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## 44 **1. Introduction**

45 During the recent years, many studies have demonstrated that conductive diamond  
46 electrochemical oxidation (CDEO) is a very robust and effective technology for the  
47 treatment of wastewaters polluted with a great variety of organic pollutants [1-13]. In  
48 fact, it can get the complete mineralization of the organic load without the formation of  
49 refractory compounds and it can also attain current efficiencies of 100 % in the the  
50 treatment of highly concentrated wastewaters (1,500-20,000 mg COD dm<sup>-3</sup>). However,  
51 in the treatment of diluted wastewaters (below 1,500 mg COD dm<sup>-3</sup>), electrolyses may  
52 be controlled by the mass transfer rate of pollutant from the bulk to the anode surface  
53 and thus, the current efficiency decreases linearly with COD concentration [14]. This is  
54 what used to be observed in the treatment of wastewaters polluted with persistent  
55 organic pollutants (POPs), in which these species are typically found at very low  
56 concentrations because of their low solubility.

57

58 The harsh oxidation conditions attained with CDEO is usually explained in terms of the  
59 oxidation mechanisms involved in the process. It is well documented [15] that besides  
60 direct electrooxidation on the surface and oxidation by means of hydroxyl radicals in a  
61 region close to the electrode surface, the oxidation mediated by other oxidants  
62 electrogenerated on the diamond surface from the electrolyte salts should be taken into  
63 account, as it can counterpart the mechanisms of oxidation in this kind of  
64 electrochemical technology, and it contributes to increase the global oxidation  
65 efficiency [16]. However, recent studies have shown that the oxidation efficiency of the  
66 oxidants produced electrochemically is much more significant than that show by  
67 commercial oxidants [17]. This fact seems to point out that it is necessary the activation

68 of these oxidants to promote the mediated oxidation. This activation can be carried out  
69 by chemical reactions or by irradiation of ultrasound or ultraviolet-light (UV) [18-31].

70

71 Recent studies coupling ultrasounds to CDEO (Conductive-Diamond Sono  
72 Electrochemical Oxidation, CDSEO) have shown that process efficiency can be also  
73 increased because of the improvement of the mass transfer, promotion of the  
74 decomposition of water producing hydroxyl radicals, formation of new radical species  
75 and components and the electrohydraulic cavitations, growth and cyclical collapse of  
76 gas bubbles [18-24]. These changes are complementary and even synergistic with those  
77 taking place during electrolyses, resulting in very effective processes.

78

79 On the other hand, it has been also demonstrated that coupling UV irradiation to CDEO  
80 (Conductive-Diamond Photo Electrochemical Oxidation, CDPEO) leads to a synergistic  
81 effect explained either by heterogeneous (external bias contribute to a decrease in the  
82 electron-hole pair recombination process and the UV-photons reaching the electrode  
83 surface form excited radicals) and/or homogenous (photo activation of  
84 electrochemically generated reactive species) catalytic processes [25-31].

85

86 Progesterone have been often selected as model of POPs and its removal from waters  
87 and wastewaters has been studied by oxidation with potassium permanganate [32],  
88 ozonation [33, 34], photocatalysis [35], or solar photo-Fenton [36] but, to the authors'  
89 knowledge, not a study has been made till now coupling UV and US irradiation  
90 technologies with CDEO. A previous work of our group [37] clarified the mechanisms  
91 and performance of CDEO in the removal of progesterone. In that paper, different

92 parameters, such as current density, initial concentration of pollutant or nature of the  
93 supporting electrolyte were studied.

94

95 Thus, this work focuses on the improvement of the process efficiency by coupling US  
96 and UV irradiation to CDEO in the degradation of progesterone from wastewaters. Thus,  
97 the treatment of wastewaters polluted with this compound is studied by CDEO,  
98 sonolysis, fotolysis, CDSEO, CDPEO and Conductive Diamond Sono-Photo  
99 Electrochemical Oxidation (CDSPEO). Results will be discussed at the light of the  
100 influence of the operating conditions on mineralization and reaction intermediates  
101 formation.

102

## 103 **2. Materials and methods**

### 104 **2.1. Chemicals**

105 Water-Soluble Progesterone (WSP) or Progesterone / 2-hydroxypropyl- $\beta$ -cyclodextrin  
106 (7/93), where 2-hydroxypropyl- $\beta$ -cyclodextrin is a stabilising agent [38]. This  
107 compound was supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim,  
108 Germany). Anhydrous sodium sulphate, used as supporting electrolyte, was analytical  
109 grade purchased from Fluka. All solutions were prepared with high-purity water  
110 obtained from a Millipore Milli-Q system, with resistivity  $> 18 \text{ M}\Omega \text{ cm}$  at  $25 \text{ }^\circ\text{C}$ .  
111 Sulphuric acid and sodium hydroxide used to adjust the solution pH were analytical  
112 grade and supplied by Panreac Química S.A. (Barcelona, Spain).

113

### 114 **2.2. Analytical procedures**

115 The Total Organic Carbon concentration was monitored using a Multi N/C 3100  
116 Analytik Jena analyzer. Measurements of pH and conductivity were carried out with an

117 InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively. The  
118 concentrations of the compounds were quantified by HPLC (Agilent 1100 series). The  
119 detection wavelength used to detect progesterone was 248 nm. The column temperature  
120 was 25 °C. Volume injection was set to 50 µL. The analytical column used was  
121 Phenomenex Gemini 5 µm C18. Solvent A was composed by 25 mM of formic acid  
122 water solution and Solvent B was acetonitrile. A linear gradient chromatographic  
123 elution was obtained by initially running 10 % of Solvent B ascending to 100 % in 40  
124 min. Samples extracted from electrolyzed solutions were filtered with 0.20 µm Nylon  
125 filters before analysis. Moreover, the acids intermediates formed during the experiments  
126 were detected with a detection wavelength of 190 nm. The ion exchange column used  
127 was SUPELCOGEL™ H Carbohydrate Columns from Sigma-Aldrich and dilute  
128 H<sub>3</sub>PO<sub>4</sub> (0.022 M) was employed as the solvent.

129

### 130 **2.3. Electrochemical cells**

131 Electrolyses were carried out in a single compartment electrochemical flow cell  
132 working under a batch-operation mode [39]. Conductive –Diamond Electrodes (p-Si–  
133 boron-doped diamond) were used as anode and a stainless steel (AISI 304) as cathode.  
134 Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm<sup>2</sup> and  
135 an electrode gap of 9 mm. Boron-doped diamond films were provided by Adamant  
136 Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical  
137 vapour deposition technique (HF CVD) on single-crystal p-type Si <100> wafers (0.1  
138 Ωcm, Siltronix).

139

140 The ultrasound horn was a UP200S (Hielscher Ultrasonics GmbH, Germany) equipped  
141 with a titanium glass horn of 40 mm diameter, length 100 mm, emitting 24 kHz and

142 maximum ultrasonic power of 200 W. The output can be continuous or pulsed with  
143 varying percentage of cycle duty ranging from 10 to 100%.

144

145 The ultraviolet lamp was a Filtered Lamp Vilber Lourmat VL-215.MC with a power of  
146 4 W. The wavelength used was 254 nm (UV-C).

147

#### 148 **2.4. Experimental procedures**

149 Bench-scale electrolyses of 1000 cm<sup>3</sup> of wastewater were carried out under  
150 galvanostatic conditions. The current density employed was 30 mA cm<sup>-2</sup>.

151

152 The cell voltage did not vary during electrolysis, indicating that conductive-diamond  
153 layers did not under go appreciable deterioration or passivation phenomena. Prior to use  
154 in galvanostatic electrolysis assays, the electrode was polarized during 10 min in a  
155 0.035 M Na<sub>2</sub>SO<sub>4</sub> solution at 15 mA cm<sup>-2</sup> to remove any kind of impurity from its  
156 surface.

157

158 The wastewater was stored in a glass tank and circulated through the electrolytic cell by  
159 means of a centrifugal pump (flow rate 21.4 dm<sup>3</sup> h<sup>-1</sup>). A heat exchanger coupled with a  
160 controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to  
161 maintain the temperature at the desired set point (25 °C).

162

#### 163 **3. Results and discussion**

164

165 Fig. 1 shows the changes in the concentration of progesterone (part a) and TOC (part b)  
166 during the treatment of synthetic wastewater polluted with 100 mg dm<sup>-3</sup>, using different

167 technologies (semi-logarithmic scale is used for a better comparison). Operation  
168 conditions of each experiment are detailed in the Figure caption.

169

170 Regarding oxidation of the progesterone molecule (part a of Fig. 1), an efficient  
171 degradation can be observed when single CDEO is used, just the opposite of that  
172 observed for single sonolysis and photolysis technologies, which only entail a slight  
173 removal of progesterone. On the contrary, coupling UV light and US irradiations with  
174 CDEO seems to have a very positive effect, improving results obtained by single CDEO  
175 very significantly. Anyhow, enhancement observed seems to be different in both  
176 combined technologies. CDSEO enhancement is observed only for reaction times  
177 higher than 200 minutes, just when the mass transfer control limitations should be more  
178 important for the single CDEO technology (according to the concentration of pollutants  
179 which is diminished in one fold at this time). Hence, it could be suggested that this  
180 mechanical irradiation should improve the turbulence of the electrolyte and  
181 consequently the transfer of pollutants to the conductive-diamond surface, and this  
182 improvement in mass transfer has a clear positive effect on the degradation rate.  
183 CDPEO improves process efficiency from the initial time, being the final improvement  
184 higher than with CDSEO. In this case, the most probable reason is the promotion of the  
185 formation of radicals from oxidants produced electrochemically, because UV light  
186 irradiation is known to favor this type of activation and obviously, it does not have any  
187 influence on mass transfer.

188

189 A different behavior is found when the TOC vs. time plot is studied (part b of Fig. 1).  
190 As it can be observed, no mineralization is attained by single sonolysis or photolysis  
191 processes. This result indicates that the slight degradation of progesterone is due only to

192 the break-up of the molecule into intermediates and no mineralization at all is achieved,  
193 meaning that degradation of intermediates is prevented. Hence, soft oxidation  
194 conditions are obtained with the single application of both irradiation technologies.  
195 Opposite, single CDEO obtains an efficient mineralization, although the rate is  
196 significantly improved when UV or US are irradiated simultaneously with the  
197 electrolysis. Again the enhancement is attained from the start up in the CDPEO, and  
198 only after 200 minutes of electrolysis in the case of CDSEO. Contrary to what it could  
199 be expected, the combined action of UV and US irradiation on electrolysis does not  
200 further improve but even make lower the rate of the pollutant mineralization with  
201 respect to CDPEO or CDSEO. This is interesting because this combined irradiation of  
202 the electrolytic technology did not show this clear negative effect on the removal of the  
203 raw progesterone, meaning that it should be related to the destruction of more oxidized  
204 intermediates such as carboxylic acids, in which the effect of many oxidants on their  
205 removal should be smaller.

206

207 Experimental results shown in Fig. 1 clearly fit straight lines meaning that they can be  
208 modeled with a first order kinetic approach, regardless of the treatment technology. For  
209 UV and US irradiation, this is a typical model, and the kinetic constants depend on the  
210 energy irradiated. In electrolytic processes, this type of model could be easily explained  
211 in terms of a mass transfer control of the rate (Eq. 1) and/or in terms of a pseudo steady  
212 state concentration of oxidants produced in the bulk (Eq. 2), for direct or mediated  
213 electrochemical processes, respectively. This approach has been proposed and applied  
214 successfully in previous works for CDEO of POPs [37, 40].

215 
$$r = k_m \cdot A \cdot [\text{Pollutant}] = K [\text{Pollutant}] \quad (1)$$

216 
$$r = k' [\text{Oxidant agents}][\text{Pollutant}] = K [\text{Pollutant}] \quad (2)$$

217

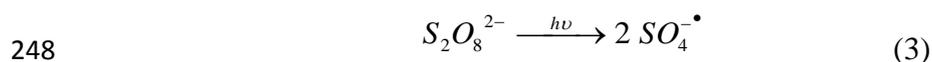
218 Taking into account this model approach, Fig. 2 shows the first order kinetic constants  
219 calculated in terms of TOC for the experiments shown in Fig. 1. This Figure also  
220 compares these values with the values calculated by the addition of the different single  
221 contributions. Synergistic effects of irradiating UV light and US are clearly observed,  
222 because the effect of the combination is greater than the addition of the effects of the  
223 single technologies. This synergistic effect is much lower for the case of the combined  
224 UV+US irradiation as it was pointed before, but it is still over the value of the addition  
225 obtained with the single processes. Hence, from the viewpoint of reaction rate,  
226 irradiations of UV or US have a clear positive effect on results, although this does not  
227 mean a greater efficiency and a direct recommendation of applicability.

228

229 To account for the efficiency is important to consider the energy supplied with the  
230 different technologies and, in this point, differences are very important. Thus, power  
231 dosed with the electrochemical cell in the CDEO of Fig. 1 is around 11.8 W (current  
232 intensity 2.36 A, cell voltage 5.0 V), power irradiated with the US horn is 200 W and  
233 power irradiated with the lamp is 4 W. Effect of UV light irradiation on rate is even  
234 higher than that of US irradiation, even taking into account that US irradiation  
235 consumes 50 times more energy. This means that CDSEO and CDSPEO should not be  
236 recommended at this point, at least with such a great energy application. On the contrary,  
237 the increase in the demand of energy of the CDPEO process with respect to the CDEO  
238 is only of 33% and it attains an improvement in the rate of mineralization of 77%, being  
239 a really synergistic process, not only from the improvement of rate but also from the  
240 energy point of view.

241

242 Regarding mechanisms related to the improvement found in CDPEO, they should be  
243 related to the activation of oxidants produced in the electrolytic process as pointed out  
244 before. CDEO of wastes containing sulfates is known to produce persulfates and, light  
245 irradiation is known to promote the production of sulfate radical from persulfate (Eq. 3)  
246 [41, 42]. This activation enhances process reaction rate because the sulfate radical reacts  
247 typically  $10^3$ – $10^5$  times faster than the anion persulfate [43].



249 In addition, other oxidants are known to be produced and activated by UV-light  
250 irradiation and it is particularly important the production of hydroxyl radicals. Eqs. 4  
251 and 5 show two of the main reactions involved in these mechanisms [44].

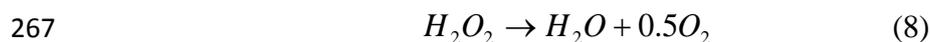


254 Opposite to single electrolytic process, the effect of these radicals can be extended to  
255 the bulk in a photoelectrolytic process, because in spite of their short lifetime, they are  
256 produced not on the anodic surface but in the bulk by decomposition of more stable  
257 oxidants. Its activity can account for the improvement observed in the CDPEO.

258

259 When the ultrasound horn and the ultraviolet-light lamp are used together with the  
260 electrolysis, the degradation of progesterone by CDSPEO is improved in respect of  
261 CDSEO but not in respect of CDPEO. This behavior might be explained, according to  
262 eqs. 6-9, in terms of an excessive formation of radicals which instead of attacking  
263 organic species, combine among them to form more stable and less aggressive oxidants  
264 which have a smaller oxidation capability and can decompose forming oxygen.





269

270 Regarding intermediates found during the oxidation of progesterone, CDEO behaves as  
271 a cold incineration process for concentrations as low as those used in this work [37] and  
272 intermediates are present in very small concentrations and almost negligible if  
273 compared with the 100 mg dm<sup>-3</sup> of progesterone contained in the raw synthetic  
274 wastewater. In fact, only 2-hydroxypropyl-β-cyclodextrin was measured in significant  
275 concentration, and this species is not an actual intermediate but an additive of  
276 progesterone to increase its water solubility.

277

278 Taking into account this, Fig. 3 compares the maximum concentration measured of  
279 these compounds for each technology in respect of the chromatographic area found for  
280 CDSEO, process where these areas were lower. The main intermediates found by HPLC  
281 are 2-hydroxypropyl-β-cyclodextrin and oxalic and formic carboxylic acids. Comparing  
282 technologies, only 2-hydroxypropyl-β-cyclodextrin appears in all treatments (but it is  
283 not an intermediate) and maximum concentration of the other intermediates monitored  
284 is very low. Carboxylic acids are only measured for the CDPEO because in the single  
285 sonolysis and photolysis, oxidation progress is not large enough to attain them (nil  
286 mineralization). In single CDEO, these intermediates should be completely depleted in  
287 the nearness of the electrode surface. In CDPEO it is expected a bulk oxidation and this  
288 reflects in the presence of these highly oxidized intermediates. The non detection of  
289 these carboxylic acids in CDSEO suggests that this technology does not favor bulk  
290 radical reactions in the experimental conditions used, but only improvements in mass

291 transfer of pollutants (hence carboxylic acids formed are depleted in the nearness of the  
292 electrode surface, as in single CDEO, and not measured in the bulk).

293

294 Coming back to CDSEO, it was clear that US irradiation improves the rate of the  
295 degradation of progesterone and TOC by CDEO, but energy required to attain this  
296 enhancement was too much high, especially if compared to that applied in the CDPEO  
297 device to get a better performance. These results advice against the application of  
298 CDSEO. In order to assess if the same effect could be obtained with less US-energy  
299 irradiated, two strategies were assessed:

- 300 • Decrease in the amplitude of the UV wave (energy dosed with US irradiation is  
301 related to the square of the amplitude of the US wave).
- 302 • Decrease in the period of application of ultrasounds (energy dosed is directly  
303 related to the US emission time, and can be diminished using a pulse input).

304

305 Fig. 4 shows the changes in concentration of progesterone and TOC during CDSEO  
306 experiments carried out with an initial concentration of pollutant of  $100 \text{ mg dm}^{-3}$ , a  
307 current density of  $30 \text{ mA cm}^{-2}$  and using  $\text{Na}_2\text{SO}_4$  as supporting electrolyte (0.035 M).  
308 The experiments are made with values of emission mode of 0.5/ 1 (pulse or continuous)  
309 and power of 50/ 200 W in order to check the two strategies of energy minimization  
310 pointed out. As it can be observed, there is a clear influence of the US-energy irradiated  
311 on progesterone removal and mineralization. These differences are small during the  
312 initial stage of the electrolysis and they become greater at longer reaction times when  
313 concentration of pollutants decreases, suggesting the clear role of US irradiation in the  
314 improvement of mass transfer of pollutants to the electrode surface [18-20, 23, 24].

315

316 Regarding the two strategies used to decrease the energy irradiated, a clear effect of  
317 emission period and amplitude of ultrasound is seen when the different experiments are  
318 carried out, although it does not correlate directly with the energy dosed in every case.  
319 As expected, the higher reaction rates are achieved with the higher values of these  
320 parameters when the emission time or the amplitude is kept constant (only one pure  
321 strategy is applied). Thus, CDSEO with emission mode of 0.5 (pulse signal with half of  
322 the time emitting US and hence dosing 100 W) performs worse than with emission  
323 mode of 1 (continuous emission of US and hence dosing 200 W). Likewise, CDSEO  
324 experiment in which US amplitude decrease by a half (energy dosed 50 W) gets worse  
325 results than that obtained in the base experiment (energy dosed 200 W).

326

327 The interesting point comes when the comparison is made in terms of the strategy. As it  
328 can be observed, it is more interesting to decrease the amplitude of the US than to use  
329 pulsed inputs (and hence to decrease the emission periods). Thus, progesterone  
330 degradation and mineralization are more effective in terms of rate when applying 50 W  
331 of continuous signal than when applying 100 W of pulsed-US. This might be explained  
332 in terms of a negative effect on the promotion of turbulence of the interruption in the  
333 emission of US and maybe because of prevention in the formation of radicals by US  
334 irradiation. At this point, it is interesting to take into account that single sonolysis  
335 produced a decrease in the progesterone concentration and it could only be explained in  
336 terms of this oxidation mechanism.

337

338 Regarding intermediates found in CDSEO, only 2-hydroxypropyl- $\beta$ -cyclodextrin (that it  
339 is not a real intermediate but a raw matter associated to the pollutant) was detected in  
340 appreciable concentrations. Fig. 5 compares the values with respect to those obtained in

341 the CDSEO with continuous mode and 200 W, experiment where cyclodextrin is found  
342 at the lowest concentration. Comparing the different technologies, it is clear the positive  
343 effect of US irradiation in CDSEO and also the negative effect of a pulsed mode,  
344 because the cyclodextrin remains in higher concentrations under these conditions. No  
345 carboxylic acids or any other intermediates are detected. This observation supports our  
346 previous discussion and suggests that US irradiated mainly affects to the mass transfer  
347 and that carboxylic acids formed may be rapidly depleted in the nearness of the  
348 electrode surface by the same electrolytic processes that occur in CDEO [37].

349

350 Finally, Fig. 6 shows the kinetic constant calculated in term of TOC for the different  
351 processes CDSEO experiments carried out. In terms of oxidation rate, the application of  
352 a pulsed US radiation seems to have an antagonist effect on the efficiency of the  
353 removal of progesterone, because the resulting rates are lower than those obtained by  
354 the addition of the rates of the two singles processes (sonolysis and CDEO). Opposite,  
355 when the US is continuously irradiated, there is a synergistic effect and resulting rates  
356 are much higher than that obtained by addition of single processes. In terms of energy,  
357 results are not positive, because an increase in the energy of  $50 \text{ w dm}^{-3}$  attains an  
358 improvement in the rate 4.76% while an increase of  $200 \text{ w dm}^{-3}$  obtains 20.24 %,  
359 meaning that enhancement ratio is kept (linear relationship), although at a very  
360 expensive price.

361

#### 362 **4. Conclusions**

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

364

- 365 - Single CDEO is able to attain efficient degradation of progesterone and  
366 mineralization. Single sonolysis and photolysis technologies only entail a slight  
367 removal of progesterone and nil mineralization.
- 368 - Synergistic effects of irradiating UV light and US are clearly observed in the  
369 oxidation rate, due to the improvement of mass transfer to the conductive-  
370 diamond surface in the case of CDSEO, and to the promotion of the formation of  
371 radicals in the bulk solution from oxidants produced electrochemically in the  
372 case of CDPEO.
- 373 - Energy required to attain a significant improvement in the oxidation rate with  
374 CDSEO and CDSPEO prevents against their application in the removal of  
375 progesterone from wastewater. On the contrary, CDPEO is a really synergistic  
376 process, not only from the improvement of rate but also from the energy point of  
377 view.
- 378 - Application of a pulsed US radiation shows an antagonist effect on the  
379 efficiency of the removal of progesterone just the opposite that the effect  
380 obtained with continuously irradiation. Improvements with US irradiation  
381 depend linearly on the energy irradiated.

382

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387

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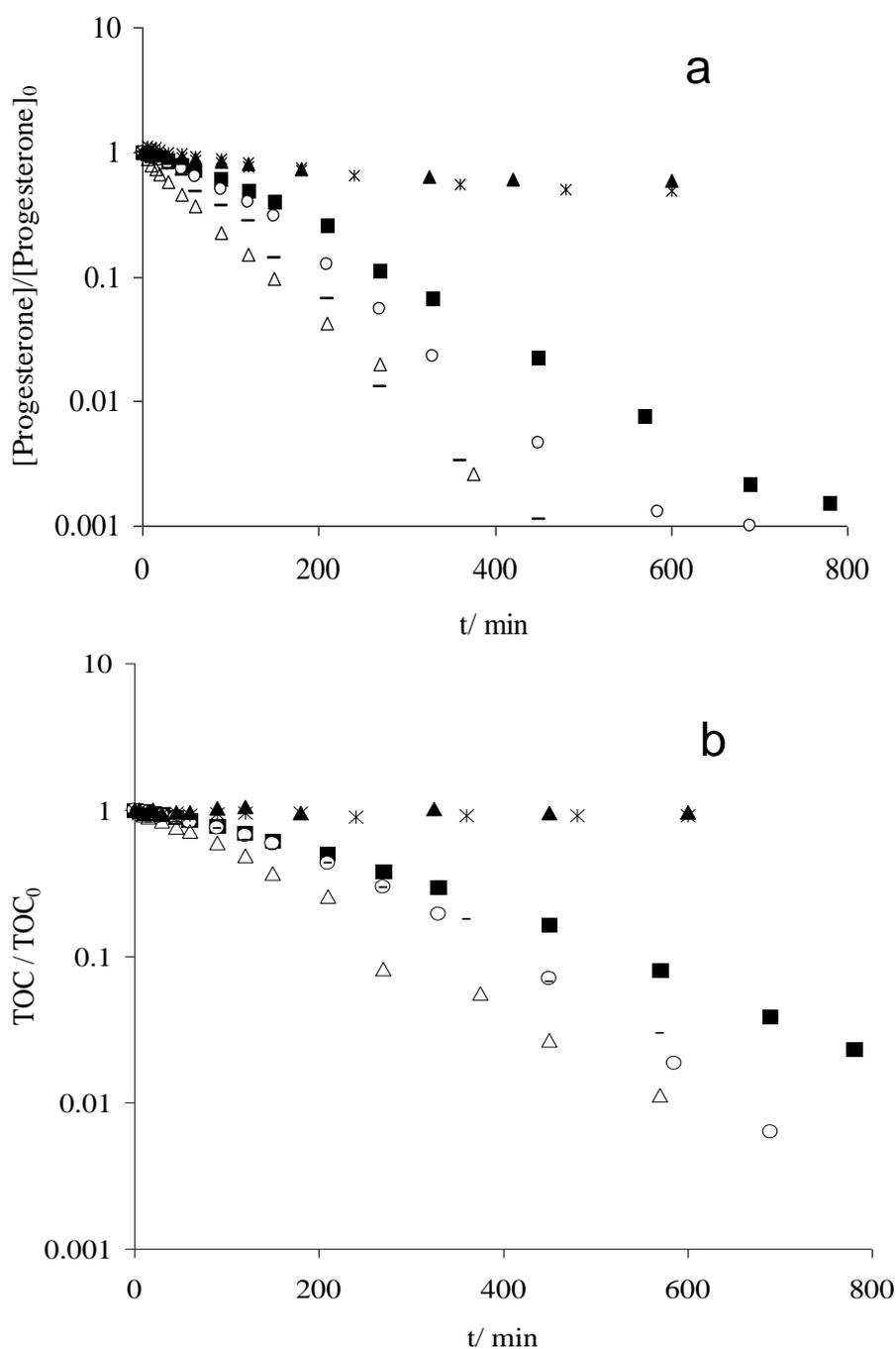
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534 **Figure**

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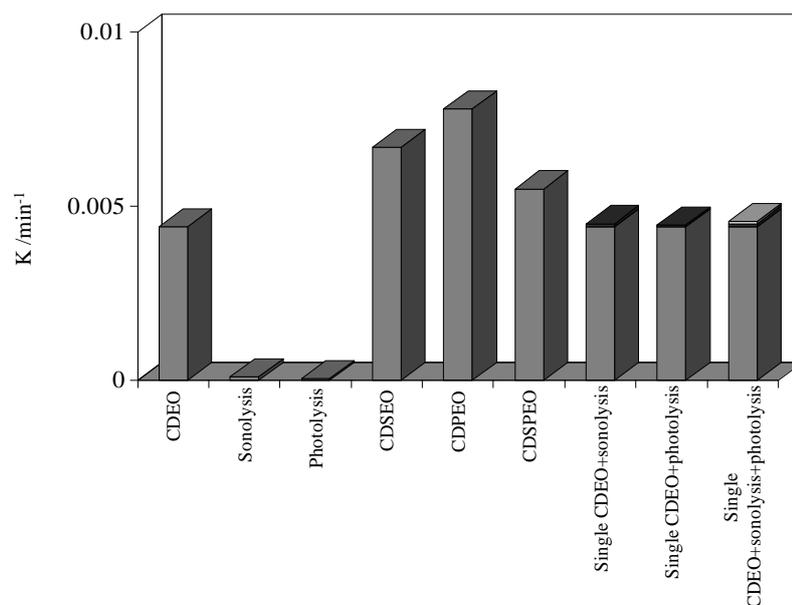
536

537 **Figure 1.** Progesterone concentration (a) and TOC (b) profiles for the experiments

538 carried out by CDEO (■), sonolysis (\*), photolysis (▲), CDSEO (○), CDPEO (Δ) and

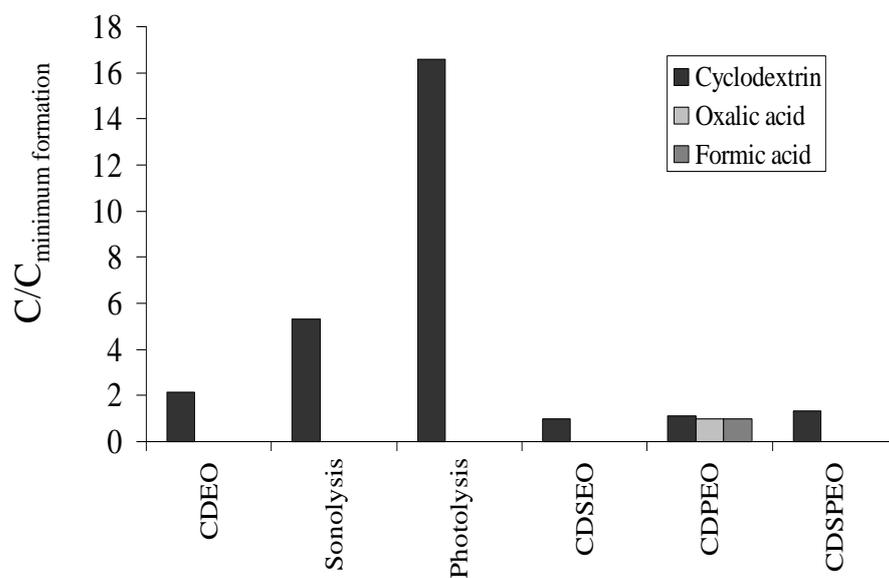
539 CDSPEO (-).  $[\text{Progesterone}]_0$ :  $100 \text{ mg dm}^{-3}$ ,  $j$ :  $30 \text{ mA cm}^{-2}$ ,  $0.035 \text{ M Na}_2\text{SO}_4$ .

540 Ultrasound wave: continuous mode/200 W. Ultraviolet light: 254 nm.



541

542 **Figure 2.** Kinetic constants calculated for the different processes and comparison with  
 543 the values calculated by the addition of the different single contributions.

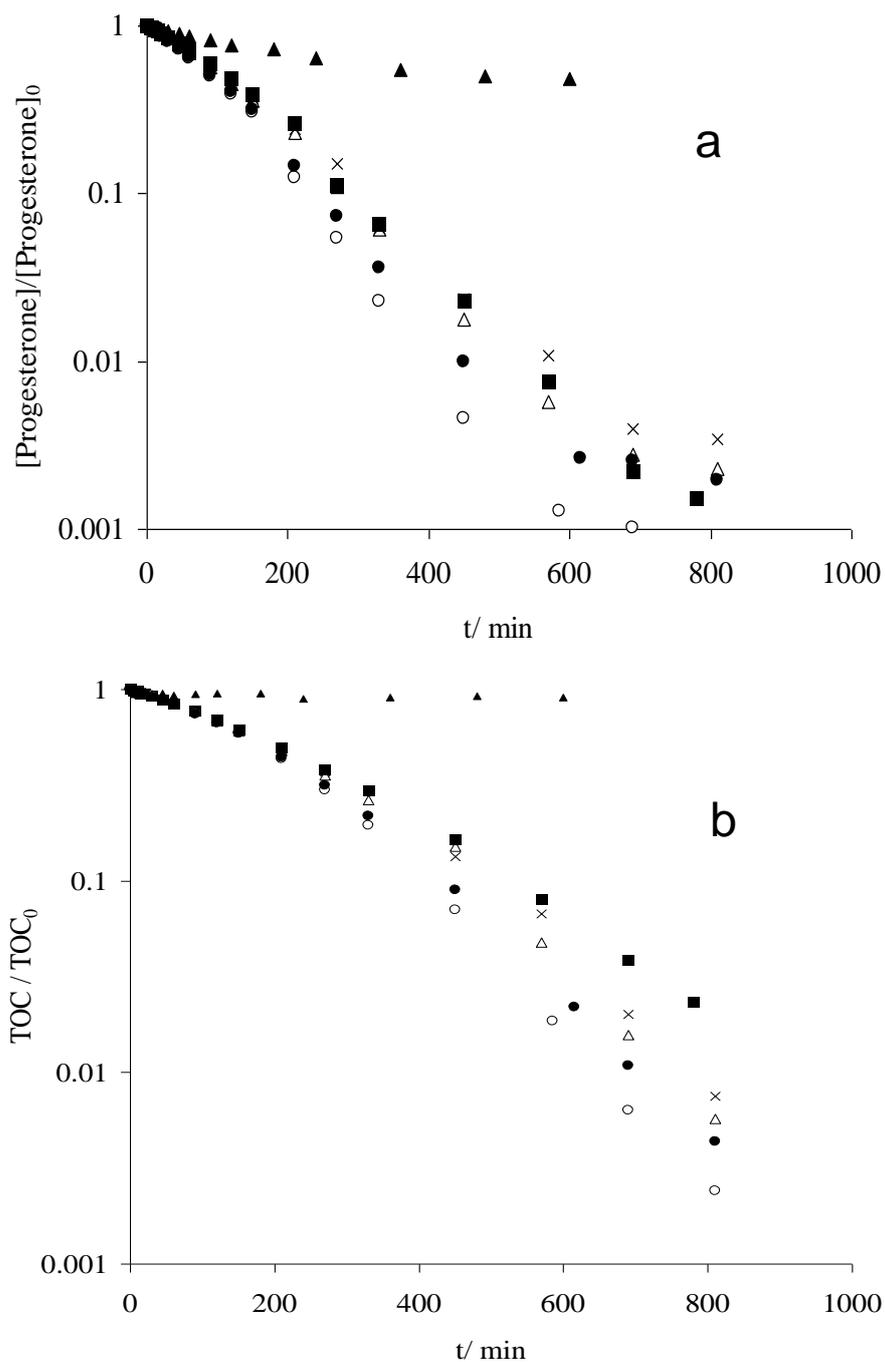


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545 **Figure 3.** Maximum concentration of reaction intermediates found for the different  
 546 studies in respect of the formation by sonoelectrolysis process. (■) 2-hydroxypropyl- $\beta$ -  
 547 cyclodextrin, (■) oxalic acid, (■) formic acid.

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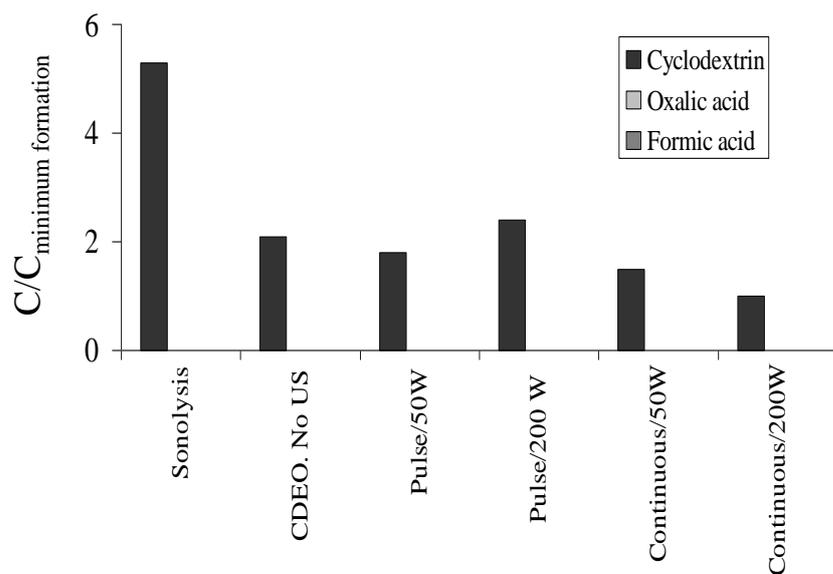


550

551 **Figure 4.** Influence of emission period and power of ultrasonic wave on the  
 552 progesterone (a) and TOC (b) removal profiles. ■ CDEO, without US, Emission  
 553 period/power: ○ continuous/200 W, △ pulse/200 W, ● continuous/50 W, □ pulse/50 W.  
 554 ( $[\text{Progesterone}]_0$ : 100 mg dm<sup>-3</sup>, j: 30 mA cm<sup>-2</sup>, 0.035 M Na<sub>2</sub>SO<sub>4</sub>).

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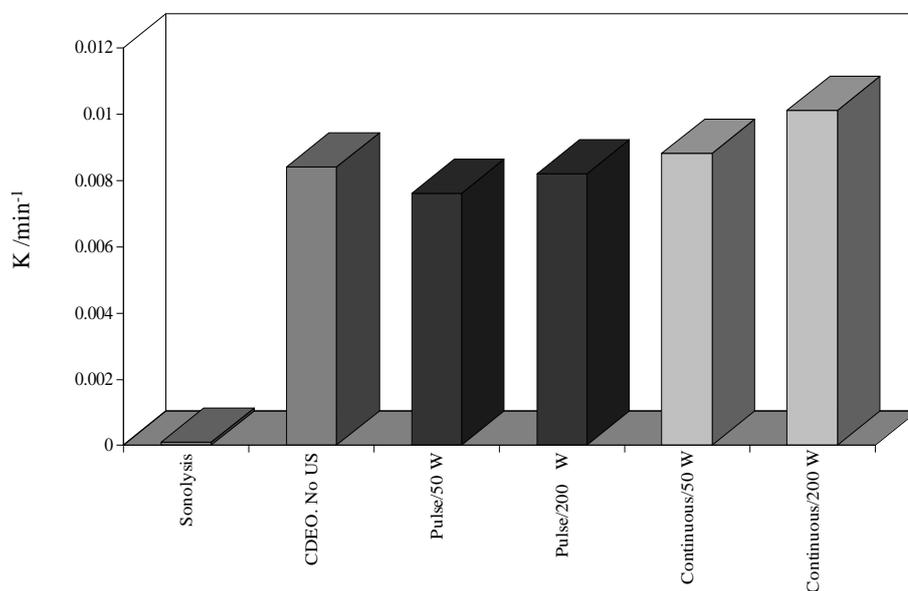
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558 **Figure 5.** Maximum concentration of intermediates compounds formed in the different  
 559 electrolysis processes with respect of the formation by continuous emission mode and  
 560 200 W. (■) 2-hydroxypropyl- $\beta$ -cyclodextrin, (□) oxalic acid, (▒) formic acid.

561



562

563 **Figure 6.** Kinetic constants calculated in term of TOC for the different ultrasound  
 564 processes.