

1 Solar-powered CDEO for the treatment of wastewater 2 polluted with the herbicide 2,4-D

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10

11 **Abstract**

12

13 In this work, the remediation of wastewater polluted with 2,4-D via conductive-diamond
14 electrochemical oxidation using solar energy as a direct electrical power source has been
15 investigated. The changes in operating conditions during the solar test are clearly related
16 to the day-night cycle, with a maximum solar irradiation intensity of 450 W m^{-2} at noon
17 and an average daily charge supplied of $22.5 \text{ Ah m}^{-2} \text{ d}^{-1}$. A solar irradiation intensity
18 greater than 100 W m^{-2} is necessary to produce current, and values over 200 A m^{-2} are
19 required for efficient solar-powered processes. Despite fluctuations in the intensity
20 supplied to the electrochemical cell, electrolysis with diamond electrodes can attain
21 complete depletion of 2,4-D and its mineralization, although the changing operating
22 conditions applied during the electrolysis powered by solar energy favor the accumulation
23 of many intermediates. In contrast, only very low concentrations of two intermediates
24 were detected during electrolysis powered galvanostatically with a power supply at 3.0
25 A , indicating that the intensity highly influences the oxidation rate involved in the
26 electrolysis.

27 **Keywords:** Solar energy, direct connection, herbicide, diamond anode, electrochemical
28 oxidation

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36 **1. Introduction**

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39 Conductive-diamond electrochemical oxidation (CDEO) has been widely used to treat
40 different types of wastewater [1, 2]. In general, this technology attains the almost
41 complete mineralization of the organics contained in wastewater with very high current
42 efficiencies due to the combination of several oxidation mechanisms, such as direct
43 electrooxidation, hydroxyl radical-mediated oxidation, and oxidation mediated by
44 oxidants generated during the treatment from the salts contained in the waste [3, 4].
45 Consequently, the operating costs are lower than those required by other electrochemical
46 technologies, and this technology can even compete with other advanced oxidation
47 processes from an economic perspective [5-8].

48 However, despite the considerable scientific effort of several research groups devoted to
49 studying the technical feasibility of CDEO [6, 9-16], industries are reluctant to employ
50 this technology because one of the key factors for CDEO is the requirement of large
51 amounts of electricity. In this context, the use of renewable energy (solar photovoltaic
52 and/or wind turbines) as an energy source for powering electrochemical reactors has
53 begun to be developed in recent years, and currently, it is a very interesting topic in which
54 both the direct powering and the use of intermediate energy storage components, such as
55 batteries, are investigated for obtaining an efficient integrated technology. In this context,
56 over the past years, several works have focused on the use of renewable energy power
57 sources to decrease both the investment and maintenance costs of wastewater treatment
58 systems. Among them, recent research studies on the electrodialysis of brackish water
59 [17-19], the electrocoagulation of dyes [20], and the electrooxidation of wastewater [21-
60 26] in which an electrochemical cell is directly supplied by photovoltaic solar energy have
61 demonstrated the technical feasibility of the technology. The direct connection of the

62 photovoltaic array to the electrochemical reactor avoids the use of a storage battery
63 system, and this clearly contributes to efficient use of the energy (no energy losses in
64 charge-discharge cycles of batteries) and to a decrease in the investment and maintenance
65 costs of storage systems. However, changes in solar irradiation intensity throughout the
66 day lead to significant energy fluctuations, and hence, the electrochemical reactor
67 becomes fed by a non-constant energy source. This power profile can influence the
68 performance and efficiency of the wastewater treatment. From this perspective, recent
69 electrooxidation studies [21, 23, 24, 26] have demonstrated that the photovoltaic array
70 configuration has a considerable influence on the use of the generated power and that the
71 optimum configuration must be redesigned depending on the intensity of the
72 instantaneous solar irradiation, conductivity of the solutions and concentration of
73 pollutant in the wastewater.

74 Over the past decades, the greatest concern regarding human exposure to pesticides has
75 been their presence in surface water bodies due to their extensive use in agriculture and
76 to the inadequate treatment of the wastewater streams produced in pesticide
77 manufacturing plants. Some pesticides are toxic to humans and animals, and their
78 continuous use is causing serious environmental contamination problems [27]. For this
79 reason, research effort is focusing on studying effective processes, such as CDEO, to
80 eliminate pesticides from the environment.

81 Based on this background, this work aims to demonstrate the feasibility and usefulness
82 of an electrooxidation system powered by solar panels. In this work, we first focus on the
83 main features of the PV solar powering of an electrolytic wastewater treatment cell and
84 then on the treatment of one herbicide as model pollutant: 2,4-dichlorophenoxyacetic acid
85 (2,4-D). The efficiency of the process in both the removal of 2,4-D and in its
86 mineralization is studied. Moreover, the influence of the power source (solar energy or

87 conventional power supply) on the performance of the conductive-diamond
88 electrochemical oxidation is evaluated. In addition, the robustness of electrochemical
89 technology powered by a non-constant energy source is assessed with a three-day test in
90 which the main parameters of this coupling are monitored.

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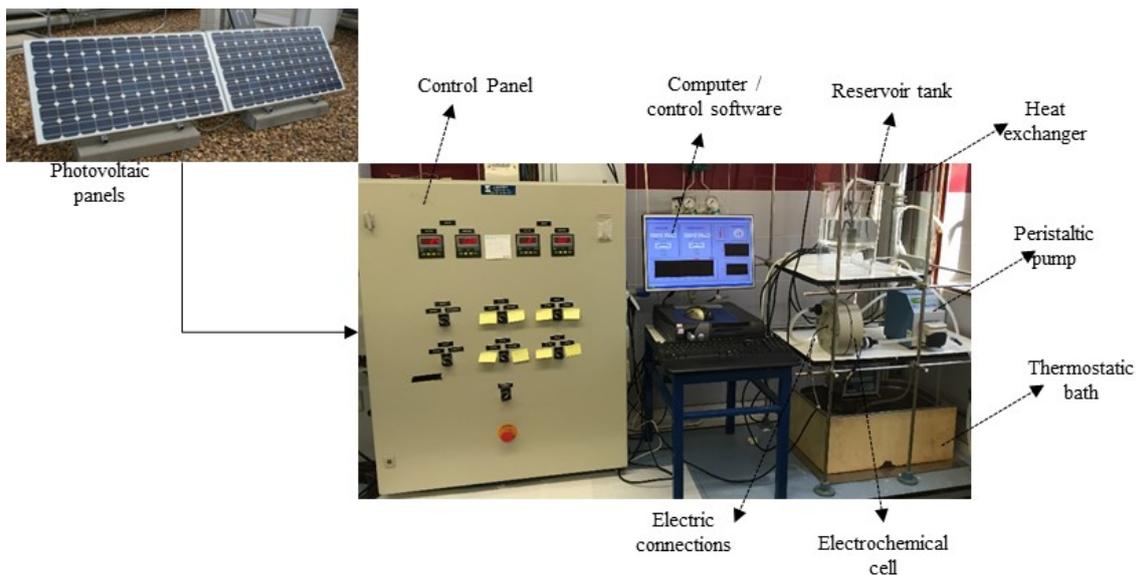
92 **2. Materials and methods**

93 **2.1 Experimental setup**

94

95 The electrooxidation processes were conducted in a DiaCell® 101 supplied by Adamant
96 Technologies (Switzerland). Boron-doped diamond electrodes (p-Si–boron-doped
97 diamond) were used as the anode and cathode. Both electrodes were circular (100 mm
98 diameter) with a geometric area of 78 cm². The BDD coating had a thickness of 2 μm,
99 resistivity of 100 mΩ cm, boron concentration of 500 ppm and sp³/sp² ratio of 76. The
100 active surface was 70 cm² per compartment, and the inter-electrode gap was 1 mm. The
101 BDD electrode was subjected to a cleaning procedure for 10 min in a 1 M Na₂SO₄ solution
102 at 150 A m⁻² prior to the electrolysis assays. Figure 1 shows a schematic representation
103 of the pilot plant designed for the WP-EO process.

104



105

106 **Figure 1.** Layout of the experimental setup.

107

108 Electricity produced by two photovoltaic panels connected in series (each panel with an
 109 area of 1.313 m²) can be used to power the electrochemical cell, or it can be stored in
 110 batteries. Computer software (Labview, National Instruments) was used to control the
 111 process, and during the tests, energy was directly supplied to the electrochemical cells.

112

113 **2.2 Analysis procedures and methods**

114 The electrooxidation of 4 dm³ of a solution containing 100 g m⁻³ 2,4-*D* at natural pH (3.5)
 115 and 3 g L⁻¹ NaCl as a supporting electrolyte was performed. The electrochemical cell was
 116 electrically powered by solar photovoltaic panels and by a conventional power supply. In
 117 the latter case, the experiment was conducted by applying 3.0 A of external current. The
 118 cell reactor was operated in batch-operation mode. The cell reactor was connected by a
 119 peristaltic pump (flow rate of 26.4 dm³ h⁻¹) to a tank through silicon tubes. A heat
 120 exchanger was coupled with a controlled thermostatic bath to maintain the temperature at
 121 25 °C. All electrolyses were performed under the same operating conditions to evaluate
 122 the efficiencies of the different power supplies.

123 All of the samples extracted from electrolyzed solutions were filtered using 0.45 μm
124 nylon filters from Whatman prior to analysis. Measurements of pH were performed using
125 an InoLab WTW pH-meter. The decay of 2,4-D and the evolution of its aromatic products
126 were followed using reversed-phase chromatography and total organic carbon (TOC).
127 The chromatography system was an Agilent 1100 series coupled to a UV detector. A
128 Phenomenex Gemini 5 μm C18 analytical column was used. The analytical conditions
129 were a mobile phase consisting of 60 % acetonitrile and 40 % water containing 2 % acetic
130 acid with a flow rate of 0.4 $\text{cm}^3 \text{min}^{-1}$, UV detection wavelength of 280 nm, oven
131 temperature of 25 $^\circ\text{C}$, and injection volume of 20 μL . Chemical Oxygen Demand (COD)
132 was monitored using standard kits from Merck. Solutions were oxidized by digestion for
133 2 h at 150 $^\circ\text{C}$ in a block ECO 25 Thermoreactor (Velp Scientifica). Then, after the ambient
134 temperature was reached, the absorbance of the samples was read at 600 nm in a
135 spectrophotometer (Hach DR 2000). The total organic carbon concentration was
136 monitored using a Multi N/C 3100 Analytik Jena analyzer.

137

138 The current efficiency (CE) was calculated with Equation 1 where COD_t and $\text{COD}_{t+\Delta t}$ are
139 the chemical oxygen demand (in $\text{g O}_2 \text{dm}^{-3}$) at times t and $t+\Delta t$ (in seconds), respectively,
140 I is the current intensity (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume
141 of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistence ($\frac{32 \text{ g O}_2 \cdot \text{mol}^{-1} \text{ O}_2}{4 \text{ mol e}^- \cdot \text{mol}^{-1} \text{ O}_2}$
142).

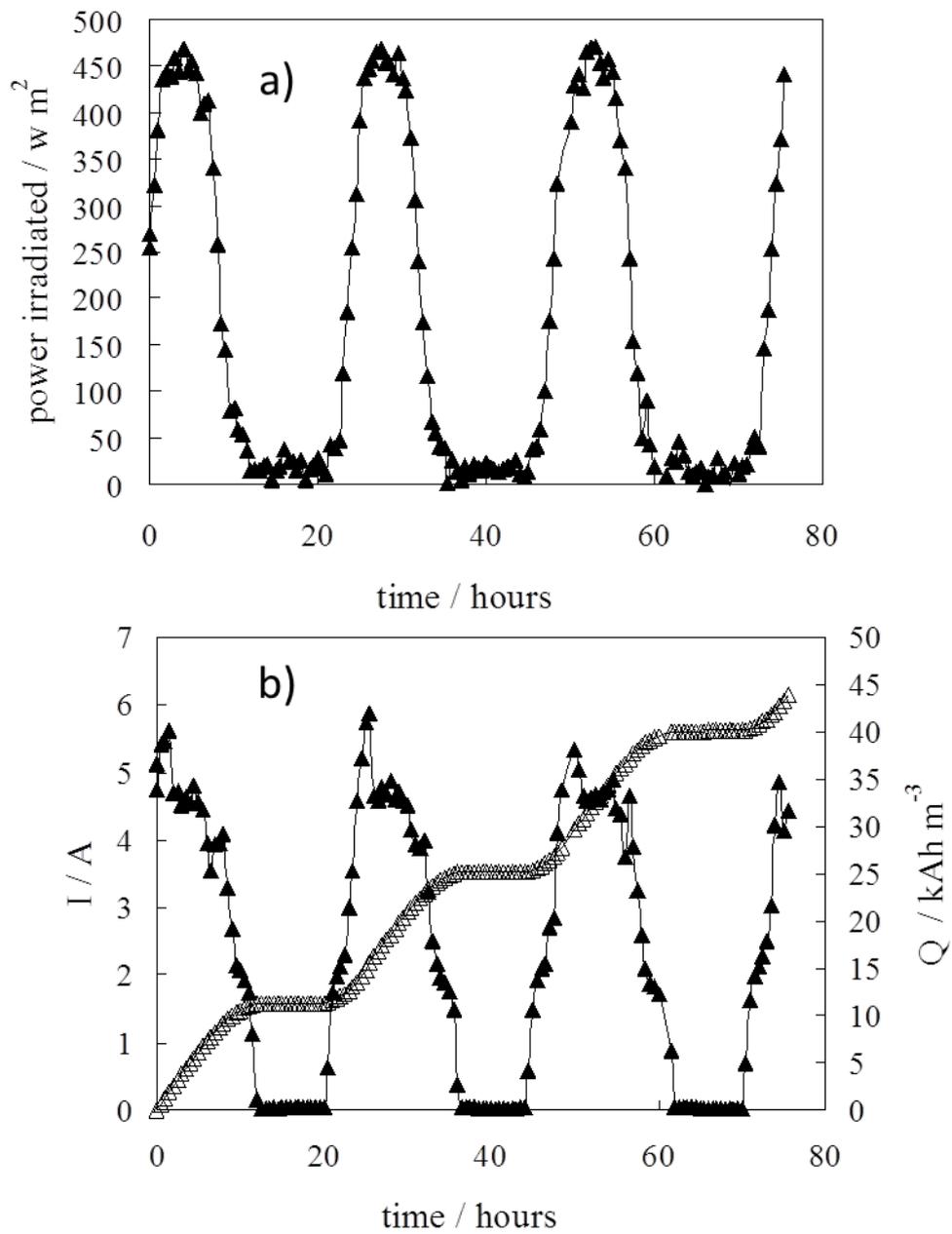
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$$CE = \frac{[(COD)_t - (COD)_{t+\Delta t}]FV}{8I\Delta t} \quad (1)$$

145

146 **3. Results and discussion**

147 **Current profiles in electrolytic cells fed with PV panels.** Figure 2 shows profiles of the
148 solar irradiation intensity applied to the electrolytic cell and total current charge passed
149 during a continuous 75-hour test in which an electrochemical cell was electrically
150 powered by the two photovoltaic solar panels and in which a synthetic wastewater with a
151 conductivity of 5.4 mS cm^{-1} was electrolyzed. This test aimed to determine the main
152 features of the electric powering of the electrochemical cells. Experiments were
153 performed during three selected (according to the weather forecast) consecutive sunny
154 days (no clouds) during the month of September 2014, and the PV panels were located
155 on the roof of the E3L Lab (38.59 N 3.55 O) and oriented to the south.



156

157 **Figure 2.** Changes in the a) solar power irradiation intensity and b) applied current

158 intensity and total current charge passed during the test.

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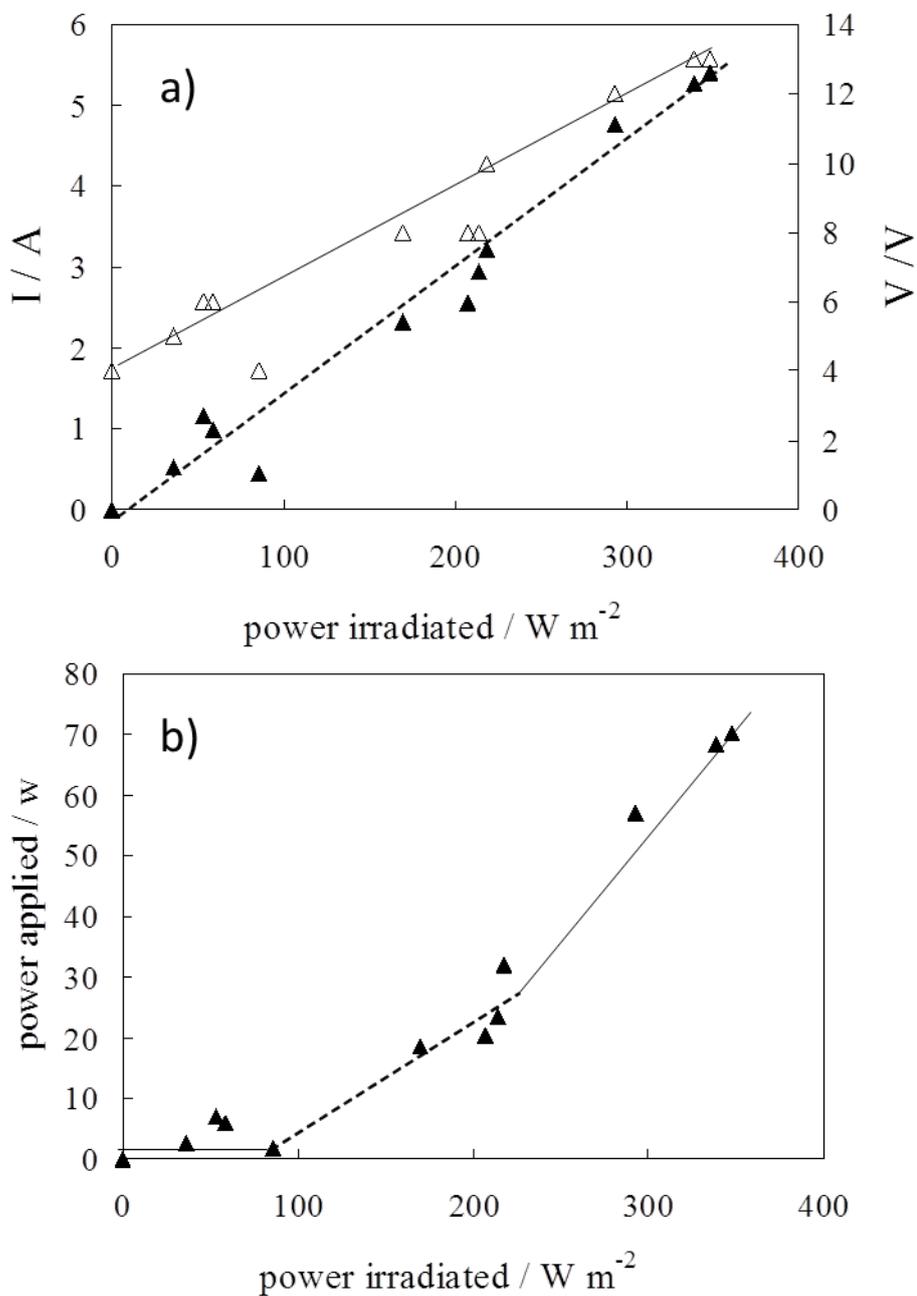
160 As expected, the solar irradiation profile (part a) was clearly related to the day-night
161 cycles, with maximum solar irradiation values (approximately 450 W m^{-2}) during the
162 noon time slot (from 12.00 h to 15.00 h) and null values during the night (from 22.00 h
163 to 06.00 h of the next day). An almost complete reproduction of the results was obtained
164 in the three days monitored. This result can be easily understood considering that they
165 were consecutive and sunny days with comparable climatologic conditions.

166 Part b of the figure shows the instantaneous intensity provided to the electrochemical
167 device when the electricity from the PV panels is directly supplied to the electrochemical
168 device. As shown, the solar irradiation profile clearly affects the current intensity supplied
169 to the electrochemical cell. The current intensity profiles follow almost the same trend,
170 with daily peaks of intensity of 5.6, 5.9 and 5.3 A, respectively, and with plateau zones
171 of zero current during nighttime (period of approximately 7.5-8.0 hours long). Current
172 intensities over 4.0 A are supplied when the irradiation is greater than 200 W m^{-2} , and
173 this power is produced for approximately 8 hours/day (7 h in the second day and 9 h in
174 the third). From this optimum period, the decay or increase in the applied energy is very
175 rapid and not completely symmetrical, which is likely due to other external factors, such
176 as the changing environmental temperature. Thus, the average current decay rate in the
177 applied current during the evening is -0.69 A/h , whereas the average current growth rate
178 is 1.05 A/h during the early morning. This pattern clearly reflects the total current charge
179 applied to the cell, which exhibits a marked stepwise trend. During the test, a total electric
180 charge of 175.3 Ah was applied to the wastewater by the 2.6 m^2 of PV panels. This value
181 indicates that the average daily charge supplied by this power source is $22.5 \text{ Ah m}^{-2} \text{ d}^{-1}$.
182 This value is not exactly the same each day; rather, it exhibits small deviations. Thus, the
183 records for days 2 and 3 show that the applied charges were 54.4 Ah and 60.0 Ah,
184 respectively, reflecting the small daily fluctuations. The results obtained on days 1 and 4

185 (which are incomplete although they correspond to one full day) confirm this slight
186 fluctuation because, in this case, the applied charge amounted to 60.9 Ah during 24 hours.
187 Figure 3 shows the changes in the applied intensity and resulting cell voltage with the
188 irradiated solar power. As shown, linear relationships between voltage and intensity and
189 the solar irradiated power are obtained. Solar irradiation intensity of greater than 100 W
190 m^{-2} is necessary to produce current (minimum voltage is 4.0 V).

191 Regarding the power applied to the electrolytic cell (product of voltage and intensity),
192 two linear trends are obtained, with ratios of power applied/power irradiated of
193 approximately 0.1 W-electricity / (W-solar m^{-2}) and 0.2 W-electricity / (W-solar m^{-2}) for
194 solar irradiation intensities below and above 200 W m^{-2} , respectively. This result indicates
195 that this type of energy supply for electrolysis cells may be very efficient if the solar
196 irradiation intensity is above this value, the efficiency markedly decreases in the range of
197 100-200 W m^{-2} , and it is completely ineffective if the solar irradiation intensity is less
198 than 100 W m^{-2} .

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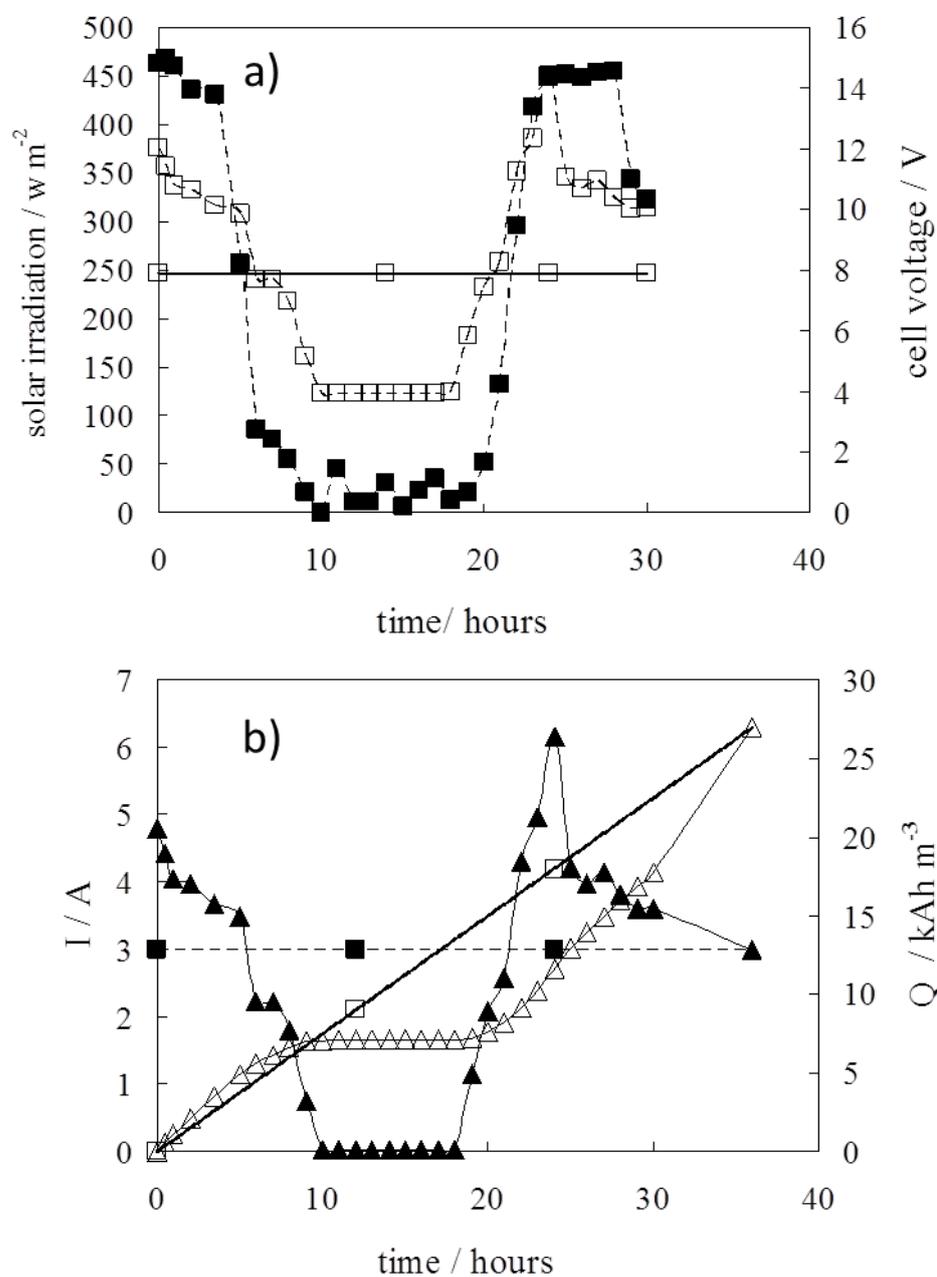
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201 **Figure 3. a)** Influences of irradiated solar power on intensity (▲) and cell voltage (△).

202 **b)** Relationship between electric power applied / irradiated solar power for the

203 electrochemical system with the PV panels.

204 **Treatment of wastewater with cells powered by PV panels.** To evaluate the influence
205 of the changing current and voltage profile on the treatment of wastewater, electrolysis
206 of synthetic wastewater containing 2,4-D was selected as a model, which was conducted
207 by powering the electrochemical cell with PV panels and with a conventional power
208 supply. In the latter case, the electrolysis was driven galvanostatically. Figure 4 shows
209 profiles of solar irradiation, cell voltage, applied intensity and total current charge passed
210 during 30 h (time required to total mineralization of the solution) in which the
211 electrochemical cell was electrically powered by solar panels.



212

213

214 **Figure 4. a)** Evolution of solar irradiation (\blacktriangle) and cell voltage (\triangle) during the
 215 electrochemical treatment of synthetic wastewater polluted with 100 g m^{-3} 2,4-D using
 216 PV panels to power the electrochemical cell. For comparison purposes, cell voltage (\square)

217 during the test with the conventional power supply. **b)** Evolution of instantaneous current
218 intensity (\blacktriangle) and total current charge passed (\triangle) during the electrochemical treatment
219 of synthetic wastewater polluted with 100 g m^{-3} 2,4-D using PV panels to power the
220 electrochemical cell. For comparison purposes, instantaneous current intensity (\blacksquare) and
221 total current charge passed (\square) during the test with the conventional power supply.

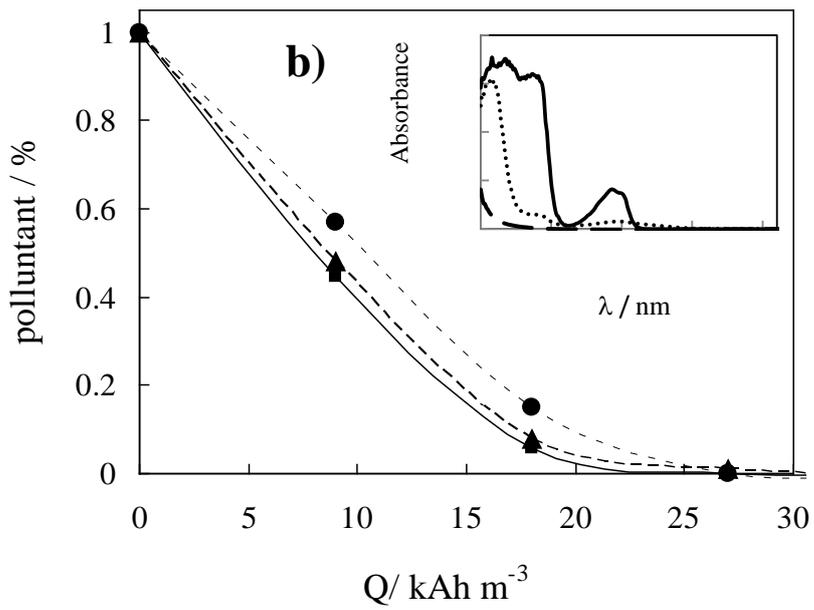
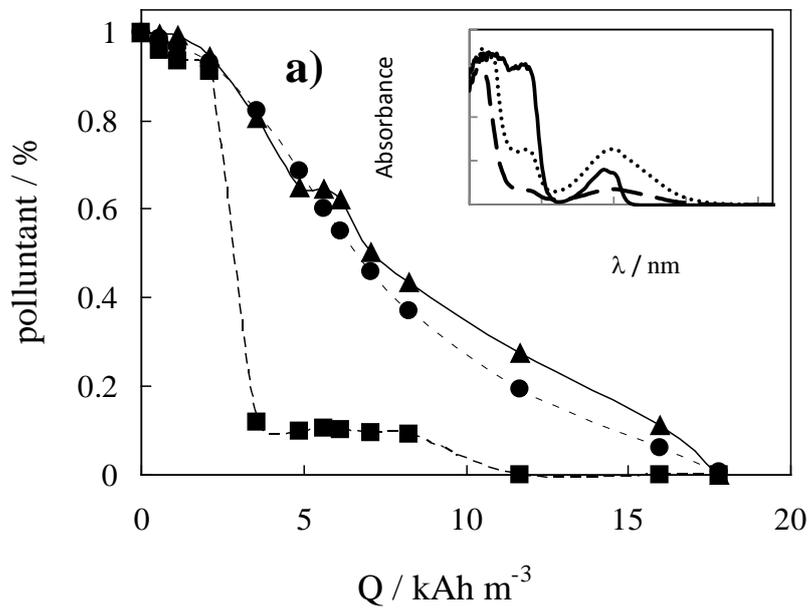
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223 As expected according to the previous tests, the applied current was not constant, and it
224 showed maximum peaks of 6.2 A, null values during the night period, and an average
225 value during the light period of 3.45 A. Consequently, after 30 h of operation, a total
226 electric charge of 18 kAh m^{-3} was applied to the wastewater. In contrast, the applied
227 current in the test with a conventional power supply was constant and set at 3.0 A
228 (galvanostatic operating conditions). For comparison purposes, Figure 4 also shows the
229 profile of cell voltage, intensity and electric charge passed during the electrolysis
230 conducted using a conventional power supply (square markers). As shown, the electric
231 powering of both systems is completely different because in the conventional test, the cell
232 voltage was maintained almost constant during the entire test (although the cell is
233 operated in galvanostatic mode, only a small decrease is observed), and the electric charge
234 linearly increases with time. Note that the experiment was designed with the aim to
235 provide comparable current charges in both systems and to apply a comparable average
236 current density.

237 Figure 5 shows the changes in the 2,4-D, COD and TOC concentrations with the applied
238 electric charge during the electrochemical treatment of synthetic wastewater polluted with
239 100 g m^{-3} of 2,4-D using both electrical connections: solar panels (part a) and power
240 supply (part b).

241 As can be observed, the 2,4-D is completely removed from the synthetic wastewater with
242 an electric charge passed of approximately 17 kAh m^{-3} in the case of the direct connection
243 of the electrochemical cell to the solar panel. Similar electric charges are also required
244 for the complete mineralization of the organic content. In contrast, the COD data show a
245 peculiar trend with a rapid decrease that is not related to either 2,4D or TOC removal.
246 Here, it is important to consider that changes in the concentration of 2,4-D only provide
247 information regarding the concentration of the raw pollutant, whereas the transformation
248 into intermediates is monitored based on COD and the transformation into carbon dioxide
249 is monitored based on TOC.

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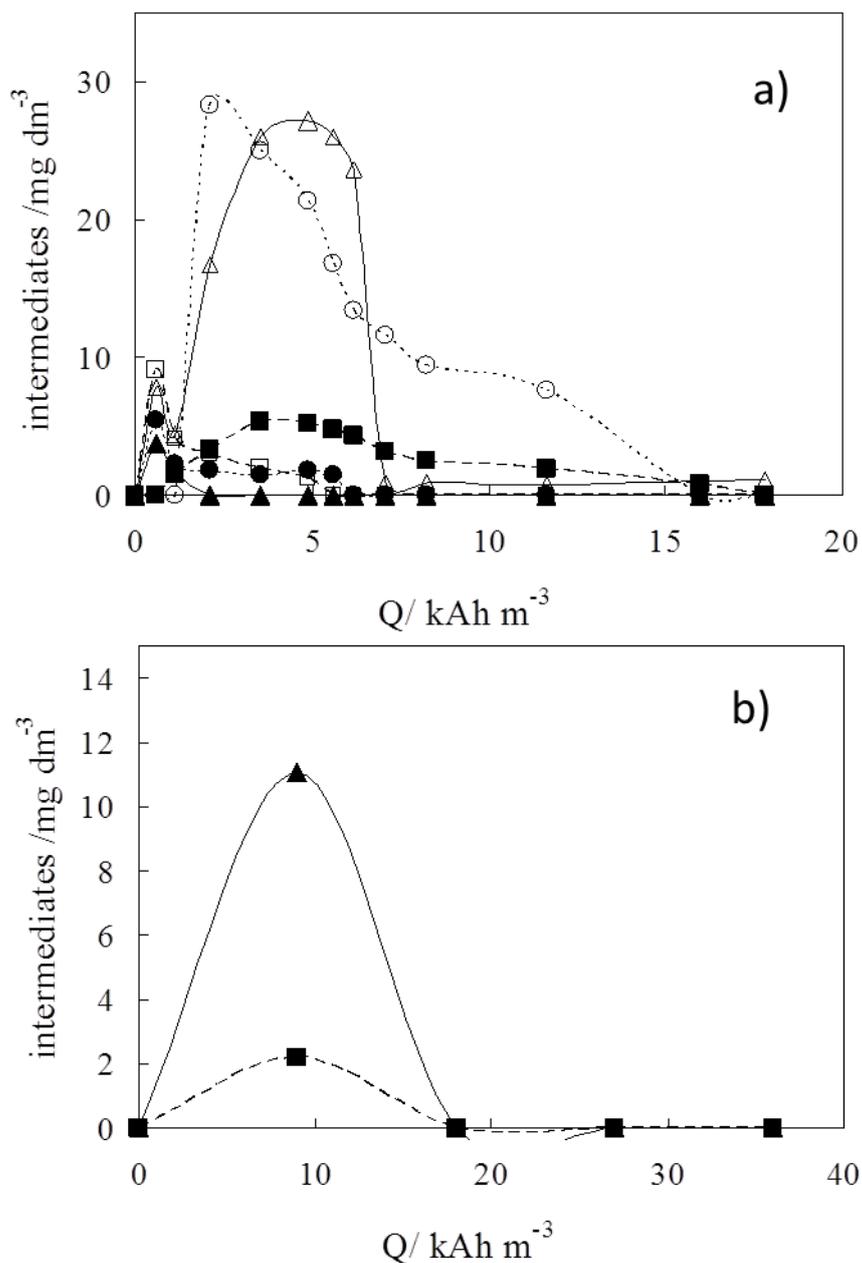
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256 **Figure 5.** Evolution of the (●) 2,4-D, (■) COD and (▲) TOC concentrations with the
257 applied electric charge during the electrochemical treatment of synthetic wastewater
258 polluted with 100 g m^{-3} of 2,4-D using **a)** solar panels to power the electrochemical cell
259 and **b)** using a conventional power supply to power the electrochemical cell. Onset:
260 Changes in the ultraviolet spectrum during the electrolysis: (–) 0 kAh m^{-3} , (⋯) 9 kAh m^{-3} ,
261 $(- - -)$ 16 kAh m^{-3} .

262

263 In the literature [28, 29], similar COD trends have been obtained during the electrolysis
264 of organics in chlorine medium, and these trends appear to be related to the formation of
265 recalcitrant intermediate species, most likely organochloride species that are not
266 oxidizable using the COD methodology. This behavior is not observed in the case of using
267 a conventional power supply to feed the electrochemical cell. In this case, 2,4-D, COD
268 and TOC decay almost simultaneously and over the same linear trend. The different
269 behavior observed in the two electrolyses may be related to the main oxidation pathways
270 involved in each case. In fact, as shown in the onsets of the figures, the UV spectra
271 obtained in the two investigated cases significantly differ. In the UV-vis spectrum of the
272 electrolysis performed using a conventional power supply, the appearance of additional
273 peaks during the treatment is not observed, and it can be assumed that once the CDEO
274 begins, the oxidation of the 2,4-D molecule continues until the formation of carbon
275 dioxide. Conversely, in the case of using solar panels as the electricity source, the
276 absorbance peak at approximately 290 nm increases during the initial stages of the
277 process, and then it begins to decrease. The average current efficiencies of both system
278 are around 6 and 2 % for conventional electrolysis and solar-powered electrolysis,
279 respectively

280 Another important point that should be noted is the plateau zones observed during the
281 removal of TOC for very low electric charge passed ($Q < 2 \text{ kAh m}^{-3}$) and approximately
282 $5\text{-}7 \text{ kAh m}^{-3}$. These zones may be related to the accumulation of intermediate species in
283 the reaction system. To clarify this point, Figure 6 shows the changes in the concentration
284 (mg dm^{-3}) of the main intermediates detected during both electrolyses. As expected, the
285 number of intermediates formed in the electrolysis performed using solar panels as the
286 energy source leads to the formation of numerous intermediates in low, but not negligible,
287 concentrations, whereas only two intermediates with relatively very low concentrations
288 are detected during the electrolysis performed using a conventional power supply.



289

290 **Figure 6.** Concentration evolution of the main intermediates detected as function of the
 291 charge applied during the electrochemical treatment of synthetic wastewater polluted with
 292 100 g m⁻³ of 2,4-D using **a)** solar panels and **b)** power supply to power the electrochemical
 293 cell. (■) 4-chlororesorcinol, (□) 2-chlorophenol, (●) 4-chlorophenol, (○) 2,4 -
 294 dichlorophenol, (▲) hydroquinone and (Δ) benzoquinone.

295 Another important observation is that during the first stages of the process ($Q < 2 \text{ kAh m}^{-3}$)
296 ³), the formation of intermediates is also favored, which can explain the lower TOC
297 removal observed during the first stages of the process. Similar behavior is observed with
298 approximately 5 kAh m^{-3} of electric charge passed. The main intermediates detected were
299 4-chlororesorcinol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, which were
300 further oxidized to hydroquinone and then to benzoquinone. Aliphatic compounds and
301 carboxylic acids were not detected in the reaction media, and thus, it can be assumed that
302 aromatic intermediates are rapidly degraded to carbon dioxide. The accumulation of
303 organochloride species in the system helps to explain the unusual COD trend obtained in
304 the electrolysis using solar panels as the electricity source (Figure 5a). In the case of the
305 electrolysis performed using a power supply to feed the electrochemical cell, only 4-
306 chlororesorcinol and hydroquinone were detected with relatively low concentrations. This
307 result is consistent with the TOC, COD and 2,4-D profiles shown in Figure 5b.

308 The differences observed in the 2,4-D and TOC removal efficiencies in the two cases
309 studied can be explained in terms of the applied electric current intensity. Note that the
310 intensity strongly influences the oxidation mechanism involved in the degradation
311 process. As well reported in the literature [3], high values of intensity favor the massive
312 production of hydroxyl radicals during conductive diamond electrochemical oxidation.
313 These species are very reactive, and they can help to form other oxidants, such as chlorine
314 or ozone [4]. The selectivity of these oxidants should be very small, and they
315 indiscriminately attack all of the intermediates formed and restrain the transfer of
316 intermediates from this reaction zone to the bulk. Nevertheless, note that a very high
317 intensity also promotes the recombination of radicals, and it leads to less efficient
318 degradation processes. Likewise, at a very low intensity, direct oxidation on the electrode
319 surface can be considered the main oxidation mechanism [3]. Taking all of these points

320 into consideration, the marked intensity fluctuations observed during the case of feeding
321 the system with solar panels can lead to periods of very soft oxidation conditions
322 (intensity < 3 A) in which the partial oxidation of 2,4-D is favored and intermediate
323 species are accumulated in the system. In contrast, the constant operating conditions of
324 the electrolysis conducted using a conventional power supply ensures hard oxidation
325 conditions throughout the entire reaction, with contributions of both direct and mediated
326 oxidation mechanisms.

327

328 **4. Conclusions**

329 The following conclusions can be drawn from the results of this study:

- 330 - CDEO can be powered using PV solar panels. During a sunny summer day, the
331 average daily charge supplied by this power source is $22.5 \text{ Ah m}^{-2} \text{ d}^{-1}$. Solar
332 irradiation greater than 100 W m^{-2} is necessary to produce current, and the ratios
333 of power applied/power irradiated are approximately $0.1 \text{ W-electricity} / (\text{W-solar}$
334 $\text{m}^{-2})$ and $0.2 \text{ W-electricity} / (\text{W-solar m}^{-2})$ for solar power irradiation below and
335 above 200 W m^{-2} , respectively.
- 336 - The complete degradation of 2,4-D can be achieved when the electrochemical cell
337 is directly powered by a PV solar panel. The mineralization efficiency (in terms
338 of applied electric charge) of 2,4-D does not significantly depend on the power
339 source used, although the fluctuations in the current intensity applied at each
340 moment appear to favor the accumulation of intermediate species in the reaction
341 system. The main intermediates detected during the oxidation were
342 organochlorinated species (4-chlororesorcinol, 2-chlorophenol, 4-chlorophenol,
343 and 2,4-dichlorophenol), hydroquinone and benzoquinone. Aliphatic compounds

344 and carboxylic acids were not detected in the reaction media, and thus, it can be
345 assumed that aromatic intermediates are transformed almost directly to carbon
346 dioxide.

347

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354

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