aromatics compounds and, therefore, it
417 increases the efficiencies on caffeine removal and the mineralization of organic
418 matter at the beginning of the process.
- 419 – Electrochemical disinfection is more efficient at bench scale due to that this is not a
420 surface process and it mainly occurs in the bulk by the attack of disinfectants
421 electrogenerated. Free and combined chlorine compounds are the main disinfectant
422 species formed and their concentration is higher at bench scale. However, chlorine
423 compounds in high oxidation state (chlorates) are generated and could limit the
424 applicability of this technology.
- 425 – It is possible to obtain a completely disinfected effluent by a photo-electrolysis
426 process at pilot plant scale. During this process, disinfectant species
427 electrogenerated are photo-activated in the bulk, favouring the formation of free
428 radicals, which contribute to inactivation of microorganisms. Likewise, the

429 formation of hazardous chlorine compounds is hindered at lower current density and
430 higher linear velocity.

431

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436

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