



26 **Abstract**

27 Background

28 In this work, the electrolysis of dimethyl phthalate (DMP, a widely-use plasticizer) with  
29 conductive-diamond anodes is studied.

30 RESULTS

31 Results show that this technology is capable of depleting this pollutant in a wide range  
32 of initial concentrations. Although mass transfer limits the kinetics of the process, there  
33 is a significant contribution of mediated oxidation and the rate of the processes improve  
34 with increasing current density, while the efficiency decreases. A first stage in the  
35 oxidation of DMP consists of the attack to the methyl ester groups and monomethyl  
36 phthalate and phthalate are the main aromatic intermediates. Further oxidation of these  
37 species results in the formation of maleic and oxalic acid, which behave as  
38 intermediates and are completely mineralized during the electrolysis. Presence of  
39 chloride in water leads to the formation of many more aromatic chlorinated  
40 intermediates coming from the action of hypochlorite on aromatics intermediates.  
41 Intermediates found and oxidation mechanisms proposed is consistent with other shown  
42 in literature for other advanced oxidation processes.

43 CONCLUSIONS

44 DMP, TOC and COD can be successfully removed using electrolysis with conductive-  
45 diamond anodes. DMP removal is faster than that of COD and TOC indicating the  
46 formation of reaction intermediates.

47 **Keywords**

48 electrolysis, conductive-diamond, phthalate, wastewater treatment

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50

51 **Highlights**

- 52 – Dimethyl phthalate can be completely depleted and mineralized under a wide  
53 range of initial concentrations (1.6-160 mg dm<sup>-3</sup>) and operation current densities
- 54 – Monomethyl phthalate and phthalate are the main aromatic intermediates and  
55 oxalic and maleic acids the main non aromatic intermediates.
- 56 – Occurrence of chlorides leads to the formation of many more aromatic  
57 chlorinated intermediates.
- 58 – Mineralization becomes less efficient as the concentration decreases.
- 59

## 60 **Introduction**

61

62 Phthalates are chemicals widely used in the manufacturing of plastics to improve some  
63 of their properties such as flexibility and durability (plasticizers). They are also used as  
64 stabilizers, lubricants, dispersants, binders, film formers or gelling, viscosity control or  
65 emulsifying agents. As a consequence, many end-products contain these species<sup>(1)</sup>  
66 including pharmaceuticals, personal care products, toys, building materials, paints, etc.  
67 Reactivity of phthalates is small and they do not combine with other compounds and  
68 they can be easily released into the environment with the ageing and/or the breaking of  
69 the material in which they are contained. Many phthalates are well-known endocrine  
70 disrupters and for some phthalates, exposure is suspected to lead to development of  
71 breast cancer<sup>(2)</sup>. Dimethyl phthalate (DMP) is methyl ester of phthalic acid (CAS #131-  
72 11-3). It is a low molecular weight phthalate (consequently good properties as solvent  
73 are expected) and it is slightly soluble in water. It is used in pesticides  
74 (ectoparasiticide), solid rocket propellants, plastics, lacquers, safety glasses, rubber  
75 coating agents, moulding powders and insect repellents<sup>(3,4)</sup>.

76 Because of its solubility in water, DMP may be present in some industrial waste streams  
77 in significant concentrations. In addition, its simplicity (it is one of the simpler  
78 phthalates because of its low molecular weight) makes it a good model to assess the  
79 viability of treatment technologies and to study the influence of different parameters in  
80 the reaction mechanisms. Thus, it allows researchers to know with great detail the  
81 intermediates formed and the final products (less difficult identification than with a more  
82 complex phthalate). For this reason, during the recent years it has been the aim of many  
83 studies. Most of these studies focus on the application of advanced oxidation  
84 technologies and in particular on the role of hydroxyl radicals in the oxidation of DMP.

85 Thus, Xu et al.<sup>(5)</sup> studied the photochemical degradation of DMP in UV/H<sub>2</sub>O<sub>2</sub> advanced  
86 oxidation process and demonstrated that photolysis and hydrogen peroxide oxidation  
87 applied separately were ineffective, and that only the combined UV/H<sub>2</sub>O<sub>2</sub> process could  
88 effectively degrade DMP, due to the huge oxidation strength of hydroxyl radical  
89 produced. With the same aim, Wu et al.<sup>(6)</sup> investigated the rate constant and mechanisms  
90 for the reaction of hydroxyl radical and hydrated electron with DMP in aqueous  
91 solutions, using pulse radiolysis and electron beam radiolysis. It was demonstrated that  
92 DMP can be completely mineralized into carbon dioxide. The mechanism of DMP  
93 degradation was elucidated and dimethyl hydroxyphthalate, benzoquinone and short-  
94 chain aliphatic carboxylic acid were identified as the main intermediates. The kinetic  
95 constant values found were  $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of  
96 hydroxyl radical and hydrated electron, respectively.

97

98 Looking for an industrial application, many authors have studied the catalytic ozonation  
99 of DMP with different catalyst on activated carbon (AC), Al<sub>2</sub>O<sub>3</sub> or zeolites supports.  
100 Thus, Wang et al.<sup>(7)</sup> investigated the catalytic ozonation of DMP in aqueous solution  
101 with ruthenium supported on activated carbon Ru/AC, and Li et al.<sup>(8)</sup> employed cerium  
102 supported on activated carbon (Ce/AC) for the same purpose. Both works demonstrated  
103 that the mineralization of DMP can be achieved via ozonation and the presence of Ru or  
104 Ce on activated carbon could greatly accelerate the mineralization rate of DMP in an  
105 ozonation process. On a different support but with the same purpose (to decompose  
106 DMP), Chang et al.<sup>(9)</sup> studied a high-gravity rotating packed bed (HGRP) as a catalytic  
107 ozonation reactor with Platinum – containing catalyst (Pt / Al<sub>2</sub>O<sub>3</sub>) and/ or ultraviolet  
108 (UV) lamp. Results indicated that all processes result in significant decomposition of  
109 DMP and mineralization, and better efficiencies were obtained with light irradiation.

110 Similar results were obtained by Chen et al.<sup>(10)</sup> when investigating DMP removal by  
111 ozonation on high silica zeolites. The complete removal of DMP was efficiently  
112 achieved via both O<sub>3</sub> and O<sub>3</sub>/UV treatments and the removal efficiencies of both  
113 chemical oxygen demand (COD) and total organic carbon (TOC) were significantly  
114 enhanced by employing the ozonation combined with UV radiation. Two years later,  
115 this group<sup>(11)</sup> studied the ozonation process of DMP combined with the catalytic and  
116 adsorptive properties of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, demonstrating a more efficient  
117 removal of DMP because of the heterogeneous photocatalytic processes occurring on  
118 the titanium dioxide. Working also with titanium dioxide, Jing et al.<sup>(12)</sup> (investigated  
119 the photocatalytic ozonation of DMP with TiO<sub>2</sub> prepared by a hydrothermal method.  
120 According to the author, the TiO<sub>2</sub> prepared with this method has a good crystalline  
121 anatase phase, greater surface area, stronger absorption to UV light wavelength and  
122 lower agglomeration than TiO<sub>2</sub> prepared by a classic sol-gel method and its use resulted  
123 in excellent efficiency for the photocatalytic ozonation of DMP.

124 Other widely employed advanced oxidation process is the Fenton process. Using this  
125 technology, Zhao et al.<sup>(13)</sup> investigated the photochemical degradation of DMP using  
126 hydrogen peroxide and Fe<sup>+2</sup> (Fenton reagent) as oxidant. The experimental results  
127 showed photo-degradation percentage as high as 81% within 120 min under the  
128 optimum conditions. Yuan et al.<sup>(14)</sup> investigated Fenton reaction involving a new  
129 catalyst Si-FeOOH under UV365 irradiation. The catalyst demonstrated a good  
130 stability, easy solid-liquor separation, high physical strength, little iron leaching and no  
131 need to be regenerated, and the process showed a good efficiency. Trabelsi-Souissi et al.  
132 <sup>(15)</sup> studied the oxidation of phthalic anhydride in aqueous medium of pH 3 by the  
133 photochemical advanced oxidation process “photo-Fenton” using UV irradiation. A  
134 value of 40 of the ratio [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>3+</sup>] and 0.1 mM of Fe<sup>3+</sup> ion as catalyst were found as

135 optimum operating parameters. Under this condition, mineralization degree of 98.7%  
136 was determined for a treatment time of 2 h.

137

138 Based on the use of iron, several photocatalytic processes have been assessed. Yuan et  
139 al.<sup>(16,17)</sup> applied a combined ferrate-photocatalytic process for the aqueous degradation  
140 of DMP. They found two different mechanisms in the oxidation of DMP, one in the  
141 presence of oxygen based on the action of hydroxyl radicals and other more efficient  
142 and promoted in the absence of oxygen base on the action of ferrates.

143 Chen et al.<sup>(18)</sup> studied the photocatalytic degradation of DMP with both, titanium  
144 dioxide-coated magnetic poly(methyl-methacrylate) (TiO<sub>2</sub>/mPMMA) and platinum-  
145 doped TiO<sub>2</sub>/mPMMA (Pt-TiO<sub>2</sub>/mPMMA) microspheres. The Pt-TiO<sub>2</sub>/mPMMA  
146 microspheres showed a remarkable improvement in terms of TOC removal compared to  
147 those with TiO<sub>2</sub>/mPMMA microspheres.

148 Regarding electrochemical technologies, Kabdasli et al.<sup>(19)</sup> investigated treatment of  
149 phthalates using DMP as a model compound by electrocoagulation employing stainless  
150 steel electrodes. After optimization of operating conditions, they found that complete  
151 removal of DMP could be achieved within reasonable operation times at relatively low  
152 specific energy consumption. The disadvantage of this method was found to be the low  
153 physic stability of the electrode and the high amount of sludge produced. Yining et al.<sup>(</sup>  
154 <sup>20)</sup> studied the anodic oxidation of DMP up to 125 mg dm<sup>-3</sup> with sodium sulfate  
155 (Na<sub>2</sub>SO<sub>4</sub>) as supporting electrolyte within the pH range 2.0-10.0 using a one-  
156 compartment batch reactor employing a boron-doped diamond (BDD) as anode. The  
157 mineralization rate of DMP was found to be pH –independent and it increases with  
158 increasing applied current density. Results indicated that kinetics of this electrochemical

159 process was subjected, at least partially, to the rate of mass transfer of organics onto the  
160 BDD surface.

161 Taking into account this background, the aim of this work has been to study the  
162 electrochemical oxidation with conductive-diamond electrodes of dimethyl phthalate  
163 paying special attention to the influence of operating condition and of the supporting  
164 electrolyte, and focusing on the main intermediates formed during the electrolytic  
165 process with the final aim to elucidate an oxidation mechanisms at the light of the  
166 existing literature.

167

## 168 **Materials and methods**

169 **Chemicals.** All chemicals, including *DMP* (a.r., Sigma-Aldrich), Anhydrous sodium  
170 sulphate and sodium chloride used as supporting electrolyte (a.r., Fluka, Spain), oxalic  
171 acid, maleic acid, tartaric acid, phthalic acid (a.r., Merck, Spain), hydroquinone, 1,4-  
172 benzoquinone, monomethyl phthalate, 4-hydroxy phthalate, 4-chlororesorcinol, 2,4,6-  
173 trichlorophenol, 2-chlorophenol, 3-chlorophenol, 2,4-dichlorophenol,  
174 chlorohydroquinone (a.r., Panreac, Spain) were analytical grade and used as received.  
175 Acetonitrile HPLC grade (a.r., Sigma-Aldrich, Spain) was used as mobile phase.  
176 Double deionized water (Millipore Milli-Q system, resistivity = 18.2 M $\Omega$  cm at 25 °C)  
177 was used to prepare all solutions.

178 **Apparatus and Analysis procedures.** All samples extracted from electrolyzed solution  
179 were filtered with 0.45  $\mu$ m nylon filters from Whatman before analysis. The  
180 concentrations of the compounds were quantified by HPLC (Agilent 1100 series) using  
181 analytical column Phenomenex Gemini 5  $\mu$ m C18. The detection wavelength used was  
182 274 nm and the temperature oven was maintained at 25 °C. Volume injection was set to  
183 50  $\mu$ L. The mobile phase consisted of 50 % acetonitrile and 50 % water with a flow rate

184 of  $0.3 \text{ cm}^3 \text{ min}^{-1}$ . The area of the peak corresponding to the *DMP* molecule was  
185 compared to the calibration curve that was previously obtained in the range of 1 to 200  
186  $\text{mg dm}^{-3}$ . Moreover, the acids intermediates formed during the experiments were  
187 detected at the wavelength of 190 nm. The ion exchange column used was  
188 SUPELCOGEL™ H Carbohydrate Columns from Sigma-Aldrich and dilute  $\text{H}_3\text{PO}_4$   
189 (0.022 M) was employed as the solvent. Total Organic Carbon concentration was  
190 monitored using a Multi N/C 3100 Analytik Jena analyzer. Reproducible *TOC* values  
191 were always obtained by subtracting the total carbon minus the inorganic carbon.  
192 Measurements of pH were carried out with an InoLab WTW pH-meter. COD was  
193 monitored until its total removal by sampling 2 mL of the electrolyzed solution at  
194 certain time intervals so were mixed in a glass tube filled with an oxidizing solution  
195 purchased from Merck. Samples containing chloride concentration up to  $2 \text{ g dm}^{-3}$  were  
196 diluted as recommended.

197

198 ***Electrochemical cell.*** Electrolyses were carried out in a single compartment  
199 electrochemical flow cell containing  $400 \text{ cm}^3$  solution. The cell reactor was connected  
200 to a peristaltic pump (flow rate  $26.4 \text{ dm}^3 \text{ h}^{-1}$ ) to a reservoir through silicon tubes. A heat  
201 exchanger coupled with a controlled thermostatic bath (Digitem 100, JP Selecta,  
202 Barcelona, Spain) was used to maintain the temperature at the desired set point ( $25 \text{ }^\circ\text{C}$ ).  
203 More details about the electrochemical system and cell configuration are described  
204 elsewhere<sup>(21)</sup>. Conductive –Diamond Electrodes (p-Si–boron-doped diamond) were used  
205 as anode and cathode, respectively. Both electrodes were circular (100 mm diameter)  
206 with a geometric area of  $78 \text{ cm}^2$ . The interelectrode gap was about 9 mm. Boron-doped  
207 diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and  
208 synthesized by the hot filament chemical vapour deposition technique (HF CVD) on

209 single-crystal p-type Si <100> wafers (0.1  $\Omega\text{cm}$ , Siltronix). Prior to use in galvanostatic  
210 electrolysis assays, the electrode was polarized during 10 min in a 1 M  $\text{Na}_2\text{SO}_4$  solution  
211 at 15  $\text{mA cm}^{-2}$  to remove any impurities from its surface. The electrooxidation was  
212 carried out galvanostatically using 0.40  $\text{dm}^3$  of a solution containing 161.8  $\text{mg dm}^{-3}$   
213 *DMP*, which corresponds to an organic carbon content equal to 100  $\text{mg dm}^{-3}$ . The  
214 investigated variables in the electrochemical degradation of the *DMP* compound were:  
215 i) the nature of the supporting electrolyte ( $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ ) by keeping the ionic  
216 strength at 0.15  $\text{mol dm}^{-3}$ , ii) the applied current density (20 – 120  $\text{mA cm}^{-2}$ ) and iii)  
217 initial concentration of *DMP*. All the experiments were carried out at 25°C. The cell  
218 voltage did not vary during the electrolysis experiments, indicating that conductive-  
219 diamond layers did not undergo appreciable deterioration or passivation phenomena.

220

## 221 **Results and discussion**

### 222 *Kinetic of the electrochemical process*

223 Figure 1 shows the changes with the applied current in the concentration of dimethyl  
224 phthalate (*DMP*), chemical oxygen demand (*COD*) and total organic carbon (*TOC*)  
225 during the electrochemical oxidation with conductive diamond electrodes of solutions  
226 containing different concentrations of *DMP* within the range 0.0082-0.82  $\text{mM}$ .

227 As it can be observed *DMP* is rapidly oxidized and depleted from the synthetic  
228 wastewaters during the three electrolyses. This observation is very interesting because  
229 electrolyses are covering a three-fold range of concentrations and results clearly indicate  
230 that the electrochemical technology is suitable to remove this particular pollutant.  
231 Another interesting remark is that the same current charge is needed to deplete *DMP*  
232 regardless of the initial concentration. Initially, this may be interpreted in terms of a less

233 efficient process, as the raw concentration in the initial wastewater decreases, because it  
234 needs the same current-charge to remove a significantly smaller amount of DMP.  
235 However, it is worth to take in mind that changes in the concentration of DMP only  
236 inform about the concentration of the raw pollutant and do not inform about the  
237 extension of the oxidation. So, DMP could be transformed into different intermediates  
238 or carbon dioxide during the process and differences would not be observed in the time  
239 or charge-course of this parameter. In fact, the first change (transformation into  
240 intermediates) should be monitored with the COD and the second (transformation into  
241 carbon dioxide) with TOC, two common characterization parameters widely used to  
242 characterize wastewaters but with a limited accuracy for assessing low concentrated  
243 wastes. Hence monitoring of parameters like COD and TOC are required to discuss  
244 about efficiency of the electrochemical process, although they should be discussed  
245 cautiously, because accuracy of the analytical methods for COD ( $\pm 10.0 \text{ mg dm}^{-3}$ ) and  
246 TOC ( $\pm 1.0 \text{ mg dm}^{-3}$ ) is much more worse than that obtained by chromatographic  
247 measurements of DMP ( $\pm 0.01 \text{ mg dm}^{-3}$ ).

248 Regarding COD and TOC, it can be clearly seem that the process is much more efficient  
249 for higher concentrations of pollutant, requiring even low charges for the same  
250 percentage of removal, in spite of the much more amount of pollution oxidized or  
251 mineralized in those conditions. Thus, the process becomes less efficient as the  
252 concentration decreases and this effect is more significant in mineralization with greater  
253 differences between the rates at different concentrations.

254 To put a figure on the efficiency of the process, many different parameters can be  
255 proposed. One very interesting consists of the slope of the log (concentration) vs.  $q$  plot  
256 because in a discontinuous electrochemical cell, like the one used in this study, it is

257 directly and simultaneously related to the rate and to the efficiency of the process. Thus,  
 258 the mass balance of the electrochemical system is as shown in eq. 1, where  $K_L$  is the  
 259 mass transfer coefficient,  $A$  is the electrode area,  $k_{mediated}$  the kinetic constant of  
 260 mediated oxidation and  $V$  the reaction volume.

$$261 \quad V \frac{d[C]_{bulk}}{dt} = K_L \cdot A \cdot C_{bulk} + k_{mediated} \cdot C_{bulk} \cdot V \quad (\text{eq. 1})$$

262 Taking into account the definition of current charge applied in a discontinuous process  
 263 (eq. 2), this mass balance can be transformed into equation 3, which can be integrated  
 264 resulting in equation 4.

$$265 \quad q = \frac{I \cdot t}{V} \quad (\text{eq. 2})$$

$$266 \quad I \frac{d[C]_{bulk}}{dq} = K_L \cdot A \cdot [C]_{bulk} + k_{mediated} \cdot [C]_{bulk} \cdot V \quad (\text{eq. 3})$$

$$267 \quad \ln \left( \frac{[C]_{bulk}}{[C]_{bulk_0}} \right) = \frac{K_L \cdot A + k_{mediated} \cdot V}{I} q \quad (\text{eq. 4})$$

268

269 In this equation, it is clearly observed that the slope of the semilogarithmic plot  $\log$   
 270 (concentration) vs.  $q$  corresponds to a specific efficiency ( $\eta$ ) defined as eq. 5 by the  
 271 change in the pollutant concentration produced by a change of one unit in the applied  
 272 electric charge.

$$273 \quad \eta \cdot [C]_{bulk} = \frac{d[C]_{bulk}}{dq} \quad (\text{eq. 5})$$

274

275 Figure 2 shows the influence of the current density on the specific efficiency of the  
 276 electrolyses with sulphate or chloride as supporting electrolyte. Efficiency decreases as  
 277 the current density increases, being the oxidation especially effective at low current

278 densities. Initially, this can be explained in terms of a diffusion control of the oxidation  
279 rate. However, the decrease in the efficiency for the largest current density assessed is  
280 smaller than expected and this can be due to an additional effect of mediated electro-  
281 oxidation processes due to the effect of peroxosulphates in sulphate medium and  
282 hypochlorite in chloride media (which affects importantly the value of  $k_{\text{mediated}}$ ).

283 Obviously the specific efficiency for each parameter is different, being greater for DMP  
284 and smaller for TOC. This can be explained because of the increased difficulty in the  
285 oxidation process. Removal of DMP can be attained by a simple oxidation process of  
286 any functional group while mineralization requires a sequence of complex oxidation  
287 reactions and much more electric current applied.

288 Regarding reaction rates, it can be clearly observed that they increase almost linearly  
289 with current density for COD and DMP but not for TOC. In addition, it is interesting to  
290 point out that values of calculated kinetic constants are close to that expected for a  
291 purely mass transfer controlled process, but not clearly over or below it. This value was  
292 calculated from a ferro-ferricyanide standard test<sup>(22)</sup> carried out in the same  
293 experimental setup and under the same flow conditions.

294 The changes in the kinetics constants are very different of that of the specific  
295 efficiencies, in spite it is worth to consider that values of kinetic rates constant are  
296 strongly related to previous specific efficiencies and calculated from them using eq. 6.  
297 This is the expected behaviour for a mass transfer controlled process with a significant  
298 contribution of mediated electro-oxidation as it can be attained from the assessment of  
299 eq. 4. The higher the current density, the higher the production of mediated electro  
300 reagents and hence the higher the kinetic constant as can be seen in Figure 3.

301 One very important point to assess in the electrolysis of an emerging pollutant is the  
302 production of intermediates, because some of them can be even more hazardous than the  
303 initial pollutant and because their relative concentration and the reaction stage (time or  
304 applied current) in which they appear is very important to propose a mechanism, which  
305 allow us to have a better understanding of the processes. Information on the influence of  
306 current density and initial concentration on this speciation may help to attain this goal.

### 307 *Degradation pathway*

308 Figure 4 shows the influence of the current density on the main aromatic and aliphatic  
309 intermediates formed. As it can be observed, monomethyl phthalate (MMP) and  
310 phthalate (PHT) are the main aromatic intermediates produced, and maleic and oxalic  
311 acid the main aliphatic ones. This speciation is in agreement with those found for  
312 radiolysis processes by Wu et al.<sup>(6)</sup> and for electrocatalytic photolysis processes by Yuan  
313 et al.<sup>(16, 17)</sup>. It indicates that attack to the methyl ester groups is the first stage in the  
314 oxidation.

315 Complete depletion of the aromatic intermediate species is observed for current charges  
316 passed below 40 kAh m<sup>-3</sup>. The maximum in the change of the concentration is attained  
317 first for PHT and short time later for MMP, in spite MMP should be a precursor of  
318 PHT. Differences are greater for the highest current density, which also lead to a shift of  
319 the maximum towards higher applied current charges. Moreover, although maximum  
320 concentration is similar in every case (varying in the range 0.005 - 0.01 mM), MMP  
321 concentration seems to be more important for highest current density and phthalate for  
322 lowest one. This can be explained by the contribution of chemical mediators in the  
323 oxidation of DMP. This is in agreement with the work of Yuan et al.<sup>(16, 17)</sup> focused on  
324 the comparison of the action of hydroxyl radicals (promoted in our system at high

325 current densities) and ferrates (chemical oxidants which behaves as persulphates in our  
326 system and whose effect could be promoted at low current densities) during the  
327 electrocatalytic photolysis of DMP. These authors found that when the reaction was  
328 conducted under a N<sub>2</sub> gas flow (formation of hydroxyl radicals was not promoted),  
329 ferrate was highly effective in scavenging the excited, conduction band electrons from  
330 the surface of the TiO<sub>2</sub> catalyst, which contributed to a substantial oxidation of DMP  
331 achieving the degradation of 83% after 120 min. However, in the presence of oxygen  
332 the resulting degradation of DMP was lower and intermediates different, indicating a  
333 different mechanisms. Thus, in the presence of typical environmental levels of oxygen  
334 (~ 9 mg dm<sup>-3</sup>) the Fe(IV)TiO<sub>2</sub>-UV process achieved a modest degree of DMP  
335 degradation (40 % in 120 min). The study of reaction pathways showed two different  
336 pathway of DMP degradation in the TiO<sub>2</sub>-UV-Fe(VI) and TiO<sub>2</sub>-UV-O<sub>2</sub> reaction  
337 systems. The radicals hydroxyls formed in the TiO<sub>2</sub>-UV-O<sub>2</sub> reaction system preferably  
338 attack the aromatic ring of DMP, forming as main intermediate products dimethyl 3-  
339 hydroxy phthalate and dimethyl 2-hydroxy phthalate, while the radicals formed in the  
340 TiO<sub>2</sub>-UV-Fe(VI) reaction system (most likely an iron axo-species) attack the alkyl chain  
341 of DMP forming as main intermediate product phthalate.

342 Regarding aliphatic intermediates, the concentration of oxalic acid is at least one fold  
343 over that of maleic acid in the complete range of current densities assessed. Although,  
344 the behaviour observed is characteristic of an intermediate (and carbon dioxide is  
345 formed according to TOC measurements), the maximum concentration is not sharp,  
346 meaning that oxalic acid is more difficultly oxidized than other intermediates and that  
347 DMP<sup>(23-26)</sup>. An unknown intermediate (not identified with any of the potential  
348 intermediates tested by HPLC) was also monitored, although its concentration  
349 (according to the chromatographic area) is far away from that of oxalic or maleic acid.

350 Figure 5 shows the effect of concentration of DMP on the production of intermediates  
351 during the electrolytic process. As expected the concentration of intermediates depends  
352 strongly on the initial concentration of the raw pollutant, being almost negligible for the  
353 experiment done with a very low concentration of DMP. This means that oxidation of  
354 DMP at low concentrations can be considered as a direct incineration of the pollutant.  
355 Oxalic acid is the main intermediate in the complete range of concentration studies and  
356 two unknown intermediates present a very low concentration (close to the detection  
357 limit of the chromatographic technique used) are observed although at very different  
358 current charges applied.

359 The number of intermediates increases significantly when chloride ions are present in  
360 the electrolyte. This is clearly observed in Figure 6, in which it is shown the species  
361 formed during the electrolyses at three different current densities. In addition to MMP  
362 and phthalate, some chlorinated phenolic derivatives are formed suggesting chlorination  
363 by hypochlorite formed electrochemically of phenolic species. This is important  
364 because these phenolic species were not observed in the experiments in sulphate media,  
365 maybe because they are rapidly oxidized to maleic and oxalic acid.

366 Regarding acids, tartaric acid is detected in addition to oxalic and maleic acid in the  
367 electrolysis with chloride anions. Oxalic behaves more clearly as an intermediate,  
368 meaning that this electrolytic medium promotes its complete mineralization. Although  
369 expected according to literature<sup>(27, 28)</sup>, no halogenated organic acids were detected  
370 (including among many others were checked by HPLC, those typically formed in the  
371 electrolysis of aromatics such as chloroacetic, dichloroacetic, trichloroacetic acids  
372 which result in nil concentration) although an unknown species with a significant  
373 chromatographic area but not corresponding to any of the expected compounds was  
374 observed.

375 With this information about intermediates, and taking into account previous  
376 mechanisms proposed in the literature<sup>(29, 30)</sup> the mechanisms shown in Figure 7 can be  
377 proposed for the electrochemical oxidation of DMP with conductive-diamond anodes.  
378 Hydroxyl radicals formed by water oxidation transform the DMP sequentially in MMP  
379 and phthalic acid. This acid can be transformed either in 4-hydroxyl phthalate<sup>(20)</sup> or in  
380 salicylic acid . In the first case, breakage of the molecule to lead to 4-hydroxyl phthalate  
381 lead to the formation of maleic acid which afterwards is oxidized with a well-known  
382 transformation into tartaric acid and oxalic acid to finally yield carbon dioxide<sup>(25, 31, 32)</sup>.  
383 In the second case, hydroquinone, catechol and benzoquinone are formed, via salicylic  
384 acid<sup>(33-36)</sup>. Mineralization of this species through carboxylic acid formation is also well  
385 known, and consistent with the intermediates found in this work. Differences in the  
386 speciation found in chloride media can be explained in terms of the very active role of  
387 hypochlorite<sup>(37, 38)</sup>. This oxidant is produced by disproportionation of anodically formed  
388 chlorine. Its presence promotes chemical oxidation pathways with formation of many  
389 chlorinated intermediates formed by substitution or addition reactions of hypochlorite  
390 with the species described in the mechanisms of Figure 7<sup>(27, 28)</sup>.

## 391 **Conclusions**

392

393 From this work the following conclusions can be drawn:

394

- 395 – Dimethyl phthalate can be successfully removed using electrolysis with  
396 conductive-diamond anodes. This technology is capable to deplete its  
397 concentration down to HPLC undetectable limits for a wide range of initial  
398 concentrations in the waste covering from values close to its solubility (0.82  
399 mM) down to two folds below (0.0082 mM). No refractory species are formed

400 in any of the conditions studied and TOC and COD are completely removed  
401 down to undetectable limits during electrolyses.

402

403 – Mass transport rate influences strongly on the kinetics of the electrochemical  
404 process, but there is a significant contribution of mediated oxidation processes.  
405 Current density promotes the formation of mediators and rate of the electrolyses  
406 improves with increasing this parameter. Opposite efficiency decreases with an  
407 increase in current density.

408

409 – Monomethyl phthalate and phthalates are the two main aromatic intermediates  
410 found in the electrolyses of dimethyl phthalate, meaning that initial stages in the  
411 oxidation process consists of the attack of methyl ester groups of the raw  
412 molecule. The oxidation of these molecules lead to the formation of maleic and  
413 oxalic acid. Both carboxylic acids behave as intermediates and they are  
414 completely depleted during the treatment. Concentration of intermediates  
415 depends strongly on the initial concentration of pollutant and it becomes  
416 negligible for the lowest concentration studied ( $1.6 \text{ mg dm}^{-3}$ ) allowing to  
417 consider the process as a cold incineration.

418

419 – Electrolysis with chlorides leads to many chlorinated intermediates formed by  
420 the action of hypochlorite on the different organic intermediates. Anyhow,  
421 complete depletion of COD and mineralization is also obtained in this  
422 supporting electrolyte medium.

423

424

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430

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555

556 **Figure captions**

557 **Figure 1.** Removal of [DMP], COD and TOC as a function of the charge applied per unit  
558 volume of electrolyzed solution ( $Q_{ap}$ ) with conductive- diamond anodes, for different values of  
559 initial concentration of DMP: (●) DMP (■) COD and (▲) TOC. Black points 161 mg dm<sup>-3</sup>;  
560 grey points 16 mg dm<sup>-3</sup>; white points 1.6 mg dm<sup>-3</sup>. Conditions: 20mA cm<sup>-2</sup>, 25 °C and the ionic  
561 strength was kept at 0.15 mol dm<sup>-3</sup> through addition of Na<sub>2</sub>SO<sub>4</sub>, as supporting electrolyte.

562 **Figure 2.** Influence of the current density on the specific efficiency of the electrolysis of 161  
563 mg dm<sup>-3</sup> DMP solution. Relative decay of (◆) DMP; (■) COD and (▲) TOC in a) Sulphate  
564 media b) chloride media. The ionic strength was kept at 0.15 mol dm<sup>-3</sup> through addition of  
565 specific salts.

566

567 **Figure 3.** Influence of the current density on the oxidation rate of the electrolysis of 161 mg dm<sup>-3</sup>  
568 DMP solution. Relative decay of (◆) DMP; (■) COD and (▲) TOC in a) Sulphate media b)  
569 chloride media. The ionic strength was kept at 0.15 mol dm<sup>-3</sup> through addition of specific salts.

570 **Figure 4.** Influence of the current density on the intermediates detected by HPLC during the  
571 electrolyses of 161 mg dm<sup>-3</sup> DMP solution. (▲) monomethyl phthalate, (◆) phthalic acid, (●)  
572 maleic acid, (■) oxalic acid, (\*) unknown 1. Current densities: 20 mA cm<sup>-2</sup> (black points) 60  
573 mA cm<sup>-2</sup> (grey points) 120 mA cm<sup>-2</sup> (empty points). The ionic strength was kept at 0.15 mol  
574 dm<sup>-3</sup> through addition of Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte.

575 **Figure 5.** Influence of the initial concentration on the intermediates detected by HPLC during  
576 the electrolyses of 161 mg dm<sup>-3</sup> DMP solution. (▲) monomethyl phthalate, (◆) phthalic acid,  
577 (●) maleic acid, (■) oxalic acid, (\*) unknown 1. Current densities: 20 mA cm<sup>-2</sup> (black points)  
578 60 mA cm<sup>-2</sup> (grey points) 120 mA cm<sup>-2</sup> (empty points). The ionic strength was kept at 0.15 mol  
579 dm<sup>-3</sup> through addition of Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte.

580 **Figure 6.** Influence of the current density on the intermediates detected by HPLC during the  
581 electrolyses of 161 mg dm<sup>-3</sup> DMP solution. Part a) (▲) monomethyl phthalate, (◆) phthalic

582 acid, (●) 3- chlorophenol, (\*) 2,4 dichlorophenol, (■) 2,4,6 trichlorophenol, (+) 4-  
583 chlororesorcinol. Part b) (▲) tartaric acid, (●) maleic acid, (■) oxalic acid, (◆) unknown 5.  
584 Current densities: 20 mA cm<sup>-2</sup> (black points, continuous line) 60 mA cm<sup>-2</sup> (grey points,  
585 discontinuous line large) 120 mA cm<sup>-2</sup> (empty points, discontinuous line short). Supporting  
586 electrolyte: sodium chloride

587 **Figure 7.** Proposed degradation pathway of DMP for the electrochemistry oxidation in sodium  
588 sulphate.

589