

1 **Degradation of dye Procion Red MX-5B by electrolytic**
2 **and electro-irradiated technologies using diamond**
3 **electrodes**

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12 **Abstract**

13 This work focuses on the treatment of synthetic wastewater polluted with dye Procion
14 Red MX-5B by different electrochemical advanced oxidation processes based on
15 diamond anodes. The influence of the current density and the supporting electrolyte has
16 been studied on dye removal and total mineralization of the organic matter. Results
17 show that electrolysis with diamond electrodes is a suitable technology for an efficient
18 degradation of dye. Nonetheless, the process efficiency increases when using chloride
19 as supporting electrolyte because of the electrochemical generation of hypochlorite in
20 wastewater which significantly contribute to dye removal. Opposite to that, the total
21 mineralization of the organic matter is more efficient when working in sulfate media. In
22 this case, large amounts of peroxodisulfate are electrogenerated, favoring the complete
23 removal of total organic carbon (TOC). On the other hand, lower current densities (10

24 mA cm⁻²) lead to a more efficient removal of both dye and TOC due to the mass transfer
25 limitations of the technology. Finally, the coupling of UV light irradiation or ultrasound
26 to electrolysis significantly improves the process performance, being photoelectrolysis
27 the most efficient technology for the treatment of wastewater polluted with Procion Red
28 MX-5B. This fact is due to the potential production of free chlorine or sulfate radicals
29 that takes place by the activation of the electrogenerated oxidants. These species are
30 more reactive than oxidants and, therefore, they quickly attack to the organic matter
31 present in wastewater.

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33

34 **Keywords:** diamond, dye, electrolysis, photoelectrolysis, sonoelectrolysis.

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38 **Highlights**

- 39 - Procion Red MX-5B can be completely removed by EAOPs based on diamond
40 electrodes.
- 41 - Chlorine compounds in high oxidation state are generated in chloride media.
- 42 - Electroirradiated technologies improve the complete mineralization of dye.
- 43 - Free sulfate and chlorine radicals play a key role on the removal of dye and
44 TOC.
- 45 - Photoelectrolysis is the most efficient process for the Procion Red MX-5B
46 removal.

47 **1. Introduction.**

48 In last decades, the increased industrial activities in different sectors such as agriculture,
49 petroleum, textile, pharmaceutical... has caused an increase in the volume of industrial
50 wastewater ([Kolpin et al., 2002](#)). These wastewaters contain high concentration of
51 organic pollutants which are not possible to completely degraded by traditional
52 processes located in Wastewater Treatment Plants (WWTP). Hence, these pollutants are
53 considered as Persistent Organic Pollutants (POPs) ([Bueno et al., 2012](#)). One of the
54 industries that produces large amounts of wastewater polluted with POPs is textile.
55 Specifically, textile effluents contain high concentration of different types of reactive
56 dyes which are used to provide color in clothes ([Vandevivere et al., 1998](#); [O'Neill et al.,](#)
57 [1999](#)). These compounds are characterized by a large number of carbons in their
58 structure as aromatic rings. Likewise, dyes can also contain chlorine, sulfur or nitrogen
59 in their molecule. This last one forms azo groups where two nitrogen atoms are linked
60 to each other by a double bond and each one is linked to a carbon (C-N=N-C). For this
61 reason, they are commonly called azo dyes and depending on the number of N=N
62 bonds, they can be classified as monoazo, diazo, triazo...

63 Based on the above, dyes are hazardous compounds that should be removed from
64 wastewater before discharge to WWTP ([Alves de Lima et al., 2007](#)). Therefore, it is
65 necessary to develop clean and efficient technologies that guarantee the complete
66 removal of these pollutants. In this context, Electrochemical Advanced Oxidation
67 Processes (EAOPs) can be considered as a good alternative due to their high efficiencies
68 in the removal of other types of organic pollutants such as pharmaceuticals or pesticides
69 among others ([Rodrigo et al., 2014](#); [Sirés et al., 2014](#)). These technologies are based on
70 the production of large amounts of hydroxyl radicals, a powerful oxidant which
71 significantly contribute to the degradation of the organic matter. Among EAOPs,

72 electroFenton has been successfully checked on the removal of different pollutants
73 (including dyes) by Brillas' and Oturan's groups. During this process, it is required the
74 addition of iron salts to promote Fenton's reaction with the electrogenerated hydrogen
75 peroxide over the cathode surface by oxygen reduction ([Brillas et al., 2009](#)). Likewise,
76 in order to favor the production of large amounts of hydrogen peroxide, pH solution
77 should be maintained around 3. Under these conditions, it has been recently reported the
78 complete removal and even the total mineralization of the organic matter of wastewater
79 polluted with different organics such as tetracaine ([Ridruejo et al., 2018](#)), naproxen
80 ([Coria et al., 2016](#)), fluometuron ([Diaw et al., 2017](#)) and dyes ([Panizza and Cerisola,
81 2009b](#)).

82 On the other hand, electrochemical oxidation with diamond electrodes is considered
83 another promising EAOP for the removal of a great variety of organic pollutants
84 ([Panizza and Cerisola, 2009a](#)). Diamond anodes present an excellent electrocatalytic
85 properties towards the production of large amounts of hydroxyl radicals by water
86 oxidation over its surface ([Marselli et al., 2003](#)). Likewise, this material allows to
87 generate other powerful oxidants from the electrolysis of the ions naturally contained in
88 wastewater which also contribute to the mineralization of the organic matter ([Cañizares
89 et al., 2009b](#)). For this reason, it is not necessary the addition of chemicals to improve
90 the process performance and, therefore, electrolysis with diamond anodes is especially
91 suitable for the treatment of wastewater polluted with POPs. Nonetheless, the main
92 drawback of this technology is the mass transfer of the pollutant to the anode surface
93 ([Coñizares et al., 2006](#); [Bebelis et al., 2013](#)). In this context, the application of
94 ultrasound to electrolysis (sonoelectrolysis) can promote the mass transfer in the
95 system, favoring the degradation of the organics present in wastewater. In addition,
96 ultrasound can encourage the production of free radicals from water sonolysis when

97 working with high frequencies. These radicals also contribute to the degradation of the
98 organic matter and, therefore, enhance the electrochemical treatment ([Adewuyi, 2005](#);
99 [Almazán-Sánchez et al., 2017](#); [Cotillas et al., 2018](#)). Likewise, the irradiation of UV
100 light to electrolysis (photoelectrolysis) favors the potential production of free radicals
101 from the photo-activation of the oxidants present in wastewater ([Cotillas et al., 2016](#);
102 [Rubí-Juárez et al., 2016](#)). Therefore, both technologies (ultrasound and UV light
103 irradiation) enhance the removal rate of electrolysis with diamond electrodes ([Martínez-
104 Huitle et al., 2015](#)).

105 With this background, the main aim of the present work is to study the removal of
106 Procion Red MX-5B as model of dye by electrolysis, photoelectrolysis and
107 sonoelectrolysis using diamond anodes. This compound has been selected because it is
108 one of the most dyes used in textile industry. The influence of the current density (10-
109 100 mA cm⁻²) and the supporting electrolyte (Na₂SO₄; NaCl) has been checked because
110 these parameters significantly affect the process efficiency ([Araújo et al., 2015b](#)).

111

112 **2. Material and methods.**

113 **2.1. Chemicals.**

114 Procion Red MX-5B (C₁₉H₁₀Cl₂N₆Na₂O₇S₂, dye content 40 %), sodium sulfate and
115 sodium chloride (Sigma Aldrich) were analytical grade and use as received. Double
116 deionized water (Millipore Milli-Q system, resistivity: 18.2MΩcm at 25°C) was used to
117 prepare all solutions.

118 **2.2. Analytical techniques.**

119 The concentration of Procion Red MX-5B (PR) was followed by spectrophotometry
120 using a Cary Series UV-Vis Spectrophotometer (Agilent Technologies) at 538 nm. TOC

121 concentration was monitored using a TOC concentration was monitored using a Multi
122 N/C 3100 Analytik Jena analyzer. The concentration of hypochlorite was determined by
123 titration with 0.001 M As_2O_3 in 2 M NaOH ([Wilpert, 1957](#); [Freytag, 1959](#)). Chlorate
124 and perchlorate were measured by ion chromatography (Metrohm 930 Compact IC
125 Flex) coupled to a conductivity detector. A Metrosep A Supp 7 column was used and
126 the mobile phase consisting of 85:15 v/v 3.6 mM Na_2CO_3 /acetone with a flow rate of
127 $0.8 \text{ cm}^3 \text{ min}^{-1}$. Persulfate concentration was analyzed iodometrically according to
128 Kolthoff & Carr ([Kolthoff and Carr, 1953](#)) and also, spectrophotometrically according
129 to the procedure described by Liang et al. ([Liang et al., 2008](#)). pH and conductivity were
130 measured using a multiparameter analyzer SESSION+ MM150DL (Hach).

131 **2.3. Electrochemical cell.**

132 Electrolyses were carried out in a single compartment electrochemical flow cell. Boron
133 doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The
134 electrodes were circular with a geometric area of 78 cm^2 . The main characteristics of the
135 diamond electrode used in this work are: boron concentration of 500 mg dm^{-3} , a
136 thickness of $2.62 \text{ }\mu\text{m}$, sp^3/sp^2 ratio of 206 and p-Si as support. The electrode gap
137 between anode and cathode was 5 mm and, the electric current was provided by a Delta
138 Elektronika ES030-10 power supply (0-30 V, 0-10 A). Photoelectrolyses were carried
139 out by using an UVG ERG-11 lamp (Baquias Cabre i Berga, S.L.) and an Epoch 650
140 ultrasound horn (Olympus) was used during sonoelectrolyses. Both devices were
141 introduced in the bulk solution during the treatment. The UV lamp irradiated 4 W
142 whereas the ultrasound horn emitted 10 MHz and a power of 200 W. Wastewater was
143 stored in a glass tank (1 dm^3). Synthetic wastewater consisted of a solution containing
144 100 mg dm^{-3} of dye and $3,000 \text{ mg dm}^{-3}$ of supporting electrolyte (Na_2SO_4 or NaCl). All
145 experiments (1 dm^3) were carried out under galvanostatic conditions and discontinuous

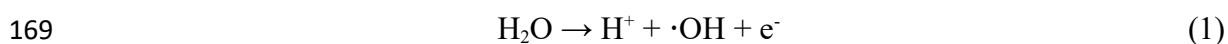
146 mode. The current density applied ranged from 10 to 100 mA cm⁻² and the temperature
147 was maintained at 25°C.

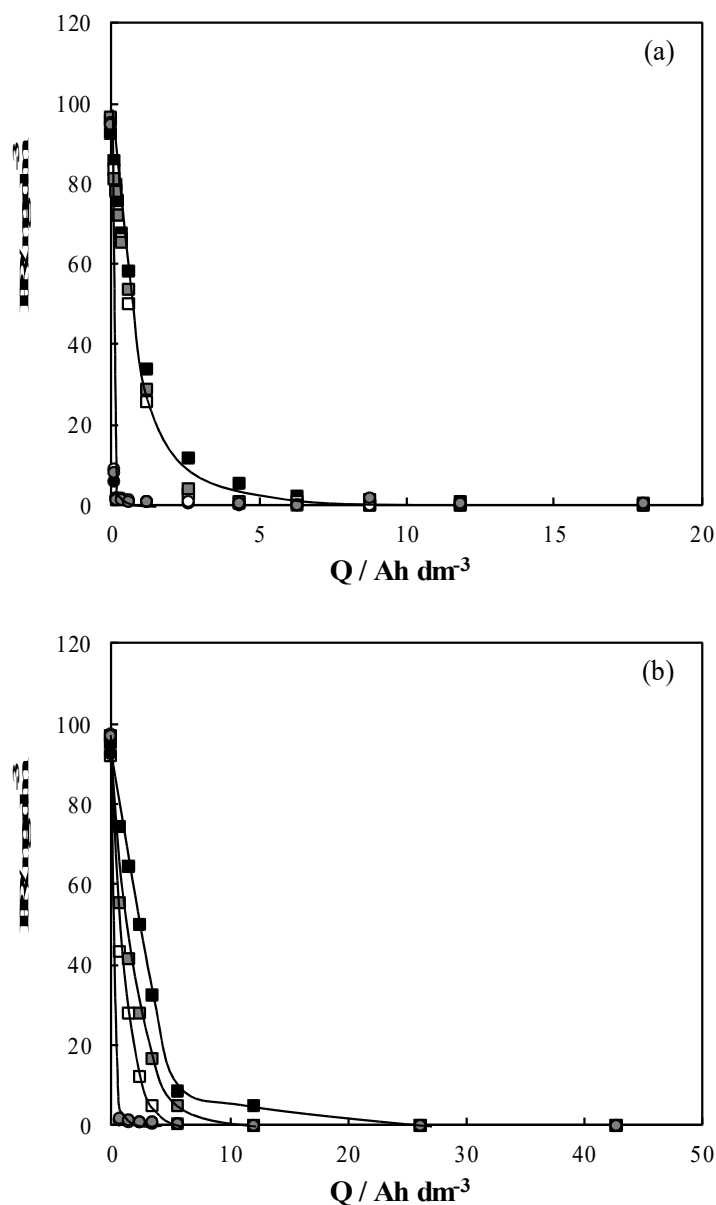
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149 **3. Results and discussion.**

150 Figure 1 shows changes in Procion Red MX-5B concentration during the electrolysis,
151 photoelectrolysis and sonoelectrolysis of synthetic wastewater polluted with 100 mg
152 dm⁻³ of dye at different current densities. Sulfate and chloride were used as supporting
153 electrolytes.

154 As can be observed, the concentration of dye decreases with the applied electric charge
155 for all the tests carried out, regardless the current density and the supporting electrolyte.
156 However, the process efficiency is clearly influenced by these parameters. In this
157 context, the use of low current densities (Figure 1a) requires applied electric charges
158 lower than 15 Ah dm⁻³ to attain a complete removal of the dye whereas values higher
159 than 20 Ah dm⁻³ are needed for a total depletion of the pollutant at 100 mA cm⁻² (Figure
160 1b). This behavior is most remarkable during the electrolysis in sulfate media and it is
161 related to mass transfer limitations of the pollutant to the anode surface (direct
162 electrolysis) and the production of large amounts of hydroxyl radicals from water
163 oxidation at higher current densities (Eq. (1)). These species present a high oxidant
164 capacity and they can attack to the organic matter present in the effluent, favoring its
165 complete degradation (indirect electrolysis). Nonetheless, these electrogenerated
166 hydroxyl radicals can be also wasted in other secondary reactions during the treatment,
167 decreasing the process efficiency in terms of pollutant removal at 100 mA cm⁻² ([Panizza](#)
168 [and Cerisola, 2005](#)).



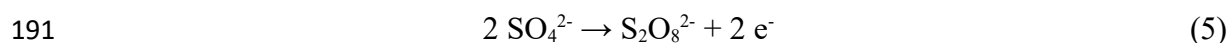
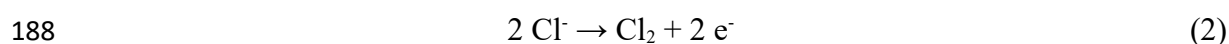


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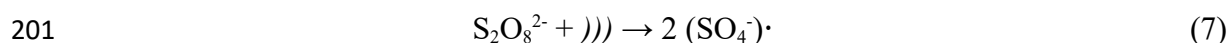
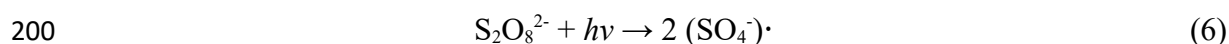
171 **Figure 1.** Dye decay as function of the applied electric charge during the electrolysis
 172 (E), photoelectrolysis (PE) and sono-electrolysis (SE) of synthetic wastewater containing
 173 100 mg dm^{-3} of Procion Red MX-5B and $3,000 \text{ mg dm}^{-3}$ of supporting electrolyte. Black
 174 points: E; white points: PE; grey points: SE. ($\blacksquare, \square, \blacksquare$) Na_2SO_4 ; (\bullet, \circ, \bullet) NaCl ; $\text{UV}_{254 \text{ nm}}$: 4
 175 W; US: 200 W; (a) j : 10 mA cm^{-2} ; (b) j : 100 mA cm^{-2} .

176 Regarding the influence of the supporting electrolyte, the removal rate of Procion Red
 177 MX-5B is higher when using chloride salts. This fact is related to the potential

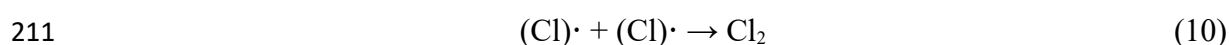
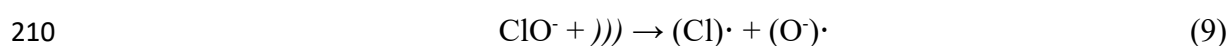
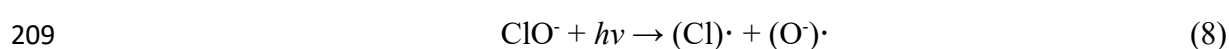
178 production of hypochlorite from the electrooxidation of chloride which significantly
 179 contribute to the removal of the pollutant (Eqs. (2)-(4)) ([Brillas and Martínez-Huitle,](#)
 180 [2015](#)). Likewise, sulfate can be oxidized during the treatment with BDD anodes,
 181 favoring the generation of peroxodisulfate (Eq. (5)) ([Serrano et al., 2002](#)). Both
 182 compounds are powerful oxidants which contribute to the degradation of Procion Red
 183 MX-5B. However, the potential required for the generation of active chlorine is lower
 184 than that needed for peroxodisulfate (1.36 vs. 2.07 V SHE). For this reason, large
 185 amounts of hypochlorite can be generated in comparison with the concentration of
 186 peroxodisulfate in wastewater and, therefore, the process efficiency increases when
 187 working in chloride media ([Cañizares et al., 2009a](#)).



192 On the other hand, the coupling of UV light or ultrasound to electrolysis improves the
 193 removal of dye in sulfate media. Specifically, the process efficiency is higher during the
 194 photoelectrolysis followed by sonoelectrolysis and, finally, electrolysis. This fact is
 195 mainly due to the photo- and sono-activation of the electrogenerated oxidants during the
 196 treatment. In this context, peroxodisulfate can be activated promoting the generation of
 197 free sulfate radicals (Eqs. (6)-(7)) ([Araújo et al., 2015a](#); [Almazán-Sánchez et al., 2017](#)).
 198 These species are known to be more efficient several log units than peroxodisulfate for
 199 the removal of pollutants ([Mercado et al., 2018](#)).



202 In the case of chloride media, similar behaviors are observed for all the studied
203 technologies at different current densities. Nonetheless, the electrogenerated
204 hypochlorite can be also activated during the process favoring the production of free
205 chlorine radicals (Eq. (8)-(9)), even though they do not seem a great influence on dye
206 removal. These results suggest that chlorine radicals are rapidly recombined, favoring
207 the production of chlorine gas (Eq. (10)) and, therefore, a potential generation of
208 hypochlorite (Eqs. (3)-(4)).



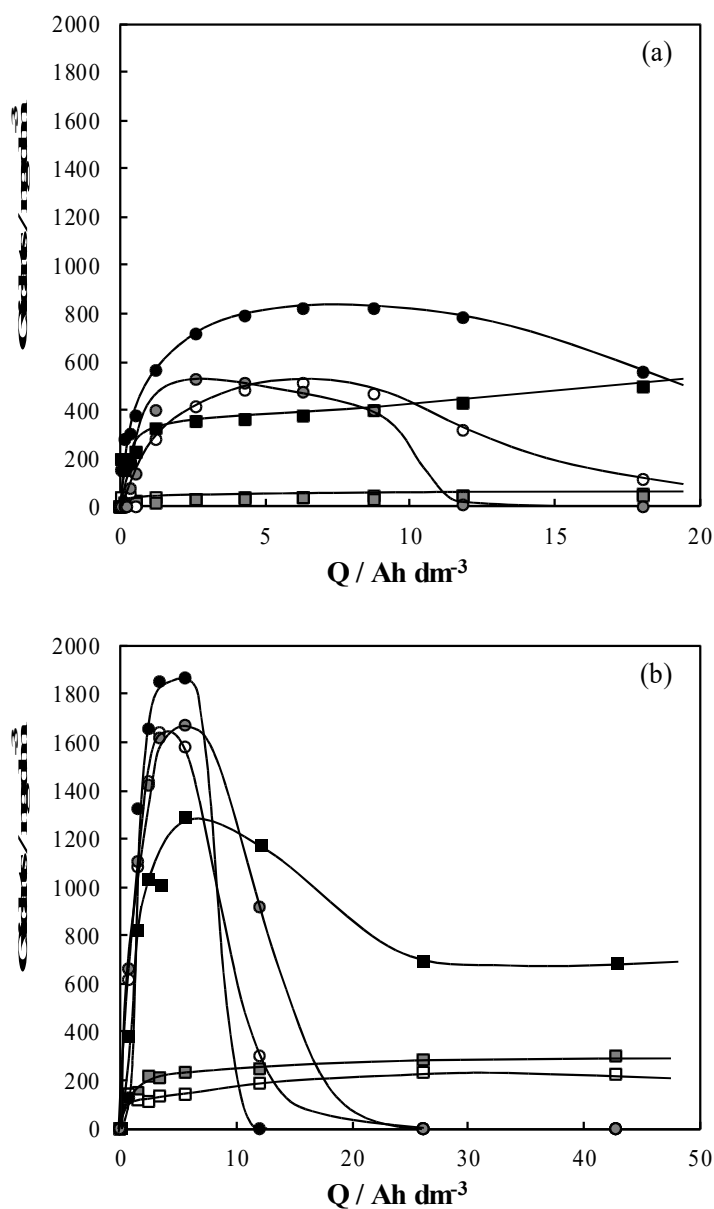
212 Figure 2 shows the concentration of oxidants electrogenerated during the removal of
213 Procion Red MX-5B at different current densities. It is important to point out that the
214 real concentration of these species is higher in the bulk, but they are continuously
215 reacting in the system. Hence, the measured concentration is referred to oxidants that
216 have not reacted yet.

217 As expected, the concentration of these species increases with the applied electric
218 charge during the electro-, photoelectro- and sonoelectrolysis of the dye. Once again,
219 different behaviors can be seen depending on the current density and the electrolyte.
220 The amount of electrogenerated oxidants is lower when working at 10 mA cm^{-2} ,
221 regardless the electrolyte used (Figure 2a). This fact is related to the different
222 mechanisms that take place during the production of oxidants by electrolysis with BDD
223 anodes ([Cañizares et al., 2007](#)). In this context, hypochlorite and peroxodisulfate are
224 mainly generated by the direct oxidation of chloride (Eqs. (2)-(4)) and sulfate (Eq. (5))
225 over the anode surface under these conditions (10 mA cm^{-2}). On the other hand, large

226 amounts of hydroxyl radicals are produced when working at 100 mA cm⁻². These
227 species not only attack to the organic matter present in the effluent but also react with
228 the anions contained in wastewater, favoring the generation of oxidants such as,
229 hypochlorite (Eq. (11)) and peroxodisulfate (Eq. (12)). For this reason, the
230 concentration of electrogenerated oxidants is higher at 100 mA cm⁻² (Figure 2b) since
231 these species can be produced by two mechanisms simultaneously: direct and mediated
232 electrolysis.



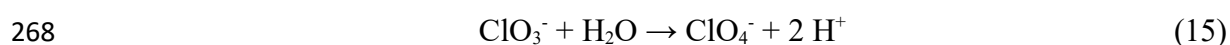
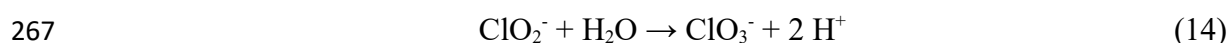
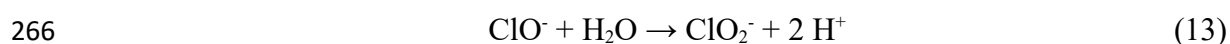
235 The maximum concentration of peroxodisulfate is lower than that obtained for
236 hypochlorite. This fact is related to the potential required for the generation of each
237 oxidant, as previously commented. Likewise, it is well known that the life-time of
238 peroxodisulfate in wastewater containing organics is lower due to its higher reactivity
239 ([Cañizares et al., 2009a](#)). On the other hand, it is important to point out that the
240 irradiation of UV light or ultrasound leads to a lower production of oxidants during the
241 treatment when working at 10 mA cm⁻² (Figure 2a). These results agree the potential
242 production of free radicals (Eqs. (6)-(9)) that takes place during the electroirradiated
243 processes ([Almazán-Sánchez et al., 2017](#)). At higher current densities, there are no
244 significant differences in the production of hypochlorite whereas the concentration of
245 peroxodisulfate follows the same behavior than that observed at 10 mA cm⁻²: the use of
246 electroirradiated technologies favors the production of free sulfate radicals from the
247 activation of peroxodisulfate and, hence, the concentration of this species (S₂O₈²⁻) is
248 lower.



249

250 **Figure 2.** Influence of the current density on electrogenerated oxidants as function of
 251 the applied electric charge during the electrolysis (E), photoelectrolysis (PE) and
 252 sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm⁻³ of Procion Red
 253 MX-5B and 3,000 mg dm⁻³ of supporting electrolyte. Black points: E; white points: PE;
 254 grey points: SE. (■, □, ▴) S₂O₈²⁻; (●, ○, ●) ClO⁻; UV_{254 nm}: 4 W; US: 200 W; (a) j: 10 mA
 255 cm⁻²; (b) j: 100 mA cm⁻².

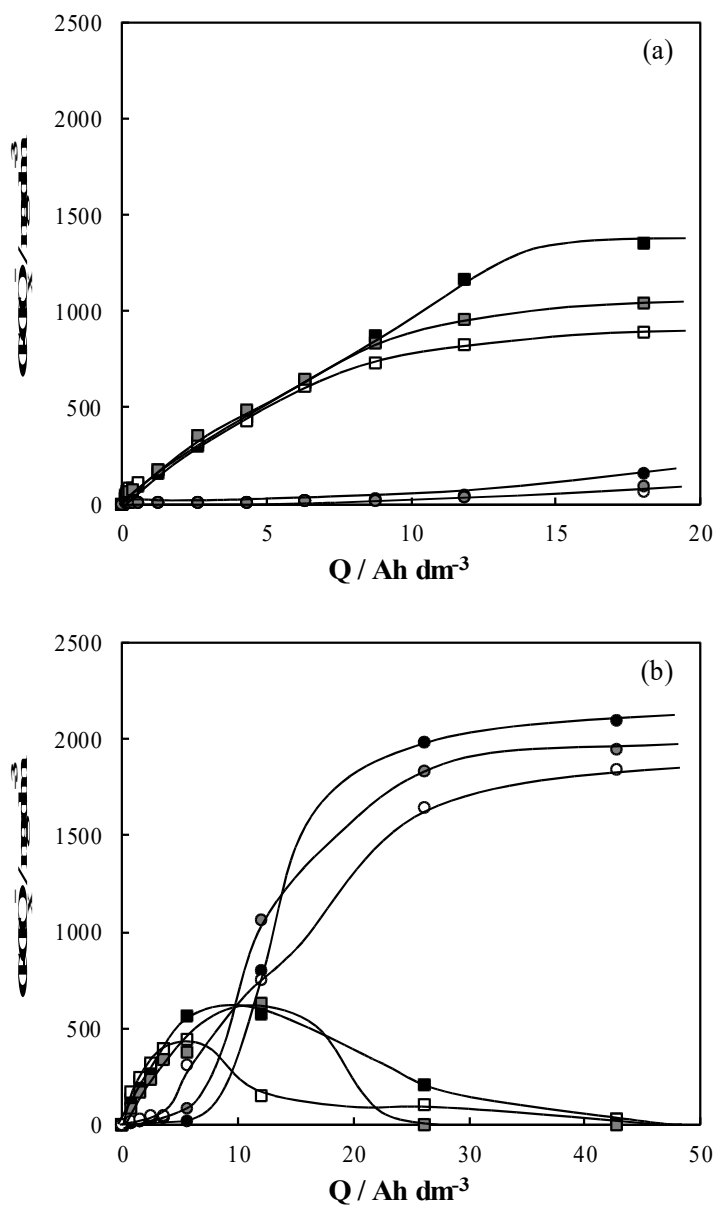
256 The last important comment is that the trend observed in peroxodisulfate concentration
 257 increases and remains constant at the end of the experiments whereas hypochlorite
 258 shows an increase followed by a decrease, reaching even zero values. In the first case
 259 (peroxodisulfate), this indicates that the generation and consumption rates of this
 260 species are similar during the process. However, the trend observed in hypochlorite can
 261 be due to the reaction between the organic matter and this compound, favoring the
 262 removal of dye; or to the evolution of hypochlorite to other chlorine compounds in high
 263 oxidation state. In this context, significant amounts of chlorate and perchlorate can be
 264 generated from the electrolysis of chlorides with BDD anodes (Eqs. (13)-(15))
 265 ([Sánchez-Carretero et al., 2011](#)).



269 Likewise, the presence of high concentrations of electrogenerated hydroxyl radicals can
 270 promote the production of chlorate and perchlorate in wastewater (Eqs. (16)-(18)).



274 Both species are toxic and harmful to human health and, therefore, their presence should
 275 be avoided in wastewater treatment. For this reason, the concentration of chlorate and
 276 perchlorate was monitored during the process. Figure 3 shows changes in the
 277 concentration of these species with the applied electric charge during the degradation of
 278 Procion Red MX-5B in chloride media by different technologies at 10 and 100 mA cm⁻².
 279 ².



280

281 **Figure 3.** Influence of the current density on chlorine speciation as function of the
 282 applied electric charge during the electrolysis (E), photoelectrolysis (PE) and
 283 sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm^{-3} of Procion Red
 284 MX-5B and $3,000 \text{ mg dm}^{-3}$ of NaCl. Black points: E; white points: PE; grey points: SE.
 285 (■, ■, □) ClO_3^- ; (●, ●, ○) ClO_4^- ; a) j : 10 mA cm^{-2} ; b) j : 100 mA cm^{-2} .

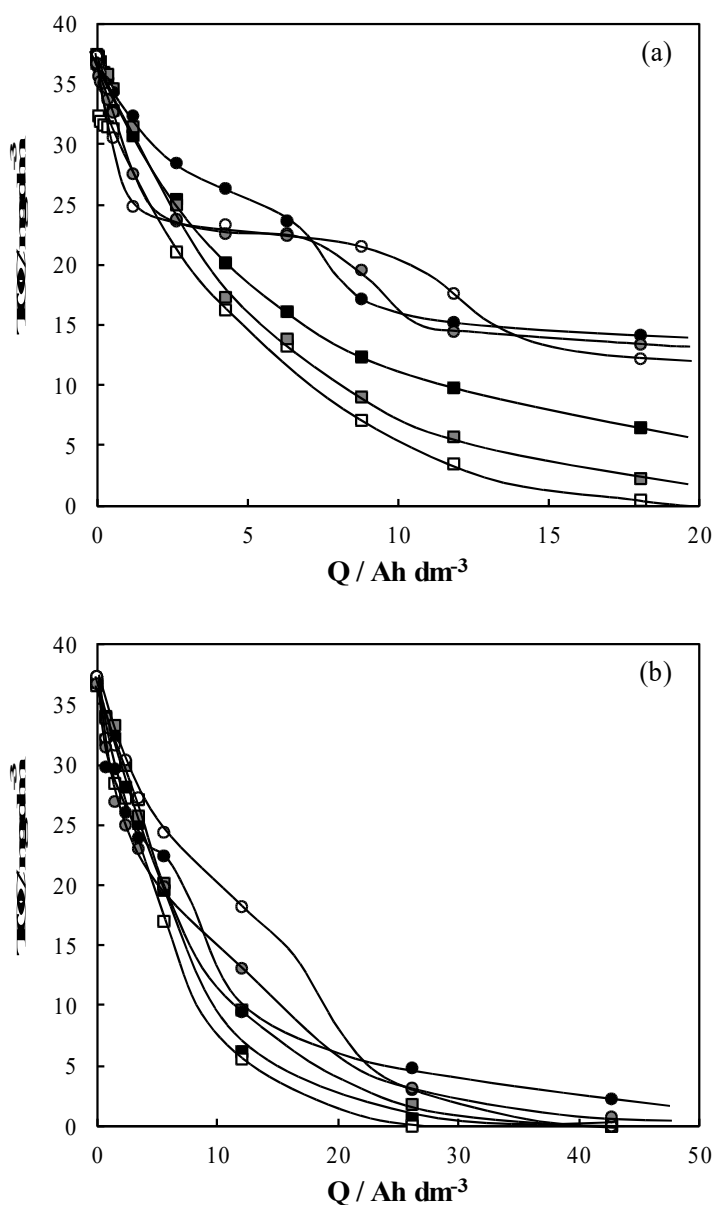
286 As can be observed, the concentration of both compounds increases with the applied
 287 electric charge, regardless the current density and the technology employed. At low

288 current densities (Figure 3a), chlorate is the predominant species in the system, reaching
289 final values higher than 1000 mg Cl dm⁻³ whereas the maximum concentration of
290 perchlorate is lower than 200 mg Cl dm⁻³. This is due to that the electrochemical
291 production of perchlorate is thermodynamically favored but not kinetically under these
292 conditions ([Sánchez-Carretero et al., 2011](#)). Opposite to that, chlorate shows an
293 intermediate profile and perchlorate is the final product when working at 100 mA cm⁻²
294 (Figure 3b). This fact is related to the large amounts of hydroxyl radicals that are
295 generated during the process at higher current densities, favoring the complete oxidation
296 of chlorides to perchlorate as final product.

297 On the other hand, it is important to highlight the influence of electroirradiated
298 technologies on chlorine speciation. As can be seen in Figure 3, the generation of
299 chlorate and perchlorate is less favored when UV light or US are coupled to electrolysis.
300 Specifically, the concentration of these oxoanions is lower during photoelectrolysis
301 followed by sonoelectrolysis and, finally electrolysis. The activation of hypochlorite to
302 produce free chlorine radicals seems to be the responsible mechanism why the
303 generation rate of these species is lower (Eqs. (8)-(9)). In this context, the promotion of
304 hypochlorite to chlorine radical competes with the electrochemical oxidation of
305 hypochlorite to chlorate and perchlorate, hindering the potential production of these
306 harmful species during the photo- and sonoelectrolysis of wastewater polluted with
307 Procion Red MX-5B. These results are highly important because reveal that the
308 coupling of UV light or US to electrolysis with BDD anodes could avoid the potential
309 generation of large amounts of chlorine compounds in high oxidation state during
310 wastewater treatment.

311 The electrolysis of synthetic wastewater polluted with Procion Red MX-5B can lead to
312 the formation of other intermediate organic compounds (even more hazardous than the

313 dye) or to the complete mineralization of the organic matter to carbon dioxide. To check
314 the possible formation of intermediates during the process, the concentration of total
315 organic carbon (TOC) was monitored. This parameter informs about the complete
316 mineralization of the organic matter present in wastewater and, therefore, it is an
317 indirect measure of the presence of intermediates in wastewater. Figure 4 shows the
318 evolution of TOC with the applied electric charge during the treatment of wastewater
319 polluted with Procion Red MX-5B at different current densities.



320

321 **Figure 4.** TOC decay as function of the applied electric charge during the electrolysis
322 (E), photoelectrolysis (PE) and sonoelectrolysis (SE) of synthetic wastewater containing
323 100 mg dm^{-3} of Procion Red MX-5B and $3,000 \text{ mg dm}^{-3}$ of supporting electrolyte. Black
324 points: E; white points: PE; grey points: SE. (■, □) Na_2SO_4 ; (●, ○) NaCl ; $\text{UV}_{254 \text{ nm}}$: 4
325 W; US: 200 W; a) j: 10 mA cm^{-2} ; b) j: 100 mA cm^{-2} .

326 As can be observed, TOC concentration decreases with the applied electric charge for
327 all the tests carried out. At low current densities (Figure 4a), photoelectrolysis shows the
328 lower TOC value at the end of the experiment in sulfate media and, therefore, the higher
329 efficiency for the mineralization of the organic matter contained in wastewater.
330 Specifically, a removal percentage of 99 % is attained under these conditions. These
331 results suggest that the generation of sulfate radicals from the photo-activation of
332 peroxodisulfate (Eq. (6)) favors not only the efficient removal of dye but also of all the
333 organics generated during the process. Likewise, sonoelectrolysis follows a similar
334 trend than that observed in TOC removal during photoelectrolysis. Nonetheless, in this
335 case, the final value registered is higher (removal percentage: 94 %). This fact can be
336 due to a lower efficiency in the production of free sulfate radicals by the application of
337 ultrasound. Finally, single electrolysis leads to the lowest efficiency in sulfate media for
338 TOC depletion, reaching a final removal of 83 %. This clearly reveals that the coupling
339 of UV light or ultrasound to electrolysis with BDD anodes significantly improves the
340 process performance in terms of both dye and TOC removal. On the other hand, final
341 TOC values are higher when working at 10 mA cm^{-2} in chloride media. Under these
342 conditions, it is not possible to attain a complete mineralization of the organic matter
343 and, hence, the production of organochlorinated intermediate compounds takes place
344 during the treatment. The trend observed indicates that there is an initial decrease
345 followed by a plateau zone and finally, the concentration decreases again. This behavior

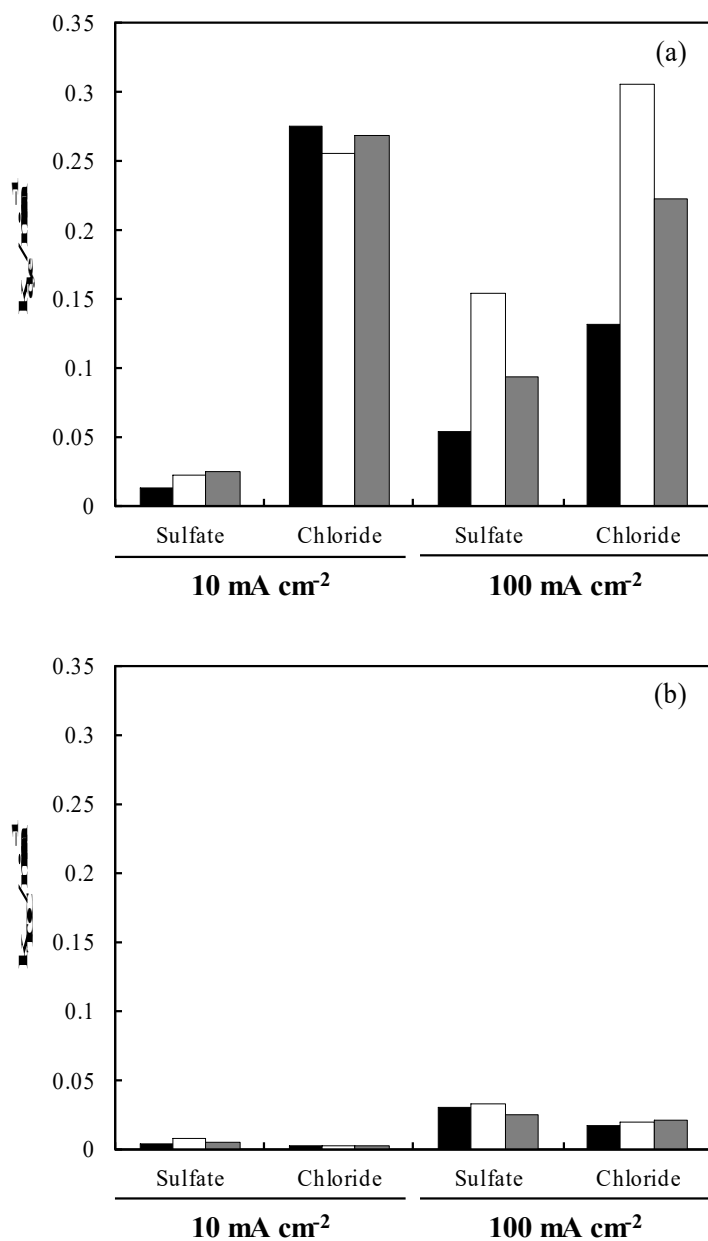
346 has been reported in literature and it is related to an accumulation of organochlorinated
347 compounds in wastewater which are more slowly degraded ([Cañizares et al., 2003](#)).
348 TOC removal efficiency is higher during photo- and sonoelectrolysis at the beginning of
349 the experiments. However, the final percentage removal is similar for all the
350 technologies studied (electrolysis: 61 %; photoelectrolysis: 67 %; sonoelectrolysis: 64
351 %). These results agree the previous obtained in dye removal (Figure 1a) where no
352 significant influence of electroirradiated technologies was observed.

353 Regarding TOC removal at 100 mA cm^{-2} (Figure 4b), it is possible to attain a complete
354 mineralization of the organic matter during all the technologies studied in sulfate media
355 and even, during photoelectrolysis when using chloride as supporting electrolyte. This
356 fact is due to the higher concentration of hydroxyl radicals electrogenerated which
357 contribute to the degradation of the organic matter present in wastewater. Likewise, as
358 pointed out before, hydroxyl radicals favor the production of large amounts of oxidants
359 during the electrolysis at 100 mA cm^{-2} and, hence, the concentration of free radicals also
360 increases during photo- and sonoelectrolysis. Both species (oxidants and radicals) attack
361 to the organic matter, improving the process performance in terms of TOC removal.
362 Photoelectrolysis is the most efficient process for the complete mineralization of the
363 organic matter, regardless the electrolyte used. These results reveal that the activation of
364 oxidants by UV light irradiation seems to be more efficient than by the application of
365 ultrasound. Nonetheless, the applied electric charge required to attain a complete TOC
366 removal is higher when working at 100 mA cm^{-2} in comparison with the results obtained
367 at 10 mA cm^{-2} . This behavior was also observed during the removal of dye (Figure 1).
368 Finally, the use of chloride as supporting electrolyte leads to the lowest efficiency in
369 TOC removal during electrolysis. Specifically, a percentage removal of 94 % is attained
370 whereas a 98 % is obtained during sonoelectrolysis and a total removal is reached when

371 coupling UV light and electrolysis. Therefore, the evolution of TOC during the
372 degradation of dye Procion Red MX-5B in chloride media clearly suggests that the
373 production of other organochlorinated compounds takes place during the process,
374 regardless the current density applied.

375 For comparison purposes, the results obtained in dye and TOC removal were fitted to a
376 first order kinetics model and removal rate constants were calculated. The values are
377 represented in Figure 5. As can be observed, the kinetic constants for dye removal
378 (Figure 5a) are higher than that obtained in the mineralization of the organic matter
379 (Figure 5b). This is an expected result taking into account that the degradation of dye is
380 faster than TOC depletion. Overall, photoelectrolysis is the fastest process for the
381 removal organic matter (dye and TOC) when working in sulfate media. Furthermore,
382 higher current densities significantly increase the values obtained for kinetic constants.
383 Hence, the degradation of Procion Red MX-5B is faster at 100 mA cm^{-2} despite the
384 process efficiency is higher at 10 mA cm^{-2} . This behavior has been previously reported
385 in literature and it indicates that the process is mainly controlled by mass transfer
386 ([Panizza and Cerisola, 2009a](#)).

387 In the case of chloride media, no remarkable differences are observed when working at
388 10 mA cm^{-2} . However, photoelectrolysis shows the highest kinetic constant for dye
389 removal followed by sonoelectrolysis at 100 mA cm^{-2} . Opposite to that, this last one
390 seems to be the fastest process for TOC removal under these conditions. These results
391 reveal that electroirradiated technologies lead to a more efficient and fast degradation of
392 organic matter than single electrolysis at higher current densities in chloride media.



393

394 **Figure 5.** Kinetic constants calculated for the removal of dye (a) and total organic
 395 carbon (b) as function of the current density and supporting electrolyte. Black bars:
 396 electrolysis; white bars: photoelectrolysis; grey bars: sonoelectrolysis.

397

398 4. Conclusions.

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

- 400 - Wastewater containing dye Procion Red MX-5B can be mineralized by
401 electrolysis, photoelectrolysis and sonoelectrolysis using diamond electrodes.
402 The use of low current densities (10 mA cm^{-2}) leads to higher efficiencies due to
403 the mass transfer limitations that take mainly place at 100 mA cm^{-2} . On the other
404 hand, the process efficiency is lower when working in chloride media because of
405 the potential formation of organochlorinated intermediate compounds during the
406 treatment which are slowly oxidized.
- 407 - The electrochemical generation of oxidants has a great influence in dye and
408 TOC removal. The concentration of these species is higher when working at 100
409 mA cm^{-2} due to the presence of large amounts of hydroxyl radicals. These
410 radicals not only attack to the organic matter but also react with the anions
411 present in wastewater favoring the production of higher concentration of
412 oxidants. Likewise, significant amounts of chlorine compounds in high
413 oxidation state are produced by hydroxyl radical mediated oxidation. These
414 compounds are harmful to human health and, therefore, their presence should be
415 avoided. For this reason, the application of this technology in effluents
416 containing chlorides could be limited.
- 417 - The coupling of UV light irradiation or ultrasound to electrolysis with diamond
418 electrodes promotes the formation of free radicals (chloride and sulfate) in the
419 bulk solution by the activation of the electrogenerated oxidants. These
420 compounds enhance the process efficiency since they are more reactive than
421 oxidants. In addition, the presence of free chlorine radicals seems to decrease the
422 potential generation of chlorate and perchlorate during the treatment. These
423 results reveal that electroirradiated technologies based on diamond electrodes

424 not only improves the degradation processes but also could decrease the
425 generation of toxic compounds.

426

427 **Acknowledgements**

428 Financial support from the Spanish Ministry of Economy, Industry and Competitiveness
429 and European Union through project CTM2016-76197-R (AEI/FEDER, UE) is
430 gratefully acknowledged.

431

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