

1 **Coupling photo and sono technologies to improve**
2 **efficiencies in conductive diamond electrochemical**
3 **oxidation**

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29

30 **Abstract**

31 In this work, the improvements obtained in the conductive-diamond electrochemical
32 oxidation (CDEO) by simultaneous coupling of ultrasounds (US) and UV-light
33 irradiation are studied for the treatment of synthetic wastes containing dimethyl
34 phthalate (DMP). Results show that both irradiation technologies improve significantly
35 the rates of oxidation and mineralization of the electrolytic process, but their coupled
36 effect on results is smaller to the effect observed when they operate separately. Results
37 are explained in terms of the formation of radicals in the reaction media by UV-light or
38 US decomposition of powerful oxidants formed electrochemically on the conductive-
39 diamond surface. Oxidation of DMP proceeds through the removal of the methyl esters
40 group, ring breakage and carboxylic acid mineralization. Concentration of intermediates
41 is very small in electrolytes with sulfates. When chlorides are present in the electrolyte,
42 chlorophenols are also observed and concentration of intermediates becomes greater. In
43 terms of energy consumed, sonolysis processes are more expensive than photolysis
44 processes to attain similar removal percentages.

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49 **Keywords**

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51 electrolysis, sono-electrolysis, photo-electrolysis, sonophoto-electrolysis, conductive-
52 diamond

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54 **1. Introduction**

55 During the recent years, many studies have demonstrated that conductive diamond
56 electrochemical oxidation (CDEO) is a very efficient technology for the removal of
57 organic pollutants. The hydroxyl radicals and many other mediated oxidants produced
58 at high concentrations on the surface of diamond are responsible for the harsh oxidation
59 conditions attained. In addition, CDEO exhibits three outstanding properties as
60 compared with other advanced oxidation technologies and with electrolyses with other
61 anodes [1]:

- 62 – Robustness, because it is the only process that can assure previously the
63 depletion of the organic load of any waste down to the limit fixed by any
64 regulation.
- 65 – Efficiency, because for concentrations over 1500-2000 mg dm⁻³ (depending on
66 the flow conditions of the cell) it uses to show an electric efficiency of 100%.
67 However, its costs depend largely on the organic load of the effluent. In
68 particular, it is very efficient for the coarse treatment of wastewaters polluted
69 with less than 15-20 g dm⁻³ COD down to the typical discharge limits to
70 municipal sewers.
- 71 – Integration capability, because CDEO technology can be easily joined to many
72 other treatment technologies either by using the anodic or the cathodic
73 processes. Some examples of this integration capability are the electro-Fenton
74 and the sono-electrolytic and the photo-electrolytic processes [2].

75

76 In spite of the large number of studies done, there is still a long way for its commercial
77 use and many topics remain as hot topics now. Two are of particular interest:

78 – The specificity of diamond electrodes and the elucidation of the influence of
79 diamond layer characteristics on the efficiency of the oxidation, because a very
80 careful selection of the properties of the electrode surface seems to improve
81 results obtained by CDEO. This is especially important in production of
82 oxidants [3], but it also influences on the treatment of wastes [4]. The
83 improvements which can be obtained by the combination of CDEO with other
84 technologies such as the irradiation of ultrasounds (US) or UV-light, because in
85 the later years light irradiation and/or ultrasounds irradiation have shown to
86 improve results of many advanced oxidation processes, in particular avoiding
87 the production of refractory organics during the oxidation of complex pollutants
88 [5-7]. This is not a problem of the robust CDEO technology, but clarification of
89 how sono- and photo - CDEO can improve results of conventional CDEO is
90 worth of investigation.

91

92 Many works have been published during the recent years on photo-electrolysis. Most of
93 them focused on the use of titanium dioxide in thin film or in mixed metal oxides
94 (MMO) anodes [8-18]. They typically study the degradation of dyes, because in addition
95 to their role as pollutants, they consist of large molecules in which synergistic effects of
96 electrochemical and photochemical technologies can be more clearly assessed.
97 However, some works are focused on pharmaceuticals or other complex molecules,
98 with the same aim: assessing the removal of a complex pollutant and, at the same time,
99 use it as a model of large molecule. Results shown in those works indicates that
100 combining photo and electrolysis technologies leads to a synergistic effect explained by
101 heterogeneous (external bias contribute to a decrease in the electron- hole pair
102 recombination process and the UV-photons reaching the electrode surface form excited

103 radicals) and homogenous (photo activation of electrochemically generated reactive
104 species) catalytic processes.

105

106 Sono-electrolysis have also been widely studied in the recent years and it has been
107 proposed for the treatment of different types of wastewaters leading to good efficiencies
108 [19-23]. Results shown in those works indicates that ultrasound irradiation is a effective
109 technology to increase mass transport and to produce important changes in the chemical
110 composition of the electrolyte because of the ultrasonic cavitation phenomenon, which
111 takes advantage of the high pressure and temperature produced during the implosive
112 collapse of bubbles irradiated with the ultrasound to form new radical species and
113 components [24,25. These changes are complementary and even synergistic with those
114 taking place during electrolyses, resulting in very effective processes.

115

116 Removal of phthalates, a widely used plasticizer commonly found in urban wastewaters
117 has been studied by sonochemical [26],photochemical [27] and electrochemical
118 methods [28] but, to the authors' knowledge, not a comparative study has been made till
119 now. The goal of this work is to compare the synergistic or antagonist effects of
120 photolysis and sonolysis on the efficiency of the conductive-diamond electrochemical-
121 oxidation of dimethyl phthalate. To do this, CDEO electrolyses, sono-CDEO, photo-
122 CDEO, and sonophoto- CDEO studies are going to be made, and results will be
123 discussed at the light of the influence of the operating conditions on efficiencies and on
124 reaction intermediates formation.

125

126 **2. Materials and methods**

127 **2.1 Chemicals.** All chemicals, including *DMP* (a.r., Sigma-Aldrich), Anhydrous
128 sodium sulfate and sodium chloride used as supporting electrolyte (a.r., Fluka, Spain),
129 oxalic acid, maleic acid, tartaric acid, phthalate (a.r., Merck, Spain), hydroquinone, 1,4
130 benzoquinone, Monomethyl phthalate, 4 - hydroxyphthalic acid, 4- chlororesorcinol,
131 2,4,6 trichlorophenol, 2-chlorophenol, 3-chlorophenol, 2,4-dichlorophenol,
132 chlorohydroquinone (a.r., Panreac, Spain) were analytical grade and used as received.
133 Acetonitrile HPLC grade (a.r., Sigma-Aldrich, Spain) was used as mobile phase.
134 Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 °C)
135 was used to prepare all solutions.

136 **2.2 Apparatus and Analysis procedures.** All samples extracted from electrolyzed
137 solution were filtered with 0.45 μm nylon filters from Whatman before analysis. The
138 concentrations of the compounds were quantified by HPLC (Agilent 1100 series) using
139 analytical column Phenomenex Gemini 5 μm C18. The detection wavelength used was
140 274 nm and the temperature oven was maintained at 25 °C. Volume injection was set to
141 50 μL. The mobile phase consisted of 50 % acetonitrile and 50 % water with a flow rate
142 of 0.3 cm³ min⁻¹. The area of the peak corresponding to the *DMP* molecule was
143 compared to the one from a calibration curve that was previously obtained in the range
144 of 1 to 200 mg dm⁻³. Moreover, the acids intermediates formed during the experiments
145 were detected with a detection wavelength of 190 nm. The ion exchange column used
146 was SUPELCOGELTM H Carbohydrate Columns from Sigma-Aldrich and dilute
147 H₃PO₄ (0.022 M) was employed as the solvent. The Total Organic Carbon (TOC)
148 concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.
149 Measurements of pH were carried out with an InoLab WTW pH-meter. The Chemical
150 Oxygen Demand (COD) was monitored using a HACH DR200 analyzer . The samples
151 containing chloride concentration up to 2 g dm⁻³ were diluted as recommended.

152

153 **2.3 Electrochemical cell.** Electrolyses were carried out in a single compartment
154 electrochemical flow cell. One of the covers of this cell was made of quartz in order UV
155 light to access into the reaction media. The other cover was made of a high chemical
156 resistance polymer. The anode was pasted to the polymer cover and a grid cathode to
157 the quartz cover in order to let light irradiates the cathode, anode surface and the
158 interelectrode gap (Figure 1). Conductive –Diamond Electrodes (p-Si–boron-doped
159 diamond) were used as anode and a grid of stainless steel as cathode. Both electrodes
160 were circular (100 mm diameter) covering a geometric area of 78 cm². The
161 interelectrode gap was about 9 mm. A UV lamp VL-215MC (Vilber Lourmat), $\lambda =$
162 254 nm, intensity of 930 $\mu\text{W}/\text{cm}^2$ and energy 4.43-6.20 eV irradiating 15 watts directly
163 to the quartz cover. The ultrasound generator was a UP200S (Hielscher Ultrasonics
164 GmbH, Germany) equipped with a titanium glass horn of 40 mm diameter, length 100
165 mm, emitting 24 kHz and maximum ultrasonic power 200 W. The output can be
166 continuous or pulsed with varying percentage of cycle duty ranging from 10 to 100%.

167

168 Boron-doped diamond films were provided by Adamant Technologies (Neuchatel,
169 Switzerland) and synthesized by the hot filament chemical vapour deposition technique
170 (HF CVD) on single-crystal p-type Si <100> wafers (0.1 Ωcm , Siltronix). Prior to use in
171 galvanostatic electrolysis assays, the electrode was polarized during 10 min in a 1 M
172 Na₂SO₄ solution at 15 mA cm⁻² to remove any impurities from its surface.

173

174 The cell reactor was connected to a peristaltic pump (flow rate 26.4 dm³ h⁻¹) to a
175 reservoir through silicon tubes. A heat exchanger coupled with a controlled thermostatic

176 bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature
177 at the desired set point (25 °C).

178

179 The electrooxidation was carried out galvanostatically using 0.80 dm³ of a solution
180 containing 161.8 mg dm⁻³ *DMP*, which corresponds to an organic carbon content equal
181 to 100 mg dm⁻³. The investigated variables in the electrochemical degradation of the
182 *DMP* compound were: i) the nature of the support electrolyte (NaCl and Na₂SO₄) by
183 keeping the ionic strength at 0.15 mol dm⁻³, ii) the applied current density (20 – 120
184 mA cm⁻²) and iii) concentration initial of *DMP*. All the experiments were carried out at
185 25°C. The cell voltage did not vary during the electrolysis experiments, indicating that
186 conductive-diamond layers did not undergo appreciable deterioration or passivation
187 phenomena.

188

189 **3. Results and discussion**

190 Figure 2 compares changes in the *DMP* concentration, COD and TOC during the
191 treatment of a synthetic waste containing *DMP* and sodium sulfate as electrolyte by
192 CDEO electrolysis and sonophoto-CDEO.

193

194 As it can be observed, the three parameters are completely depleted during the treatment
195 with both technologies, indicating that both technologies are effective in the degradation
196 of this plasticizer. In addition, a clear improvement is obtained with the use of
197 ultrasounds and UV light irradiation, in terms of a smaller requirement of electric
198 charge for the depletion of the organics. This improvement is clearly observed for COD
199 removal and mineralization (TOC removal) but not for the removal of *DMP* in which
200 the single electrolytic process (no irradiation of light and ultrasounds) seems to attain a

201 better performance. This clearly indicates that irradiation of ultrasounds or light help to
202 the progress of hard oxidation processes, but it is not very effective in the more single
203 oxidation of functional groups required to transform DMP in intermediates. Anyhow,
204 the goal of a waste treatment is not the depletion of DMP but the mineralization of the
205 waste and, consequently, light and ultrasounds irradiation exhibits a clear good effect.

206

207 Another important observation is the occurrence of a significantly high value of COD
208 when TOC is completely depleted. Not a clear explanation was found for it, although
209 two possibilities could explain the results obtained:

- 210 - the accuracy of the analytical techniques or
- 211 - the production of hydrogen peroxide that, in spite of being a well-known
212 oxidant, produces COD as a consequence of being oxidized to oxygen by COD
213 reagents. This later process should not be very important because of the well-
214 known low production with stainless steel cathodes

215

216 The important improvement found with UV and light irradiation has to be explained in
217 terms of the effect expected for both processes on the electrolytic treatment. Thus, it is
218 known that in a conductive-diamond electrochemical-oxidation process, hydroxyl
219 radicals play a very important role in the mechanism of the oxidation and on the
220 efficiency of the process. This radical is formed by water oxidation on the surface of the
221 diamond electrode (Eq. 1) and due to its very short lifetime its action is limited to the
222 nearness of the electrode surface. This explains that single CDEO processes behave
223 similarly to direct electrolysis processes, because mass transport is usually limiting the
224 kinetics of the process.



226 In addition to hydroxyl radicals, it is known that many oxidants are produced on the
 227 electrode surface. These oxidants are known to extend the oxidation of pollutants from
 228 the nearness of the electrode surface towards the bulk of the wastewater. In the case of
 229 sulfate, it is well-known [29] the production of peroxosulfates on the anode, and it is
 230 also reported the formation of ozone and hydrogen peroxide [30]. These reagents are
 231 typically found in the electrolyte during the electrolysis of wastewaters with CDEO and
 232 they are formed according to eqs. 2 to 5.

233



238

239 Light irradiation is known to promote the production of sulfate radical from persulfate
 240 as it is shown in Eq. 6 [31,32]. It is worth taking into account that the sulfate radical
 241 reacts typically 10^3 – 10^5 times faster than the anion persulfate [33].



243 In addition, other oxidants are decomposed by UV light (Eq. 7 and 8), helping to
 244 explain the better results obtained by photoirradiation because of the activation of
 245 oxidants produced electrochemically [15].



248 Opposite to single electrolytic process the effect of these radicals can be extended to the
249 bulk in a photoelectrolytic process, because in spite of their short lifetime, they are
250 produced not on the surface but in the bulk by decomposition of more stable oxidants.

251

252 Production of radicals by sono-processes is based on a different mechanism. US
253 irradiation produces huge concentrations of energy in very small places (hot spots),
254 resulting in a local temperature of several thousands of Kelvin [4]. This energy is
255 dispersed to the surroundings so that the gas temperature in the hot spot quickly returns
256 to the ambient value. However, during a very short time it can produce significant
257 changes in chemical composition and can form new radical species and components in
258 the system. Hence, in a reaction media like the one used in this study, it is expected the
259 formation of sulfate and hydroxyl radicals due to this process. These radicals are not
260 necessarily produced on the surface of the electrode but in the bulk, improving the
261 efficiency of the process.

262

263 Coming back to Figure 2, as it can be seen, charge course of experimental pollution
264 decay is exponential and so it is the time course, because the experiments were done in
265 galvanostatic conditions (at constant current density). This means that pollutant decay
266 can be properly modeled with a first order kinetic, which in electrochemical oxidation
267 processes stands for processes whose rate is controlled by mass transport or for
268 mediated electro-oxidation. As shown in eqs. 9 and 10, both kinetic can be modeled as
269 first order expression if:

270 - concentration of pollutant is considered to be nil on the surface of the electrode
271 (proper assumption in the case of mass transport) and

272
$$r_{mass_transport} = K_L A (C_{pollutant} - C_{pollutant_surface}) \approx k \cdot C_{bulk} \quad (9)$$

273 - concentration of oxidants which produces mediated processes is considered to
274 be constant (pseudo-steady state approach)

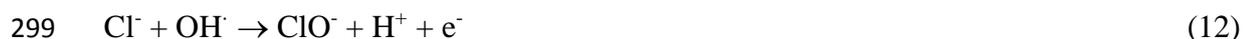
$$275 \quad r_{mediated_oxidation} = K_{ox} \cdot C_{Ox} \cdot C_{pollutant} \approx k \cdot C_{pollutant} \quad (10)$$

276

277 Figure 3 shows the kinetic constants obtained after fitting the experimental degradation
278 results to a model. This model consists of a single mass balance with a first order
279 kinetic. As states before, this model reproduces well the decay of every parameter
280 during the CDEO and sonophoto-CDEO of DMP in sulfate media. It was also observed
281 to be successful in the description of the processes in chloride-containing supporting
282 electrolyte.

283

284 As it can be observed, rates in sulfate media are higher than those fitted in chloride
285 media. Current density has a positive effect on the kinetic constant, although it is not
286 always linear, suggesting the contribution of many processes. Irradiation of light and
287 ultrasound always improves the mineralization and the oxidation progress although this
288 does not happen with DMP which exhibits a worse behavior in the irradiated
289 electrolyses in sulfate media but not in chloride media. Rates of COD removal in
290 chloride media were not calculated because of the strange behavior of this parameter
291 which was depleted very rapidly (even when significant amounts of DMP and TOC are
292 still present in the reaction media) indicating some sort of analytical problem with this
293 measurement. Main difference between the treatment of wastes containing sulfates or
294 chlorides come from the different radicals and oxidants formed. Electrolysis of chloride
295 with many electrodes lead to the formation of hypochlorite as the main final product
296 and both, the direct and the mediated oxidation mechanisms have been demonstrated
297 (eq. 11 and 12).



300 However in the case of using conductive-diamond anodes, the improved action of
301 hydroxyl radical promotes the oxidation of hypochlorite to other species, such as
302 chlorite, chlorate and perchlorate (eqs. 13 to 15), being perchlorate the final product in
303 the oxidation [34-36].



307

308 This explains that oxidation of organics in the presence of chlorine is not a very
309 effective process with diamond anodes as compared with other anodes such as those
310 containing mixed metal oxides (MMO anodes). Light irradiation effect on electrolysis
311 should be focused on the decomposition of hypochlorite. This reaction has been studied
312 in the literature [37,38], and it has been demonstrated that under non extreme pH,
313 hydroxyl and chlorine radicals are the main products resulting of the light assisted
314 degradation of hypochlorite (eqs. 16 and 17).



317 The production of these oxidants in the bulk, help to explain the better results obtained
318 by sonophoto-CDEO. However, the poorer results (as compared with those obtained in
319 the sonophoto-CDEO in supporting electrolytes with sulfates) clearly indicate that
320 sulfate radicals are playing a very important role in this processes, even more important
321 than that of chlorine or hydroxyl radicals.

322

323 Figure 4 shows the maximum concentration observed for the main intermediates
324 monitored by HPLC in the treatments of wastewaters containing sulfates as electrolyte.
325 Oxidation attained in both processes is very harsh and significance of intermediates is
326 small. Main aromatic intermediates are monomethyl phthalate, phthalic acid and 4 -
327 hydroxyphthalic acid and the main non-aromatic intermediates are maleic acid and
328 especially oxalic acid. Although small, the concentrations of this latter compound were
329 found to increase at large current densities and with light and US irradiation, opposite to
330 what it could be expected according to the effect of both technologies in other AOP
331 (promoting the depletion of intermediates). It is important to remind that, in every case,
332 these species behave as intermediates and that complete mineralization of the synthetic
333 wastewaters was obtained.

334

335 Presence of intermediates in terms of concentration is more important when chlorides
336 are contained in the supporting electrolyte, because of the very significant role of
337 chlorine and hypochlorite on the oxidation. This can be clearly observed in Figure 5, in
338 which it is important to remark that concentration of phthalate increase by one fold. In
339 addition, two new species appear as intermediates: chlorophenols and tartaric acid. No
340 chlorinated carboxylic acids were detected during the electrolyses (at least in
341 concentrations which could be detected by HPLC). This is a surprising result because in
342 previous studies of our group about the treatment of chlorophenols [39,40] the
343 chlorinated carboxylic acid seemed to play a significant role in the oxidative destruction
344 of chlorophenols. In chloride media, the irradiation of ultrasounds and light seems to
345 have a harsh effect on non-aromatic intermediates, because the concentration of oxalic

346 acids was almost nil and just small concentration of tartaric acid was detected at large
347 current densities.

348

349 Results have clearly shown that US and UV irradiation improve the performance of
350 CDEO processes in the removal of pollution. However, it is important to study the
351 separated effect of both irradiation technologies. To do this, Figure 6 compares the
352 effect of ultrasounds and light irradiation on the mineralization attained during the
353 electrolyses of synthetic wastes containing sulfates as supporting electrolyte in four
354 different cases. Electrolysis with diamond electrodes are very effective and they are
355 always capable of removing DMP within the range of current densities studied. As
356 expected in electrolytic wastewater treatment processes, the process efficiency is higher
357 at lower current densities, although it has to be taken in mind that the process rate is
358 also lower at these conditions. Irradiation of ultrasounds or light has a positive effect on
359 results leading to lower electric charges for the complete mineralization of the waste.
360 However, opposite to what it can be expected, there is not a synergistic but a clear
361 antagonistic effect on results, with the simultaneous irradiation of light and ultrasounds.
362 This effect should be explained in terms of an excessive formation of radicals which
363 instead of attacking DMP (or reaction intermediates) combine among them to form
364 more stable and less aggressive oxidants which have an smaller oxidation capability and
365 can decompose forming oxygen. Eqs 4 and 18 to 20 summarize some of the reactions
366 that could explain this behavior in our experimental system.

367



371 The same observations are applicable to electrolyses of synthetic wastes containing
372 chlorides instead of sulfates as supporting electrolyte, although in this case the effect of
373 every parameter is even clearer because curves are more separated, as it can be observed
374 in Figure 7. Electrolytic treatment with irradiation of ultrasounds clearly overcomes the
375 other treatments. In addition, comparing both supporting electrolytes, it seems clear
376 that mineralization is more efficient in sulfate media than in chloride media. This can be
377 easily explained by the more drastic oxidation of persulfates than that done by chlorine
378 reagents and by the important role suggested below for the sulfate radicals.

379

380 Finally, a point that should be clarified is the performance of the single sono and photo
381 irradiation. Figure 8 shows mineralization attained by single sonolysis and single
382 photolysis technologies in both chloride and sulfate aqueous electrolytes. As it can be
383 observed, opposite to electrolytic technologies, supporting electrolyte does not influence
384 on results in both technologies. This confirms that differences observed in the
385 electrolytic processes can be explained because of the decomposition by US or UV
386 irradiation of more stable oxidants formed on the electrode surface. In addition,
387 photolysis is much more efficient than sonolysis because it attains a faster removal even
388 with the irradiation of 10 times less energy (UV 37.5 w dm⁻³ irradiation power vs. 500
389 w dm⁻³ US irradiation power). For comparison purposes, power supplied in the
390 electrolytic treatments done in this work ranges between 15 and 240 w dm⁻³ for current
391 densities ranging between 20 and 120 mA cm⁻², respectively. This means that coupled
392 processes, in particular photo-CDEO can be very promising from the view point of
393 minimization of operation costs.

394

395 **4. Conclusions**

396

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

398

399 - Dimethyl phthalate can be successfully oxidized using conductive-diamond
400 electrochemical oxidation. Light and ultrasound irradiation improves very
401 importantly the efficiency of the electrochemical process in an integrated
402 sonophoto-electrochemical process.

403 - The improvement attained in the CDEO with the application of both irradiation
404 technologies is smaller to that of the application of them separately, indicating that
405 the combination of the two technologies with the electrochemical process show a
406 clear antagonistic effect.

407 - In single irradiation processes there are no differences caused by the electrolyte
408 composition (in particular presence of sulfate or chlorides). Improvements in the
409 electrolytic treatment attained with irradiation of UV-light and US can be explained
410 by the formation of radicals by decomposition in the bulk of the oxidants formed on
411 the surface of the electrode.

412 - Both the CDEO and the sonophoto-CDEO produce the same intermediates. Main
413 aromatic intermediates are monomethyl-phthalate, phthalic acid and 4 -
414 hydroxyphthalic acid. Main non-aromatic intermediates are maleic acid and
415 especially oxalic acid. These intermediates are found in combined and single
416 processes and also reported in literature for other AOP, indicating that oxidation of
417 DMP proceed through the removal of the methyl esters group and the breakage of
418 the aromatic ring to form carboxylic acids that are finally mineralized to carbon
419 dioxide. In the presence of chloride, production of chlorophenols and tartaric acid

420 and increases in the concentration of all intermediates are the main differences
421 observed.
422 - US irradiation is less efficient in terms of energy requirements than UV-irradiation
423 and CDEO.

424

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499
500

501 **Figure captions**

502

503 **Figure 1.** Scheme of the photo-electrochemical reactor.

504

505 **Figure 2.** Removal of pollutants during the electrolysis (●DMP; ■COD; ▲TOC) and
506 sonophoto-electrolysis (○DMP; □COD; △TOC) with conductive-diamond anodes of
507 DMP solutions in at 20 mA cm⁻²

508

509 **Figure 3.** Influence of the current density on the oxidation rate of DMP by electrolyses
510 (◆DMP; ■COD; ▲TOC) and sonophoto- electrolyses (◇DMP; □COD; △TOC) in a)
511 Sulfate media b) chloride media

512

513 **Figure 4.** Maximum concentrations of intermediates found during the electrolyses (full
514 points) and sonophoto-electrolyses (empty points) of dimethyl phthalate in sulfate
515 media. a) ◆ and ◇ monomethyl-phthalate, ■ and □ phthalic acid, ▲ and △ 4 -
516 hydroxyphthalic acid; b) ◆ and◇ maleic acid, ■ and □ oxalic acid,▲ and △ tartaric
517 acid.

518

519 **Figure 5.** Maximum concentrations of intermediates found during the electrolyses (full
520 points) and sonophoto-electrolyses (empty points) of dimethyl phthalate in chloride
521 media. a) ◆ and ◇ monomethyl-phthalate, ■ and □ phthalic acid, ▲ and △
522 chlorophenols; b) ◆ and◇ maleic acid, ■ and □ oxalic acid,▲ and △ tartaric acid.

523

524 **Figure 6.** Removal of TOC during electrolysis (●), sono-electrolysis (■), photo-
525 electrolysis (▲) and sonophoto-electrolysis (◆) with conductive-diamond anodes of
526 DMP solutions sulphate medium. a) 20 mA cm⁻²; b) 60 mA cm⁻²; c) 120 mA cm⁻²

527

528 **Figure 7.** Removal of TOC during the electrolysis (●), sono-electrolysis (■), photo-
529 electrolysis (▲) and sonophoto-electrolysis (◆) with conductive-diamond anodes of
530 DMP solutions in chloride medium. a) 20 mA cm⁻²; b) 60 mA cm⁻²; c) 120 mA cm⁻²

531

532 **Figure 8.** Removal of TOC during the sonolyses and photolysis of DMP solutions om
533 chloride or sulfate medium. ■ photolysis in chloride media; ▲ photolysis in sulfate
534 media; □ sonolysis in chloride media; △ sonolysis in sulfate media.

535

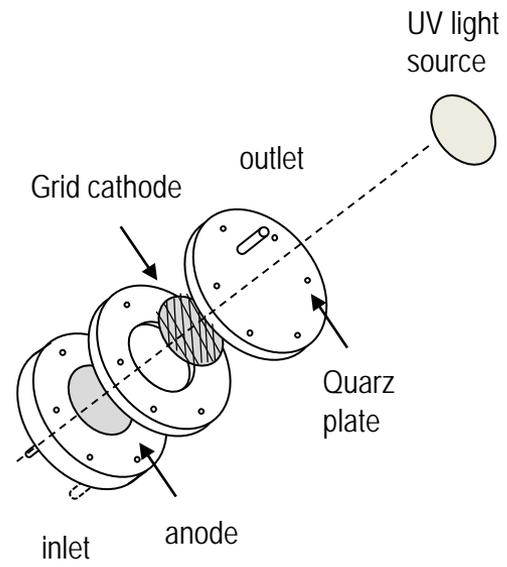


Figure 1

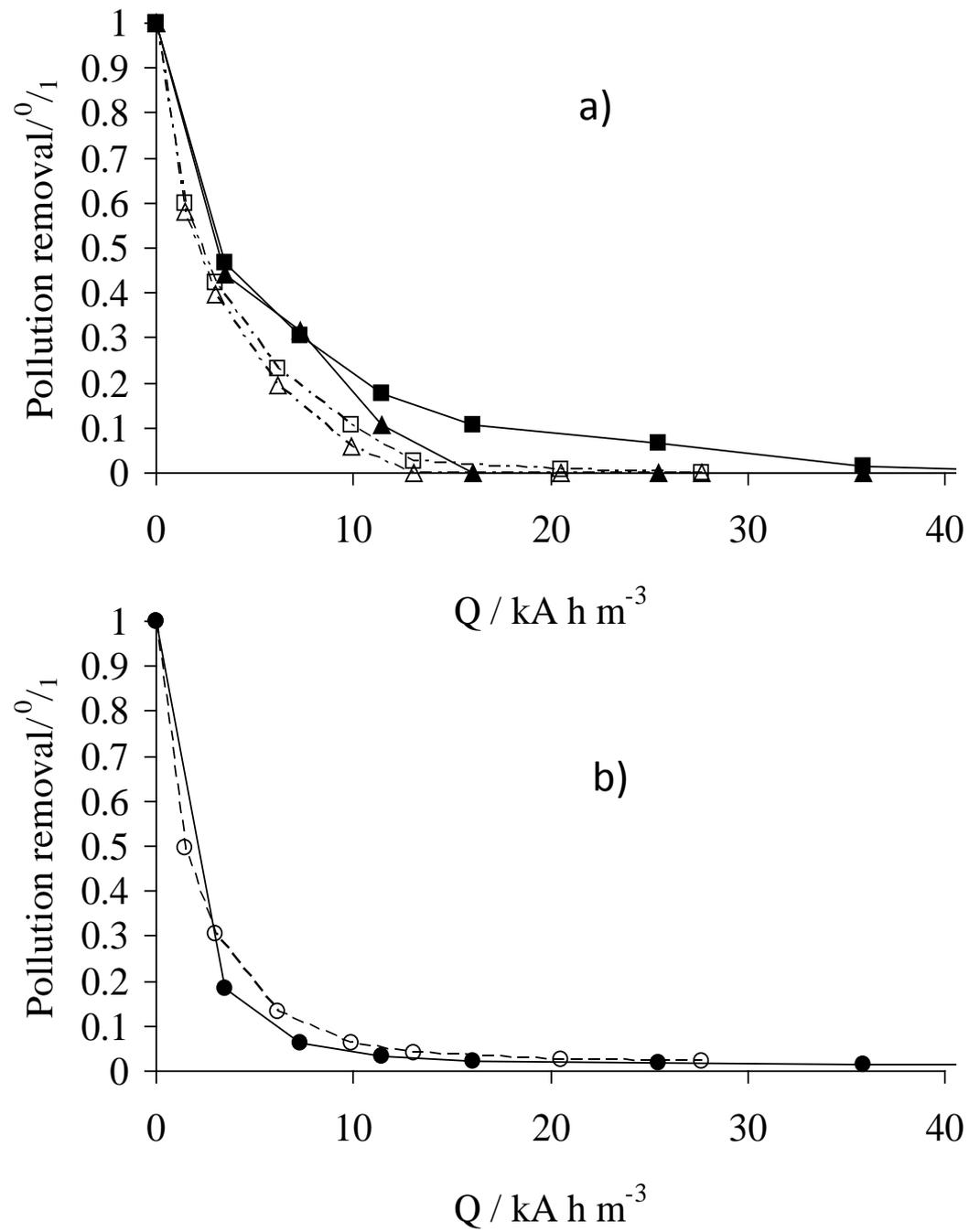


Figure 2

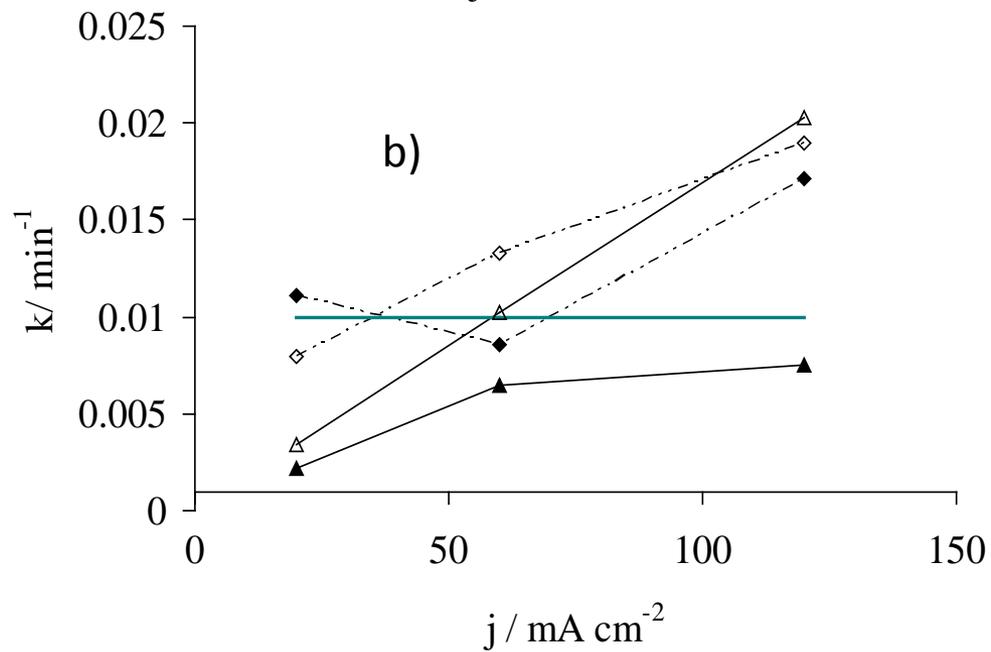
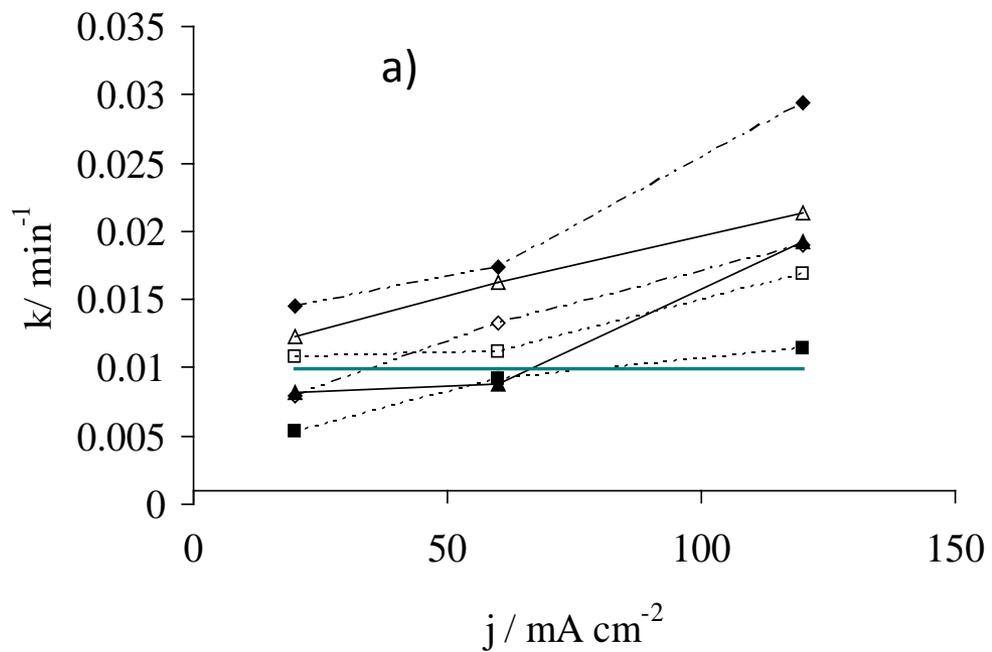


Figure 3

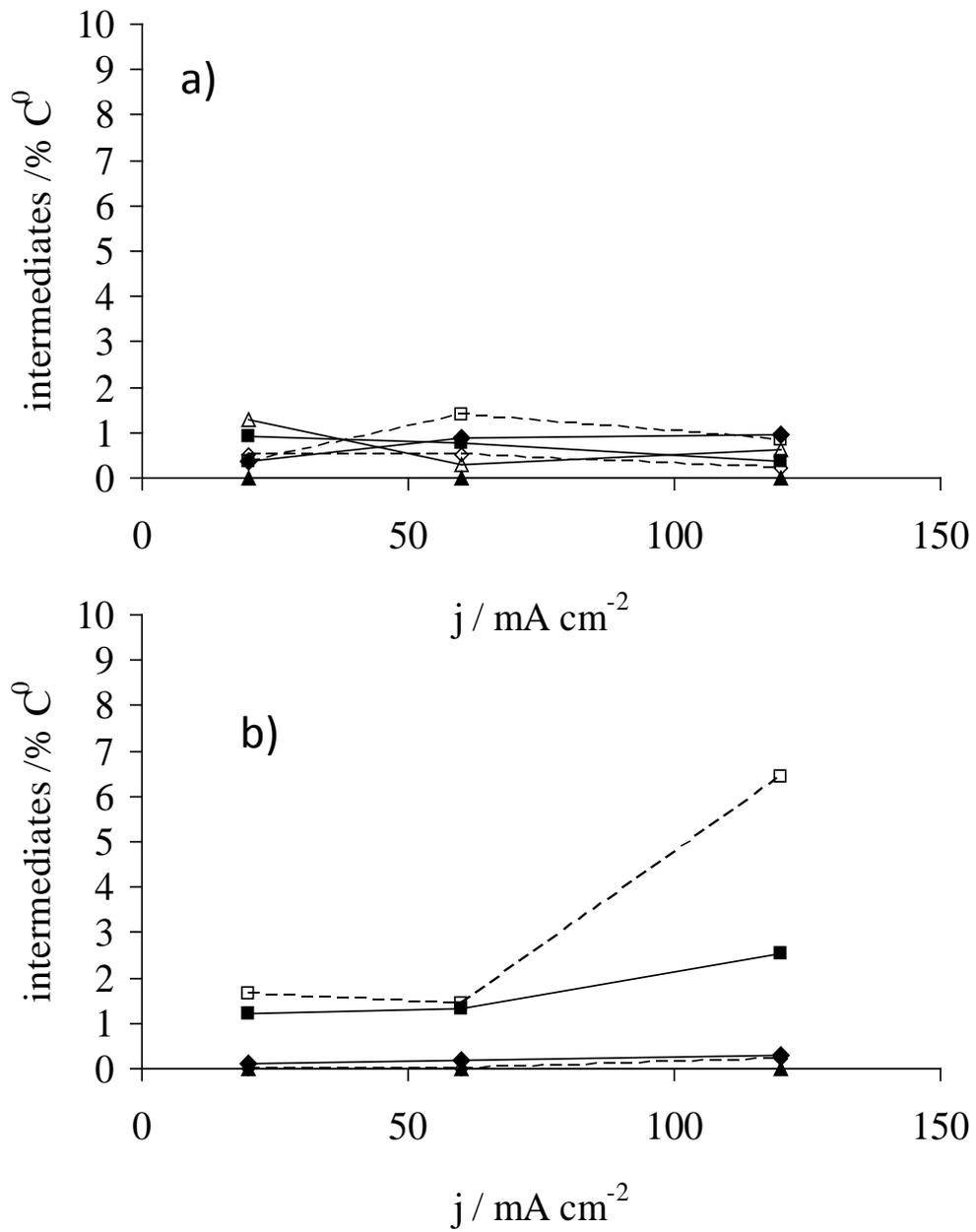


Figure 4

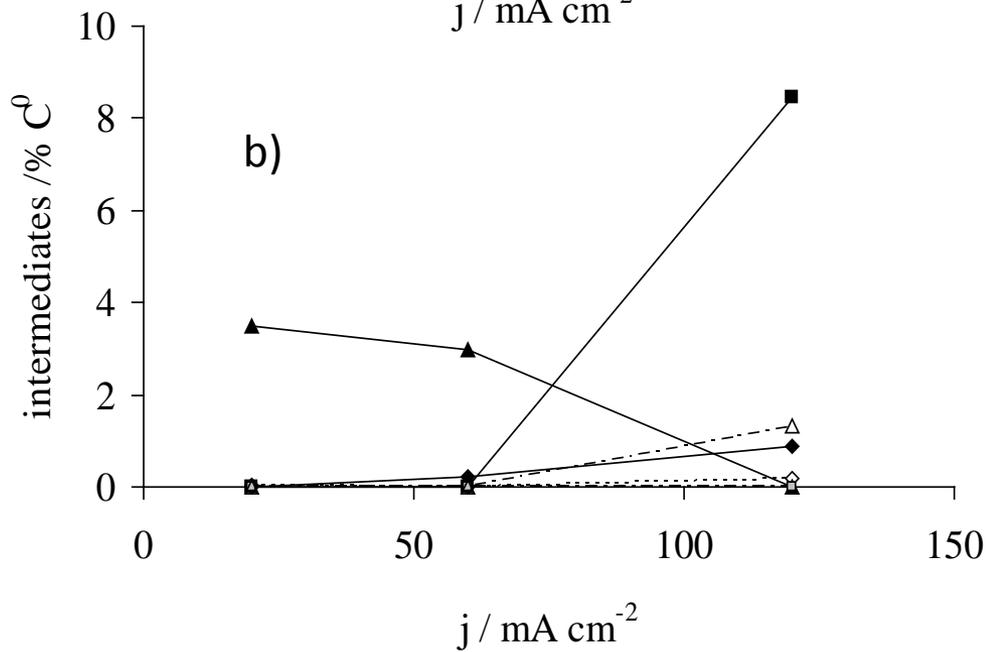
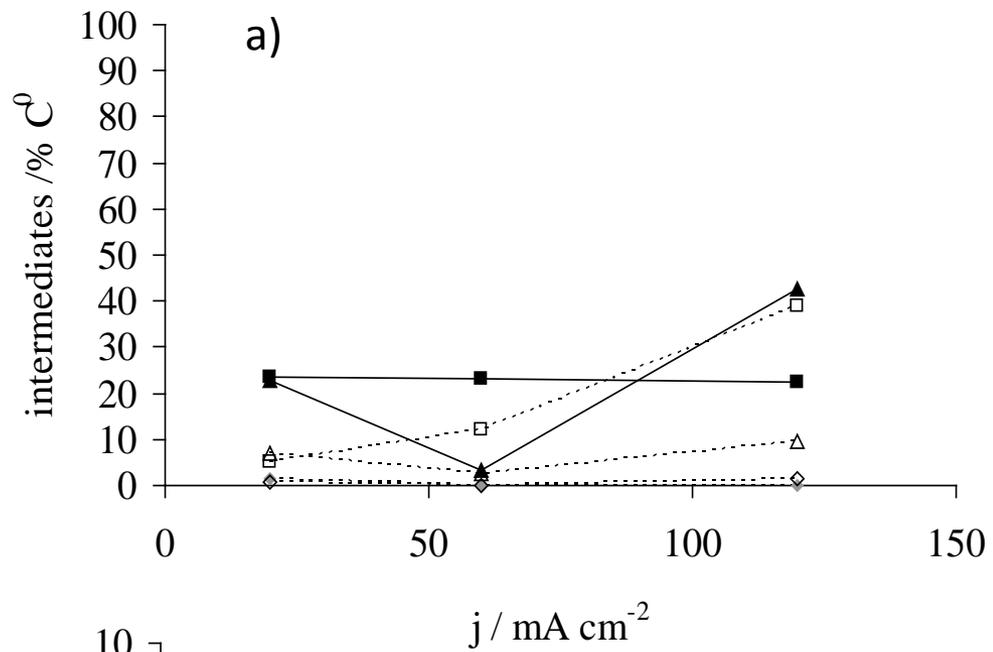


Figure 5

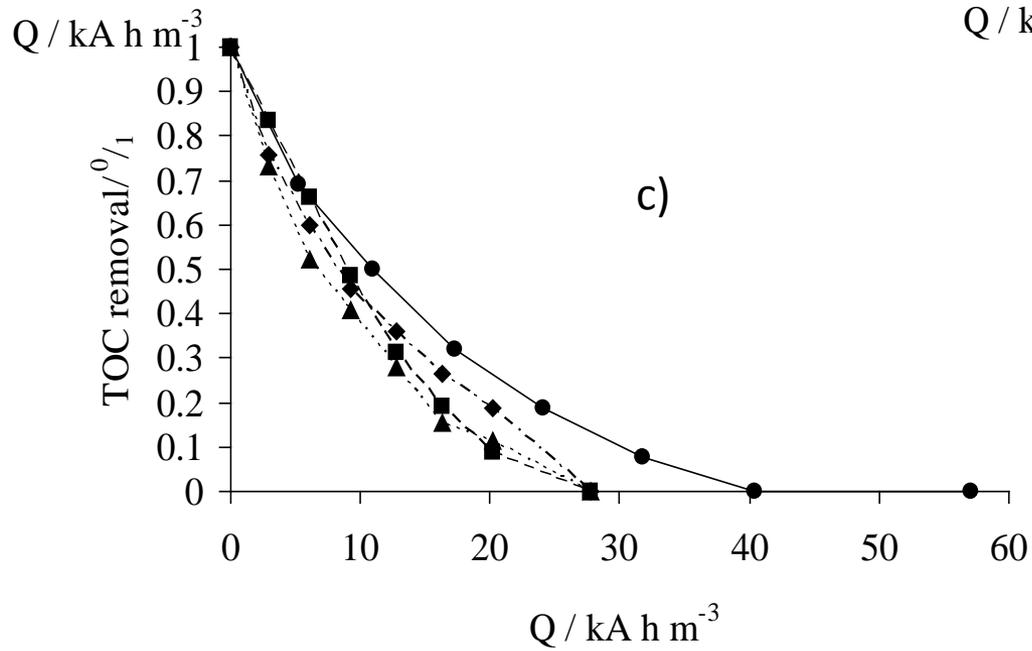
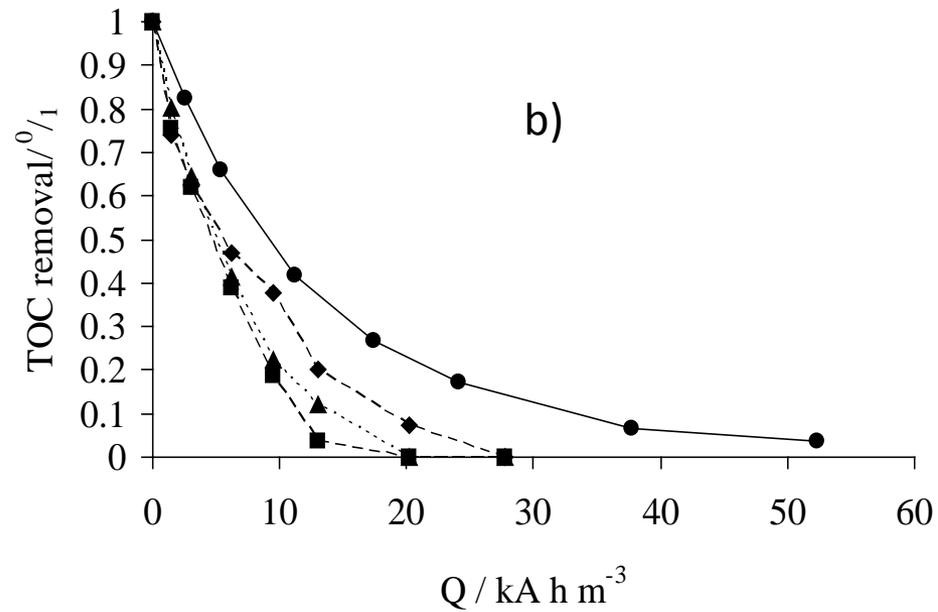
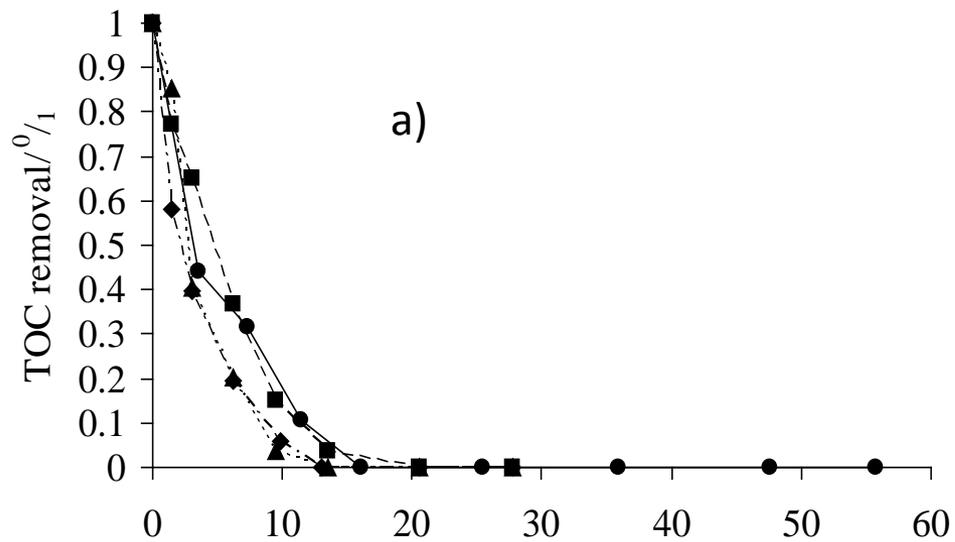


Figure 6

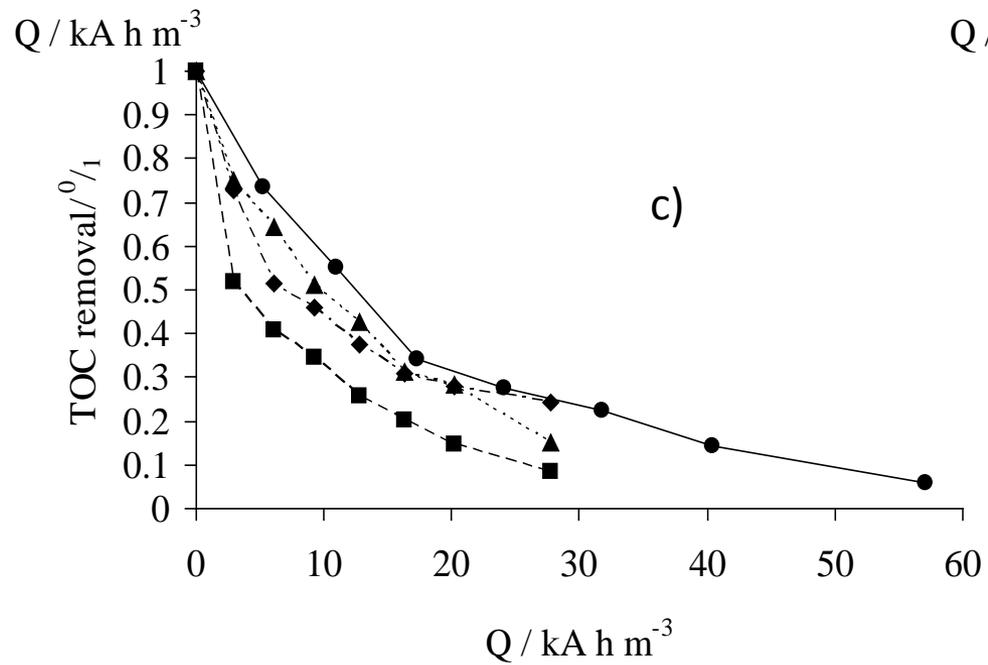
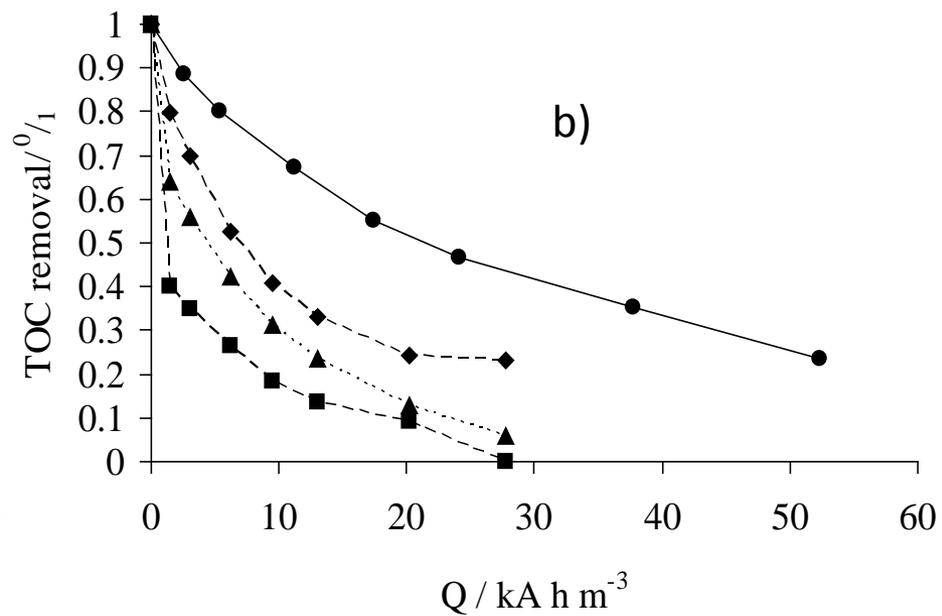
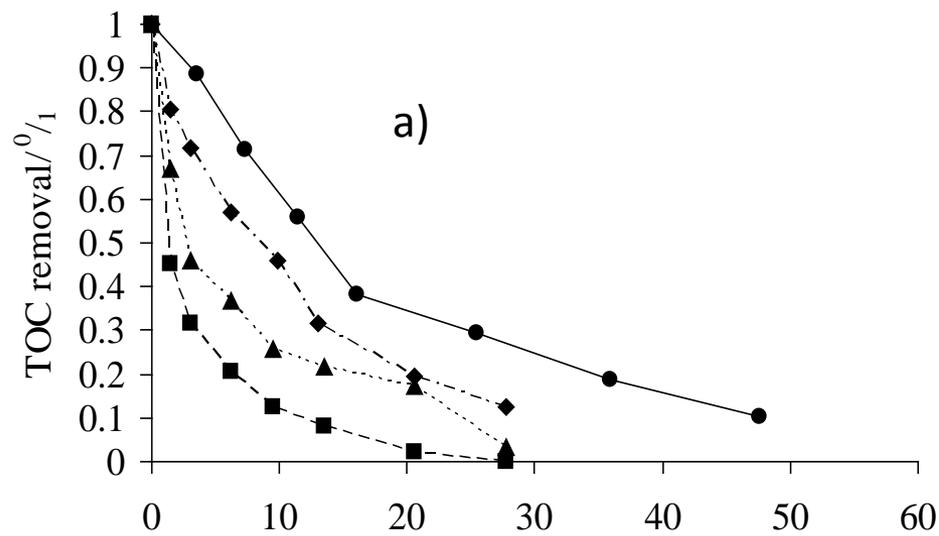


Figure 7

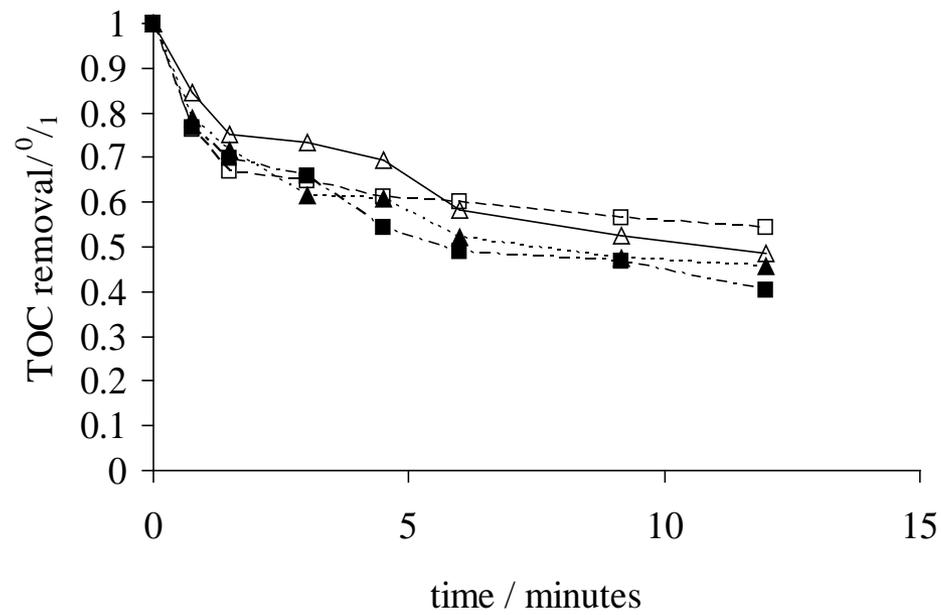


Figure 8