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**Degradation and Mineralization of Antipyrine by UV-A LED Photo-Fenton
Reaction Intensified by Ferrioxalate with Addition of Persulfate**

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38 **ABSTRACT**

39

40 The intensification of the degradation of antipyrine in aqueous solution by using
41 a UV-A-LED-photo-Fenton reaction intensified by ferrioxalate complexes and with
42 addition of persulfate anions was studied. The efficiency of the reaction was evaluated in
43 terms of antipyrine degradation and mineralization degree at different initial
44 concentrations of hydrogen peroxide, ferrous ion, oxalic acid and persulfate anion. The
45 reaction was carried out using a lab-scale photoreactor irradiated with artificial UV-A-
46 LED light emitting at 365 nm. Artificial neural networks (NNs) were implemented for
47 modelling the degradation process. Under optimal conditions, complete degradation of
48 antipyrine and 93% mineralization was reached in 2.5 and 60 min, respectively. The
49 contribution of HO• radicals in this system was evaluated running the reaction in the
50 absence and presence of appropriate quenchers such as tert-butyl alcohol and methanol.
51 In the last step of reaction, possibly different intermediates such as 2-butenedioic acid,
52 butanedioic acid, 4-oxo-pentanoic acid, acetate and formate can be generated which
53 cannot be degraded by HO• radicals or their reaction is very slow. This ferrioxalate-
54 mediated system reduces the amount of H₂O₂ needed (100 mg L⁻¹) for antipyrine
55 degradation and persulfate was not necessary because it could not be activated with UV-
56 A LED nor with Fe²⁺ since it is quickly converted to Fe³⁺ forming ferrioxalate complexes.

57

58 *Keywords: antipyrine; UV-LED; persulfate; ferrioxalate; pharmaceuticals; modelling*

59

60

61 1. INTRODUCTION

62

63 The consumption of pharmaceuticals compounds in last years has increased
64 considerably leading to the increase in their concentration in urban wastewaters [1- 3].
65 These compounds are known to be recalcitrant to biodegradation because of their
66 aromatic structure and their low solubility in water. So, they are only slightly degraded in
67 sewage wastewater treatment plants [4, 5]. For instance, antipyrine is a pharmaceutically
68 active compound detected in various natural environments [6, 7]. The percentage of
69 removal of antipyrine in effluents from conventional wastewater treatment plants is only
70 about 30% [8]. Therefore, an effective tertiary treatment for the removal of antipyrine
71 would be necessary.

72

73 Advanced Oxidation Processes (AOPs) are being proposed as valuable approaches for
74 pharmaceuticals pollutants wastewater treatment. It is well-known that the efficiency of
75 AOPs is based on the generation of highly reactive free radicals such as hydroxyl radicals
76 (HO^\bullet , $E_0 = 2.8 \text{ V}$) or sulfate radicals ($\text{SO}_4^{\bullet-}$, $E_0 = 2.6 \text{ V}$). HO^\bullet can be generated by various
77 combinations such as UV/ H_2O_2 , Fenton, photo-Fenton, ferrioxalate-based systems,
78 UV/ TiO_2 , UV/ O_3 or these processes in conjunction with ultrasound. Sulfate radicals can
79 be formed in AOPs based on systems with activated $\text{S}_2\text{O}_8^{2-}$ by UV light, transition metals,
80 hydrogen peroxide or ultrasound [9].

81

82 Several processes including direct photolysis and UV/ H_2O_2 [10, 11], Sono-photo-Fenton
83 [12], ferrioxalate-assisted solar photo-Fenton [12-14] have been investigated for the
84 removal of antipyrine.

85

86 Oxidation of antipyrine aqueous solution by UV-C/ $S_2O_8^{2-}$ [11] or by heat activated
87 persulfate [15] has also been reported in the scientific literature. The effectiveness of these
88 studies was examined in terms of antipyrine removal, but they have not reported data
89 about mineralization.

90

91 However, until now, UV-A LED lamps have not been used for the degradation of
92 antipyrine in AOPs. LEDs offer potential advantages over conventional UV lamps like
93 high efficiency, compactness, lower energy consumption, robustness, not overheating,
94 long life times, no disposal problems and no warm-up time [16, 17]. LEDs are
95 semiconductor p-n junction diodes, which, when activated, emit light due to electrons and
96 holes recombination (i.e. electroluminescence). Recombined electrons and holes become
97 more stable and release excess energy by emitting photons of the same frequency. A key
98 advantage of LEDs is that almost all electrical energy can be converted into
99 monochromatic light energy [16]. The light output is linearly proportional to the current
100 within its active region, so the light output can be precisely modulated to send an
101 undistorted signal through a fiber optic cable. A LED is a directional light source, with
102 the maximum emitted power in the direction perpendicular to the emitting surface [18].

103

104 The main objective of the present work was to optimize the degradation and
105 mineralization of an antipyrine aqueous solution by using a UV-A LED photo-Fenton
106 system using a LED lamp with a light peak emission wavelength at 365 nm. The
107 intensification of this photo-Fenton system with ferrioxalate was studied as it is a photo-
108 sensitive complex being 320-400 nm irradiation favorable for the ferrioxalate
109 photochemistry [19-20].

110 Additionally, the photolysis of ferrioxalate generates more H_2O_2 which, with
111 Fe(II) , yields more HO^\bullet radicals through the well-known Fenton reaction mechanism
112 [21,22], improving the degradation process. The addition of persulfate was also studied
113 to test the synergistic effect of its possible activation with ferrous ion and hydrogen
114 peroxide in this UV-A LED photo-Fenton process.

115

116 Experimental tests based on a Factorial Design were analyzed and results were
117 fitted using neural networks (NNs), which allowed the value of the Response Functions
118 (degradation of antipyrine or mineralization degree (mg L^{-1} TOC removed)) to be
119 estimated within the studied range as a function of the operating variables (1: initial
120 concentration of hydrogen peroxide, 2: initial concentration of Fe^{2+} , 3: initial
121 concentration of oxalic acid, 4: initial concentration of persulfate). The effects of the
122 variables on Response Functions were also determined.

123 Finally, the reaction kinetics and hydroxyl and sulfate radical contribution on the
124 mineralization reaction were also studied.

125

126 **2. EXPERIMENTAL**

127

128 **2.1. Materials and chemicals**

129

130 Antipyrine, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ (99%) (Fig. 1) was obtained from Acros. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$,
131 sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 99.5%) and tert-butyl
132 alcohol were purchased from Panreac. Hydrogen peroxide (30% w/v) was obtained from
133 Merck. Methanol was obtained from Sigma-Aldrich. All chemicals were used as received
134 without further purification.

135

136 The initial concentration of antipyrine was always 50 mg L⁻¹ (TOC= 35 mg L⁻¹).
137 For experimental runs focused on the evaluation of radical mechanism, tert-butyl alcohol
138 and methanol were added to the system as radical scavengers [23].

139

140 Figure 1

141 **2.2. UV-light emitting diodes (UV-A LED)**

142

143 The UV LED photosystem was developed with an indium gallium nitride (InGaN) LED
144 lamp (LZ4-00U600 LED ENGIN, USA) with a light peak emission wavelength at 365
145 nm (see Fig. S1, Supplementary Material). The nominal consumption of the LED lamp
146 was 1.80 W, for an applied current of 700 mA. The photon flux emission of UV-A-LED
147 was determined by potassium ferrioxalate actinometer and found to be 3.32×10^{-6}
148 Einstein s⁻¹.

149

150 **2.2. UV-A LED photocatalytic reactor**

151

152 The schematic diagram of the experimental system employed in this research is
153 shown in Fig. 2. A quartz protective plate is placed between the reactor and the UV-LED
154 lamp emitting at 365 nm. The volume of the reactor is 150 mL.

155 All experiments were carried out in a batch mode lab-scale photoreactor
156 illuminated with a UV-A LED lamp.

157

Figure 2

158 2.2. Experimental procedure

159

160 The experiments were carried out in the batch UV-A LED photoreactor indicated
161 above. The pH was adjusted to 2.8 with H₂SO₄ and NaOH solutions to avoid iron
162 precipitation. Then, FeSO₄·7 H₂O, oxalic, hydrogen peroxide and persulfate were directly
163 added to the photoreactor at the beginning of each experiment. All the experiments were
164 run at room temperature between 24 and 26 °C. For the duration of the tests, the samples
165 were periodically withdrawn from the reactor to obtain the residual concentrations of
166 antipyrine, total organic carbon (TOC), ferrous iron, hydrogen peroxide, persulfate and
167 dissolved oxygen.

168

169 Hydroxyl radical scavenging was accomplished using 1 M tert-butyl alcohol or
170 methanol to determine the contributions of the radical reactions to mineralization. Before
171 analysis, all samples were withdrawn from the reactor to determine their H₂O₂ contents
172 and were immediately treated with excess Na₂SO₃ (in solution) to prevent further
173 oxidation (this procedure was performed to avoid overestimating degradation).

174

175 2.3. Analysis

176

177 Analysis of antipyrine concentration was carried out by high-performance liquid
178 chromatography with UV detection (Agilent Technologies 1100 HPLC-UV) in isocratic
179 mode immediately after sampling. An Eclipse XDB-C18 column (5 μm, 4.6 × 250 mm)
180 was used with an 60:40 (v/v) methanol/(water with 0.1% acetic acid) mixture at acidic
181 pH as the mobile phase (detection wavelength, λ= 286 nm; flow rate of 0.6 ml min⁻¹).

182 The mineralization degree of treated wastewater was determined using a TOC analyzer
183 (TOC-5050 Shimadzu, standard deviation $< 0.2 \text{ mg L}^{-1}$). The H_2O_2 content in solution
184 was determined by Quantofix peroxide test strips (Sigma-Aldrich). The concentration of
185 soluble iron species during the mineralization reaction was measured
186 spectrophotometrically with 1,10-phenanthroline (according to ISO 6332) using a UV-
187 Vis spectrophotometer (HACH LANGE). Determination of residual $\text{S}_2\text{O}_8^{2-}$
188 concentrations in the presence of iron was performed according to the method of Liang
189 et al. [24]. Dissolved oxygen concentration was measured using a Jenway 9200 DO₂
190 meter. Experiments were conducted in triplicate and standard error was found to be
191 approximately 5%.

192

193 **2.4. Experimental design**

194

195 A Central-Composite Experimental Design was applied to investigate the effects of
196 four variables (1: initial concentration of hydrogen peroxide, 2: initial concentration of
197 Fe^{2+} , 3: initial concentration of oxalic acid, 4: initial concentration of persulfate) on the
198 chosen Response Functions (degradation of antipyrine and mineralization degree (mg L^{-1}
199 TOC removed)). The process design consisted of three series of experiments (Table 1):

200 (i) a factorial design with 2^k trials (all possible combinations of codified values
201 $+1$ and -1), which in the case of $k = 4$ variables consisted of 16 experiments
202 (1-16)

203 (ii) selection of the axial distance of the star points (codified values $\alpha = 2^{k/4} = \pm 2$)
204 consisting of $2k = 8$ experiments (experiments 17-24), and

205 (iii) replicate of the central point (three experiments, 25-27).

206 The complete experimental design and additional experiments, including variable
207 ranges and obtained Response Functions values, are also shown in Table 1.

208 Table 1

209

210 **2.5. Neural-network strategy**

211

212 The neural network applied in this work was solved with two neurons, using a
213 simple exponential activation function and a solution strategy based on a back-
214 propagation algorithm [25, 26]. Parameters were fitted using the Solver tool in a custom
215 spreadsheet in Microsoft Excel using a nonlinear fitting method. The input variables in
216 this study were 1) initial concentration of hydrogen peroxide, 2) initial concentration of
217 Fe^{2+} , 3) initial concentration of oxalic acid, 4) initial concentration of persulfate. The
218 chosen response functions were A) degradation of antipyrine and B) mineralization
219 degree (mg L^{-1} TOC removed). The effects of the studied variables on the response
220 functions were also evaluated. Finally, a measure of the saliency of the input variables
221 was made based on the connection weights of the neural networks. This study analyzed
222 the relevance of each variable with respect to the others (expressed as percentages).

223

224 **3. RESULTS AND DISCUSSION**

225 **3.1 Preliminary study**

226 An initial comparative study on the degradation of 50 mg L^{-1} antipyrine aqueous solution
227 at pH 3 under different single systems such as UV-A-LED, H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ was done.
228 Taking into account the results, we could conclude that the antipyrine degradation via
229 direct photolysis using UV-A-LED light was very inefficient (5%). On the other hand,

230 hydrogen peroxide or persulfate anion alone insignificantly affected the degradation of
231 the antipyrine which confirmed that the direct or molecular reactions between these
232 oxidant species and the possible compounds present in the antipyrine solution did not
233 occur or had slow oxidative kinetics. In these single systems, possible oxidative
234 intermediate species (mainly hydroxyl radicals) were not generated either.

235

236 Taking into account the results from this preliminary study, a central-composite
237 experimental design was applied to optimize the ferrioxalate-induced photo-Fenton
238 process under UV-A-LED and with addition of persulfate, as this catalytic system could
239 offer a practical alternative for the destruction of this type of contaminants.

240

241 **3.2 Ferrioxalate system kinetics evaluation**

242 In the ferrioxalate assisted UV-A-LED photo-Fenton reaction with persulfate
243 addition, the antipyrine degradation followed pseudo-first-order kinetics with respect to
244 the antipyrine concentration, as follows:

$$245 \quad -r = -\frac{dC_{AP}}{dt} = k_{AP}C_{AP} \quad (1)$$

246 where r is the reaction rate, C_{AP} is the concentration (mg L^{-1}) of antipyrine at a given time,
247 t (min) and k_{AP} is the pseudo-first-order degradation rate constant (min^{-1}). This equation
248 can be integrated between $t = 0$ and $t = t$, yielding:

$$249 \quad \ln \frac{C_{AP}}{(C_{AP})_o} = -k_{AP}t \quad (2)$$

250 where $(C_{AP})_o$ is the initial concentration of antipyrine. According to this expression, a plot
251 of the first term versus “ t ” must yield a straight line satisfying Eq. (2) with slope k_{AP} .

252

253 3.3. NNs fitting

254

255 The experimental results obtained for the response functions [A) pseudo-first-order
256 kinetic rate constant of antipyrine degradation (k_{AP} , min^{-1}) and B) %TOC removal of
257 antipyrine aqueous solution] under the UV-A LED photo-Fenton process intensified with
258 ferrioxalate and with addition of persulfate (shown in Table 1) were fitted with NNs,
259 resulting in an average error of less than 15% in both cases. The equation and fitting
260 parameters are shown in Table 2. N1 and N2 are general factors related to the first and
261 the second neurons, respectively. W11 to W14 are the contribution parameters to the first
262 neuron and represent the influence of each of the four variables in the process: 1) initial
263 concentration of hydrogen peroxide, 2) initial concentration of Fe^{2+} , 3) initial
264 concentration of oxalic acid, 4) initial concentration of persulfate, respectively. W21 to
265 W24 are the contributions to the second neuron corresponding to the same variables.

266

Table 2

267 The results of a saliency analysis on the input variables for each neural network
268 (%) are also shown in Table 2. From these results, it was possible to deduce the effect of
269 each parameter on the response function. Thus, it was confirmed that both the antipyrine
270 degradation and the mineralization of solution under the UV-A LED photo-Fenton
271 process intensified by ferrioxalate and with addition of persulfate process was mainly
272 influenced by the initial concentration of persulfate (although with negative effect) and
273 by the initial concentration of the catalyst Fe^{2+} (positive effect), as will be explained
274 below.

275

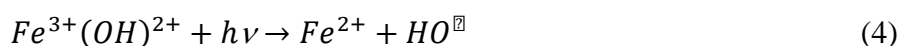
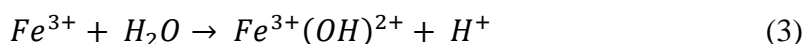
276 3.4. Antipyrine degradation and mineralization study

277

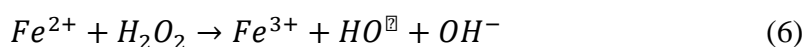
278 Equation and parameters shown in Table 2 enabled a simulation analysis of the
279 effects of the studied variables on the value of the two chosen Response Functions, 1) the
280 pseudo-first-order kinetic rate constant of antipyrine degradation (k_{AP}) and 2) %TOC
281 removal. Figs. 3 and 4 show the effects of the four variables (initial concentrations of
282 hydrogen peroxide, Fe^{2+} , oxalic acid and persulfate) on k_{AP} and TOC removal,
283 respectively. Figs. 3abc and 4abc show results corresponding to center point operating
284 conditions and Figs. 3d and 4d show results that would be obtained under the selected
285 optimal conditions using NNs.

286

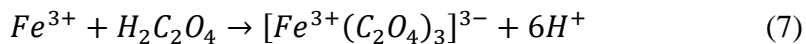
It was found that both Fe^{2+} and oxalic had a positive effect on both k_{AP} and %TOC removal over the studied range. This could be due to the continuous regeneration of Fe^{2+} via photoreduction of Fe^{3+} with 365 nm UV-A-LED light and generation of hydroxyl radicals according to Eqs. (3) and (4):



Ferric ions were formed by the oxidation of ferrous ion (added as $FeSO_4$) by dissolved oxygen (Eq. (5)) and by Fenton reaction (Eq. (6)) also generating superoxide radical anion and hydroxyl radicals as follows:



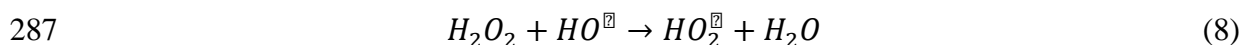
On the other hand, ferrioxalate is formed *in situ* by reaction between oxalic acid and Fe^{3+} as indicated in Eq.(7) and extra hydroxyl radicals are generated by ferrioxalate photochemistry as previously reported [27].



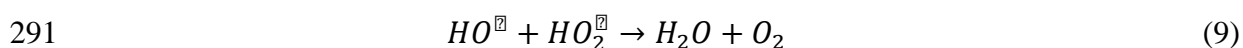
Figs. 3d and 4d show that both the antipyrine degradation constant (k_{AP}) and mineralization degree (% TOC removal) increased with the $[H_2C_2O_4]/[Fe]$ molar ratio up to 3, because at an $[H_2C_2O_4]/[Fe]$ molar ratio of 3, the Fe^{3+} ions were complexed with the maximum amount of oxalate, in the form of the saturated complex $Fe(C_2O_4)_3^{3-}$ (ferric complexed with three oxalate molecules as its limit load). As it can be seen in Figs. 3d and 4d, the optimal $[H_2C_2O_4]/[Fe]$ molar ratio is $100 \text{ mg L}^{-1} H_2C_2O_4/20 \text{ mg L}^{-1} Fe \llcorner 1.11 \text{ mM } H_2C_2O_4/0.36 \text{ mM } Fe (\approx 3)$. However, when the molar ratio is below 3, insufficient oxalate amount is present, and some of the ferric ions can precipitate as $Fe(OH)_3$, reducing the yield of Fe^{2+} ion regeneration. An excess of oxalate could act as an additional organic compound and so compete the HO^\bullet radicals with antipyrine and intermediates reducing the mineralization efficiency.

However, as it is shown in Figs. 3a and 3c, the optimal initial concentration of hydrogen peroxide over the studied range was the minimal value, 100 mg L^{-1} . In a preliminary study using H_2O_2 concentrations below this value lower k_{AP} values were obtained (see Table S1, Supplementary Material). This could be justified because ferrioxalate photochemistry provides extra sources of oxidant H_2O_2 and catalyst Fe^{2+} for the Fenton reaction to yield more HO^\bullet radicals [27, 28]. It is well-known that an increase in H_2O_2 concentration produces a higher amount of HO^\bullet radicals by Fenton reaction. However, an excess of hydrogen peroxide reduces catalytic activity since it favours

reaction (8) with a very high kinetic constant, $k= 4.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$, (where HO^\bullet reacts with peroxide), reducing the amount of radicals available to destroy antipyrine and producing the well-known *scavenger effect*.



288 Although other radicals (HO_2^\bullet) are produced, their oxidation potential is much
289 smaller than that of the hydroxyl radicals. Additionally, decomposition of hydrogen
290 peroxide to form water and oxygen is also favoured by Eqs (8) and (9).



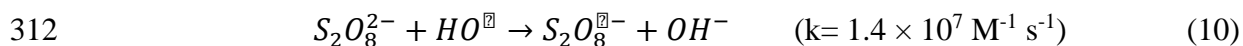
292 As shown in Figs. 3c, 3d, 4c and 4d, an increase in the concentration of oxalic
293 acid, up to 100 mg/L, resulted in a significant positive effect on antipyrine degradation
294 (Figs. 3c and 3d), while this increase merely affected process efficiency in terms of
295 intermediates' mineralization (Figs. 4c and 4d). These findings indicate that oxalic acid
296 addition plays an essential role during the first step of the degradation reaction, when
297 antipyrine oxidation takes place. Antipyrine was always totally degraded in less than 15
298 min. It was also reflected in the salience analysis (%) shown in Table 2.

299

300 With respect to the effect of persulfate on reaction, we can see in Figs. 3a and 4a
301 that it has a negative effect on both the antipyrine degradation constant and mineralization
302 degree practically in the overall studied range. This demonstrated that no persulfate
303 activation took place possibly due to two reasons: (a) the UV-A LED lamp emitted at 365
304 nm while persulfate absorbs light below 288 nm and so it could not be activated with UV-
305 A LED, and (b) persulfate was not activated by Fe^{2+} either, due to the fast conversion of
306 ferrous into ferric and formation of ferrioxalate complexes. On the other hand, when
307 initial persulfate concentration increased, the *scavenger effect* capturing hydroxyl radical

308 increased according to Eq (10) [29] decreasing the availability of HO• and so the
309 degradation efficacy. So, persulfate was not necessarily used in this ferrioxalate-
310 photochemistry-based system.

311



313

314 3.5. Reaction analysis

315

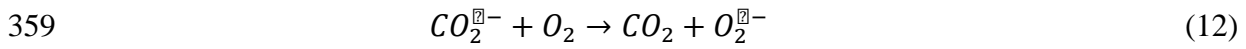
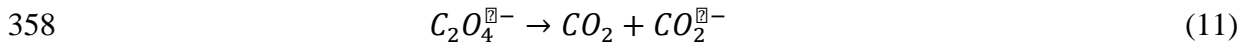
316 Fig. 5 shows the evolution of antipyrine, TOC and dissolved oxygen concentrations along
317 the reaction (average values of three replicated experiments) under the optimal operating
318 conditions selected by Factorial Design and NNs. Under these conditions ($[H_2O_2]_0= 100$
319 mg L^{-1} , $[Fe^{2+}]_0= 20 \text{ mg L}^{-1}$, $[H_2C_2O_4]_0= 100 \text{ mg L}^{-1}$, $[S_2O_8^{2-}]_0= 0 \text{ mg L}^{-1}$, temperature=
320 $24\text{-}26^\circ\text{C}$, $\text{pH}= 2.8$) antipyrine was fully degraded in 2.5 min and 93% TOC removal was
321 achieved in approximately 60 min. It was observed that mineralization degree reached in
322 the presence of UV-LED was higher than that obtained in our previous study on
323 antipyrine degradation using the ferrioxalate-assisted solar photo-Fenton process under
324 optimal conditions (83% TOC removal in 60 min). A comparison of the two alternative
325 processes is difficult because the irradiation sources and used reactors geometry are
326 different. The higher efficiency of the UV-LED system may be attributed to the fact that
327 UV-LED system emits monochromatic irradiation at 365 nm, which is very close to the
328 maximum absorbance wavelength of ferrioxalate complexes (see Fig. S2, Supplementary
329 Material). The value of the pseudo-first-order kinetic rate constant of antipyrine
330 degradation, k_{AP} , calculated from the results in optimal conditions was 1.50 min^{-1} . This
331 was the value predicted by the model shown in Fig. 3d. However, the mineralization

332 degree obtained, 93%, was different than the model predicted ($\cong 99\%$) shown in Fig. 4d.
333 It could be explained because the mathematic model did not take into account the possible
334 formation of intermediates refractory towards hydroxyl radicals and subsequently stop of
335 mineralization reaction. As it is shown, TOC abatement curve corresponding to the
336 intermediates degradation linearly decreased during the first 15 min while it only slightly
337 decreased and remained constant above around 25 min being 93% TOC removal attained
338 (Final concentration of TOC= 6 mg L⁻¹). This indicated that intermediates generated from
339 antipyrine aqueous solution degradation by ferrioxalate assisted UV-A-LED photo-
340 Fenton reaction were refractory towards hydroxyl radicals. This is in agreement with our
341 previous study about 50 mg L⁻¹ antipyrine solution mineralization under a sono-photo-
342 Fenton process where the main oxidative intermediate species was also hydroxyl radical
343 [30] and the residual TOC was 6.1 mg L⁻¹. In this ferrioxalate UV-A-LED system, where
344 mineralization was mainly attributed to hydroxyl radicals, as will be explained below,
345 different intermediates such as 2-butenedioic acid, butanedioic acid, 4-oxo-pentanoic
346 acid, acetate and formate can be formed in the last step of reaction. These compounds
347 cannot be degraded by HO• radicals or their reaction is very slow, as previously reported
348 [31].

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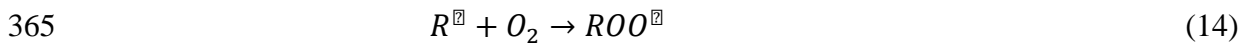
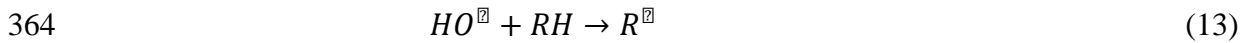
351 With respect to dissolved oxygen, once the reaction began, dissolved oxygen quickly
352 decreased to below 1.5 mg L⁻¹ during the first 20 min. After that, dissolved oxygen slowly
353 increased to 2 mg L⁻¹ and then it remained constant. It could be explained because the
354 photolysis of ferrioxalate generates oxalyl radical anion, C₂O₄•⁻, which subsequently
355 undergoes a rapid decarboxylation to form a carbon dioxide radical anion, CO₂•⁻, which
356 consumes oxygen [32].

357



360

361 On the other hand, hydroxyl radical generated from ferrioxalate photochemistry reacts
362 with organic molecule to form radicals, R^\bullet , that consumes oxygen generating peroxo-
363 organic radicals, ROO^\bullet [33].



366

367 The small increase of dissolved oxygen above 20 min could be due to the higher
368 importance of oxygen generation by Eq (9) and decomposition of peroxide into water and
369 oxygen.

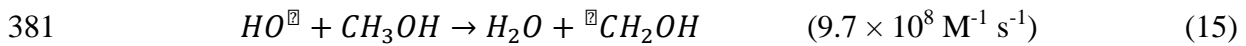
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371 **3.6 Investigation of the free radical mechanism in the ferrioxalate assisted UV-A-**
372 **LED photo-Fenton system**

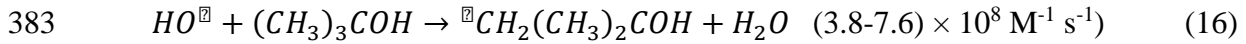
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374 In order to explain the probable contribution of hydroxyl radicals in this treatment, the
375 degradation of antipyrine was evaluated either in the absence or in the presence of
376 appropriate quenchers of HO^\bullet . Quenching studies were performed by adding a radical
377 scavenger such as tert-butyl alcohol and methanol. HO^\bullet reacts slightly faster with
378 methanol than with tert-butyl alcohol according to Eqs (15) and (16), respectively [34,
379 35]

380



382



384

385 Fig. 6 shows the antipyrine abatement curve under the optimal operating conditions in the
386 presence and absence of 1M tert-ButOH/Methanol. As it can be seen, the degradation of
387 antipyrine in the presence of both scavengers was practically negligible, indicating that
388 mainly hydroxyl radicals were involved in the degradation reaction. At the beginning of
389 the reaction with tert-butyl alcohol, we can see a slight increase in the degradation because
390 the reaction rate between the HO• and tert-butyl alcohol is lower than with methanol, and
391 so the hydroxyl radical is slower in being scavenged, as indicated above.

392

393 Fig. 6 also shows the evolution of dissolved oxygen concentration when methanol or tert-
394 butyl alcohol were added. A quick decrease of oxygen was observed at the beginning
395 while antipyrine concentration decreased by HO• not scavenged during the first 4 min, as
396 indicated above. Once hydroxyl radical availability was totally reduced by alcohols and
397 degradation of antipyrine was ceased, the concentration of dissolved oxygen continuously
398 increased up to values close to saturation by Eq (9) and decomposition of peroxide into
399 water and oxygen.

400

401 **4. CONCLUSIONS**

402

403 Intensification of UV-A-LED photo-Fenton reaction with ferrioxalate complexes
404 showed promising results in the elimination of antipyrine as a model compound of
405 emerging pollutants. The iron/oxalic acid molar ratio plays an important role on
406 degradation and mineralization of antipyrine solutions, being 3 the optimal ratio. Under
407 the optimal operating conditions ($[\text{H}_2\text{O}_2]_0 = 100 \text{ mg L}^{-1}$, $[\text{Fe}]_0 = 20 \text{ mg L}^{-1}$ and $[\text{H}_2\text{C}_2\text{O}_4]_0 =$
408 100 mg L^{-1} , $\text{pH} = 2.8$, $T = 24\text{-}26^\circ\text{C}$) the complete degradation of antipyrine and 93% TOC
409 removal were reached in 2.5 and 60 min, respectively. Antipyrine degradation kinetics
410 follows a pseudo-first-order model. Hydroxyl radicals were found to be the main
411 responsible species in the reaction. In the last step of reaction, different generated
412 intermediates cannot be degraded by HO^\bullet radicals or their reaction is very slow. This
413 ferrioxalate-mediated system reduces the amount of H_2O_2 needed (100 mg L^{-1}) for
414 antipyrine degradation and persulfate was not necessary because it could not be activated
415 with UV-A LED nor with Fe^{2+} since it is quickly converted to Fe^{3+} which did not react
416 with persulfate but formed ferrioxalate complexes.

417 This ferrioxalate-photochemistry-based UV-A-LED oxidation system is a potential
418 alternative to degrade wastewater containing emerging contaminants such as antipyrine.

419

420 **5. ACKNOWLEDGEMENTS**

421 Financial support from MINECO (CTM2013-44317-R) is gratefully acknowledged.

422

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Figure captions:

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Figure 1: Structure and properties of antipyrine.

559

560 **Figure 2:** Schematic diagram of UV-LED reactor (1: magnetic stirrer, 2: stirring bar, 3:
561 glass reactor, 4: quartz plate, 5: LED emitter, 6: heat sink, 7: cable connection to DC
562 power supply).

563

564

Figure 3: Degradation of Antipyrine aqueous solution in a UV-A LED photo-Fenton system intensified by ferrioxalate and with addition of persulfate. Reaction time: 60 min, temperature= 24-26°C. a) Effects of initial concentrations of Fe^{2+} and $\text{S}_2\text{O}_8^{2-}$; b) Effects of initial concentrations of Fe^{2+} and H_2O_2 ; c) Effects of initial concentrations of H_2O_2 and $\text{H}_2\text{C}_2\text{O}_4$; d) Effects of initial concentrations of Fe^{2+} and $\text{H}_2\text{C}_2\text{O}_4$. [a,b,c: Center point operating conditions; d: Optimal operating conditions].

565

Figure 4: Mineralization of antipyrine aqueous solution in a UV-A LED photo-Fenton system intensified by ferrioxalate and with addition of persulfate. Reaction time: 60 min, temperature= 24-26°C. a) Effects of initial concentrations of Fe^{2+} and $\text{S}_2\text{O}_8^{2-}$; b) Effects of initial concentrations of Fe^{2+} and H_2O_2 ; c) Effects of initial concentrations of H_2O_2 and $\text{H}_2\text{C}_2\text{O}_4$; d) Effects of initial concentrations of Fe^{2+} and $\text{H}_2\text{C}_2\text{O}_4$. [a,b,c: Center point operating conditions; d: Optimal operating conditions].

566

567 **Figure 5:** Evolution of antipyrine, TOC and dissolved oxygen concentrations along the
568 reaction under the optimal operating conditions: ($[\text{H}_2\text{O}_2]_0 = 100 \text{ mg L}^{-1}$, $[\text{Fe}^{2+}]_0 = 20 \text{ mg}$
569 L^{-1} , $[\text{H}_2\text{C}_2\text{O}_4]_0 = 100 \text{ mg L}^{-1}$, $[\text{S}_2\text{O}_8^{2-}]_0 = 0 \text{ mg L}^{-1}$, temperature= 24-26°C, pH= 2.8).

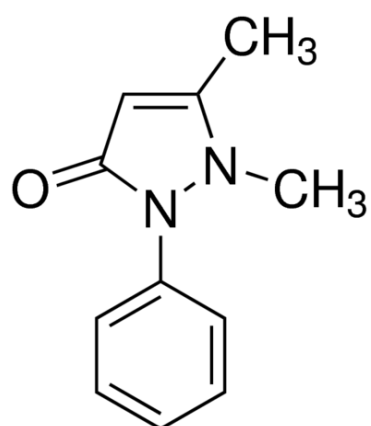
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571 **Figure 6:** Antipyrine and TOC abatement and dissolved oxygen curves under the optimal
572 operating conditions in the presence and absence of 1M tert-ButOH/Methanol. Operating
573 conditions: ($[\text{H}_2\text{O}_2]_0 = 100 \text{ mg L}^{-1}$, $[\text{Fe}^{2+}]_0 = 20 \text{ mg L}^{-1}$, $[\text{H}_2\text{C}_2\text{O}_4]_0 = 100 \text{ mg L}^{-1}$, $[\text{S}_2\text{O}_8^{2-}]_0 =$
574 0 mg L^{-1} , temperature = 24-26°C, pH = 2.8).

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580 Formula: C₁₁H₁₂N₂O

581 Molecular weight: 188.23 g mol⁻¹

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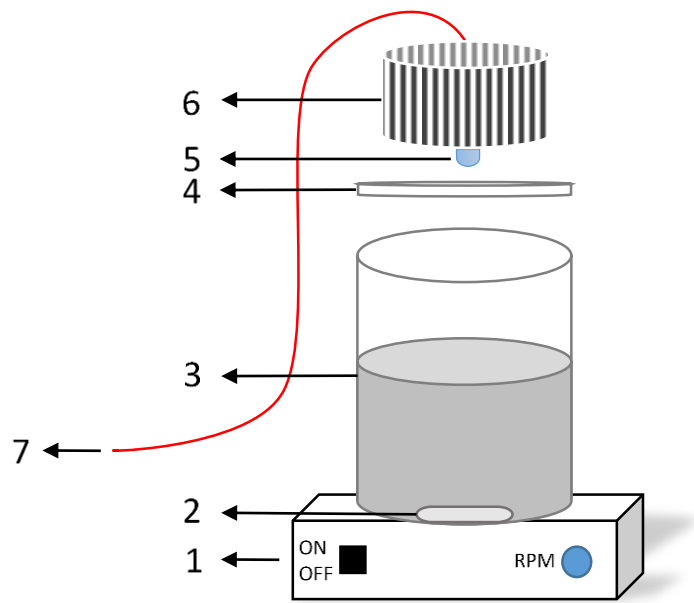
Molecular structure

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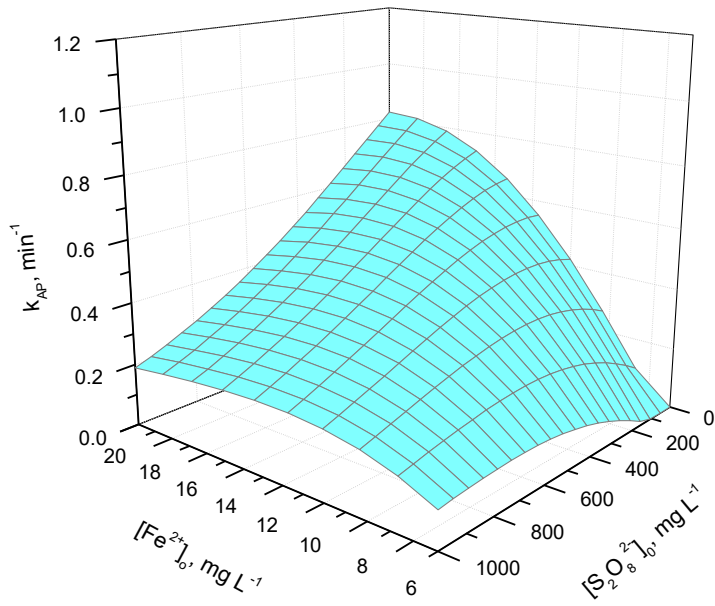


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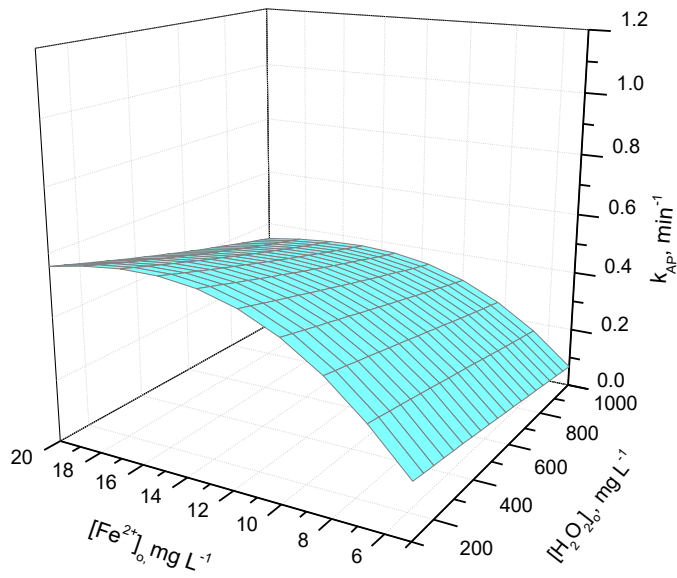
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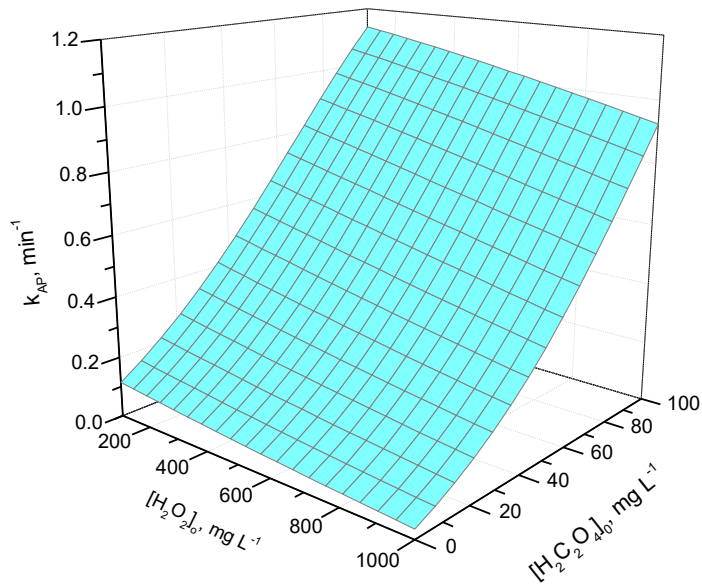
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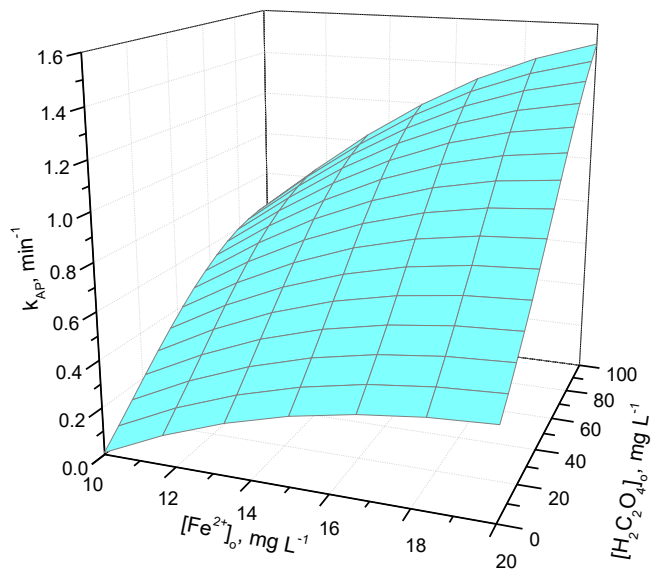
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c)

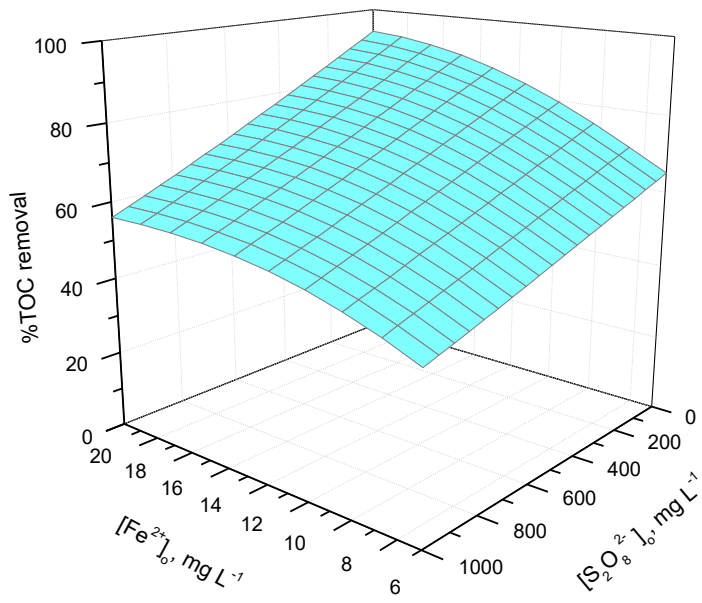
d)

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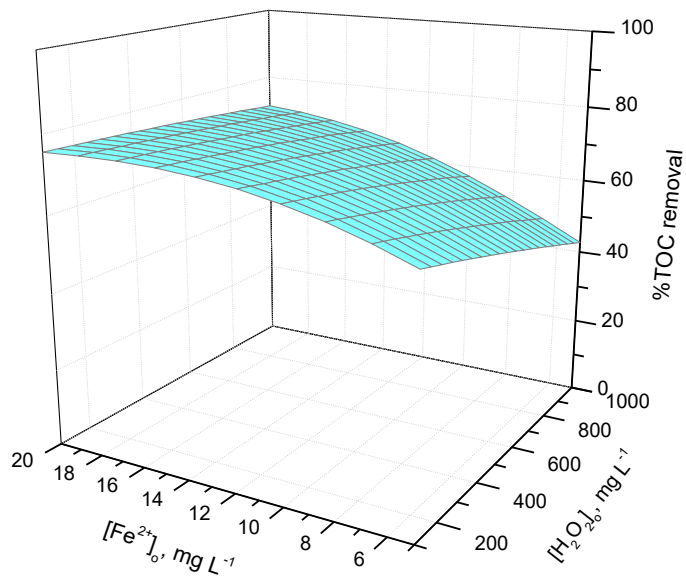
602 **Figure 3.**

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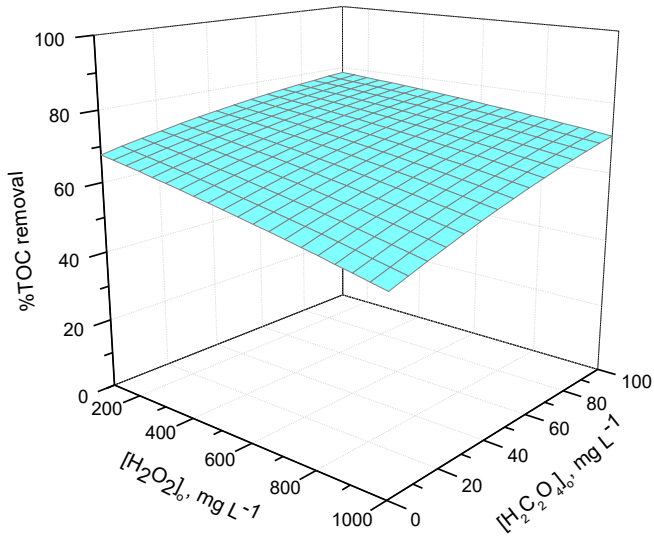
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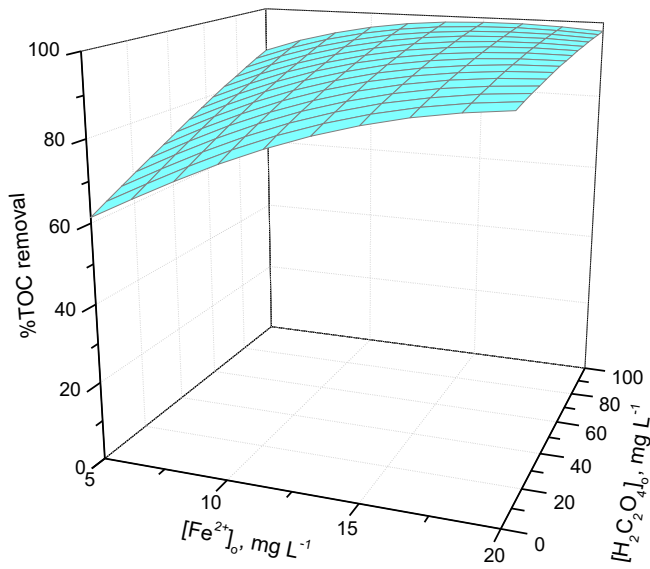
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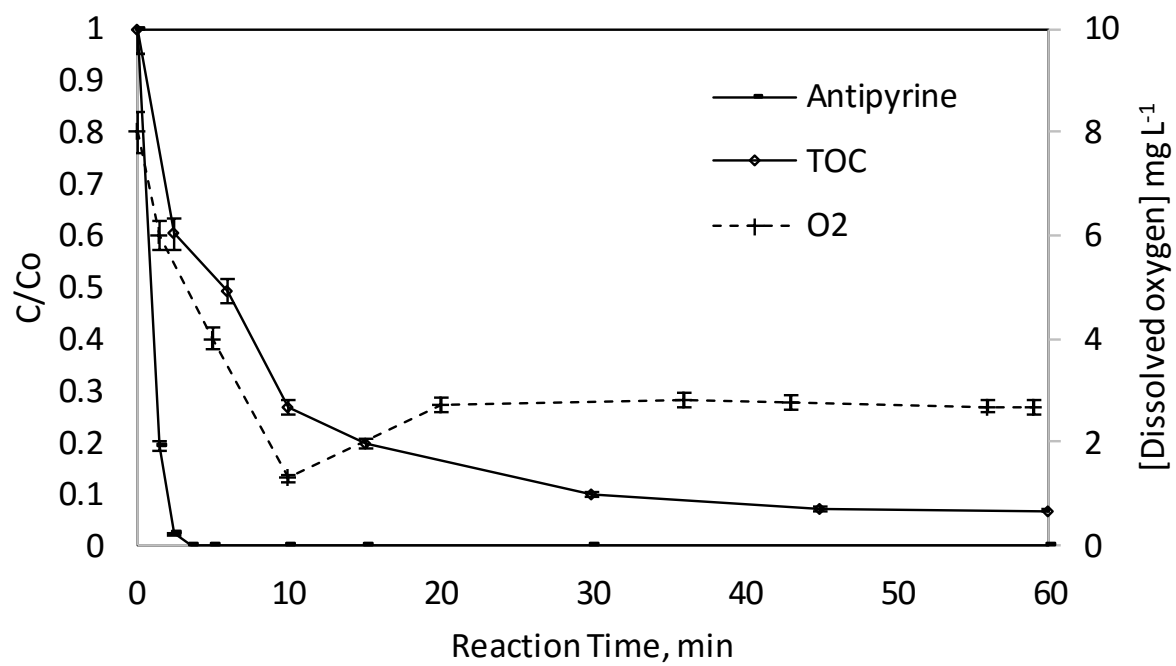
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615 **Figure 4.**

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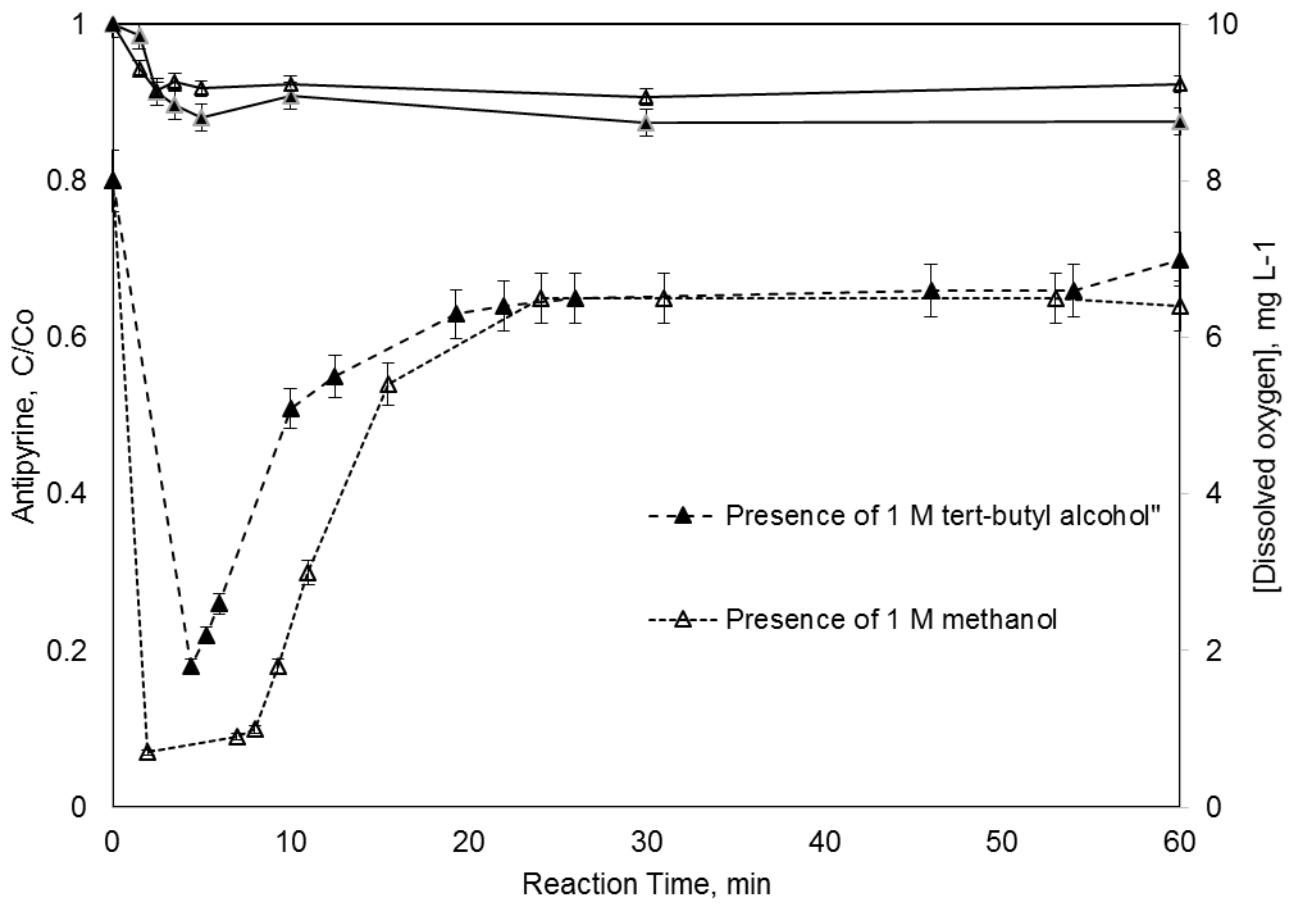
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623 **Figure 5.**

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631 **Figure 6.**

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636 **Table 1. The 4-factor Central Composite Experimental Design Matrix. Degradation**
 637 **and mineralization of an Antipyrine aqueous solution by UV-LED photo-Fenton**
 638 **intensified by ferrioxalate with addition of persulfate. [TOC]₀= 35 mg L⁻¹; pH: 2.8;**
 639 **UV-A LED lamp (11 W; λ= 365 nm).**

640

FACTORIAL DESIGN					Response Functions	
Experiment	[H ₂ O ₂] ₀ , mg L ⁻¹	[Fe (II)] ₀ , mg L ⁻¹	[H ₂ C ₂ O ₄] ₀ , mg L ⁻¹	[S ₂ O ₈ ²⁻] ₀ , mg L ⁻¹	k _{AP} , min ⁻¹	Mineralization degree, %
1	775	16.25	75	750	0.500	62.33
2	325	16.25	75	750	0.612	66.92
3	775	8.75	75	750	0.487	57.05
4	325	8.75	75	750	0.595	63.11
5	775	16.25	25	750	0.233	62.51
6	325	16.25	25	750	0.202	67.02
7	775	8.75	25	750	0.083	46.56
8	325	8.75	25	750	0.120	58.93
9	775	16.25	75	250	0.895	82.37
10	325	16.25	75	250	1.060	86.59
11	775	8.75	75	250	0.455	70.99
12	325	8.75	75	250	0.672	82.30
13	775	16.25	25	250	0.291	75.82
14	325	16.25	25	250	0.377	79.92
15	775	8.75	25	250	0.112	63.41
16	325	8.75	25	250	0.154	73.63
17	1000	12.5	50	500	0.349	64.35
18	100	12.5	50	500	0.346	67.95
19	550	20	50	500	0.551	74.07
20	550	5	50	500	0.123	51.73
21	550	12.5	100	500	1.040	74.87
22	550	12.5	0	500	0.067	57.62
23	550	12.5	50	1000	0.403	60.11
24	550	12.5	50	0	0.612	81.86
25	550	12.5	50	500	0.432	63.38
26	550	12.5	50	500	0.431	63.80
27	550	12.5	50	500	0.431	63.54
Coded levels		Natural levels				
(+α)	1000	20	100	1000		
(-α)	100	5	0	0		
(+1)	775.00	16.25	75.00	750.00		
(-1)	325.00	8.75	25.00	250.00		
(0)	550	12.5	50	500		
ADDITIONAL EXPERIMENTS						
28 ^a	100	20	100	0	1.51	93.00
29 ^b	100	20	100	0	0.016	-
30 ^c	100	20	100	0	0.028	-

641 ^a: Optimal conditions642 ^b: Optimal conditions in the presence of methanol643 ^c: Optimal conditions in the presence of tert-butyl alcohol

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Table 2. Equation and parameters of Neural Network fittings for the two Response Functions: 1) pseudo-first order kinetic rate constant of antipyrine degradation 2) Mineralization Degree of Antipyrine aqueous solution. UV-A LED photo-Fenton system intensified by ferrioxalate with persulfate addition.

Equation*

$$\text{Response Function} = N_1 \times (1/(1+1/\text{EXP}([\text{H}_2\text{O}_2]_o) \times W_{11} + ([\text{Fe}(\text{II})]_o) \times W_{12} + ([\text{H}_2\text{C}_2\text{O}_4]_o) \times W_{13} + ([\text{S}_2\text{O}_8^{2-}]_o) \times W_{14})) + N_2 \times (1/(1+1/\text{EXP}([\text{H}_2\text{O}_2]_o) \times W_{21} + ([\text{Fe}(\text{II})]_o) \times W_{22} + ([\text{H}_2\text{C}_2\text{O}_4]_o) \times W_{23} + ([\text{S}_2\text{O}_8^{2-}]_o) \times W_{24}))$$

Weight factors	Parameter	Values of neurons and factors	
		$k_{\text{AP}}, \text{min}^{-1}$	%TOC removal
N₁	Neuron	-3.6600	-1.3037
W ₁₁	[H ₂ O ₂] _o	-0.3770	0.7156
W ₁₂	[Fe(II)] _o	-2.4656	-2.066
W ₁₃	[H ₂ C ₂ O ₄] _o	0.7370	-1.026
W ₁₄	[S ₂ O ₈ ²⁻] _o	-1.9863	-0.832
N₂	Neuron	2.7738	2.5320
W ₂₁	[H ₂ O ₂] _o	-0.5871	0.024
W ₂₂	[Fe(II)] _o	-1.1411	-0.3002
W ₂₃	[H ₂ C ₂ O ₄] _o	2.2131	-0.0696
W ₂₄	[S ₂ O ₈ ²⁻] _o	-2.0302	-0.8043

* Parameter values in equation must be previously normalized to the (0.1) interval

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Saliency analysis of the input variables for the neural network (%).

Neural network output	Parameters			
	[H ₂ O ₂] _o	[Fe(II)] _o	[H ₂ C ₂ O ₄] _o	[S ₂ O ₈ ²⁻] _o
k_{AP}, min⁻¹	8.30	31.70	25.15	34.84
%TOC removal	8.74	34.78	13.97	42.52

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668 **Appendix A. Supplementary Information**

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670 **Degradation and Mineralization of Antipyrine by UV-A LED Photo-Fenton**

671 **Reaction Intensified by Ferrioxalate with Addition of Persulfate**

672

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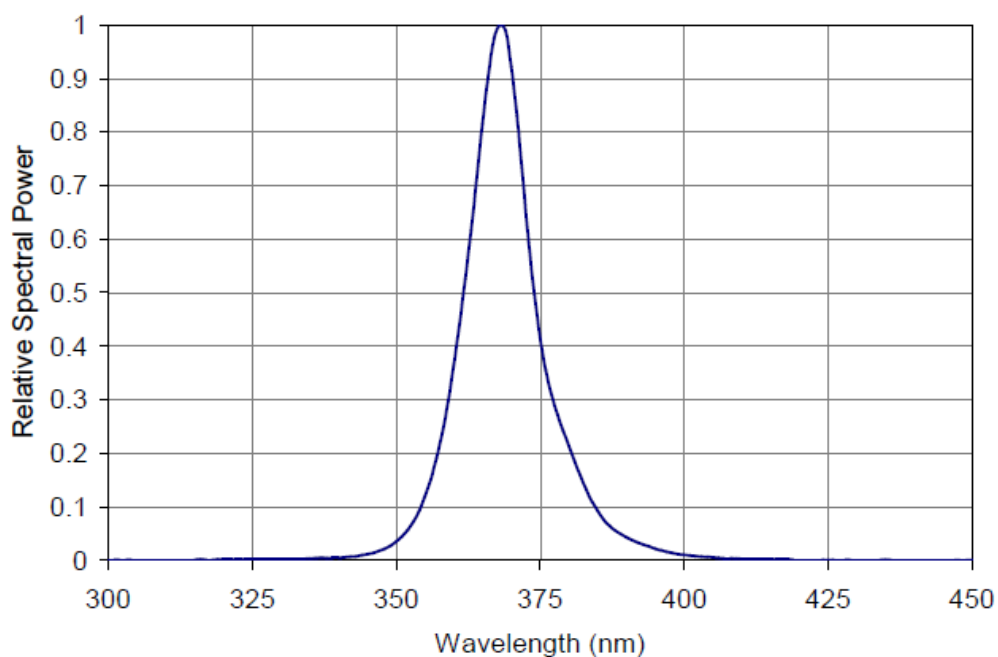


Fig. S1: Typical Relative Spectral Power Distribution

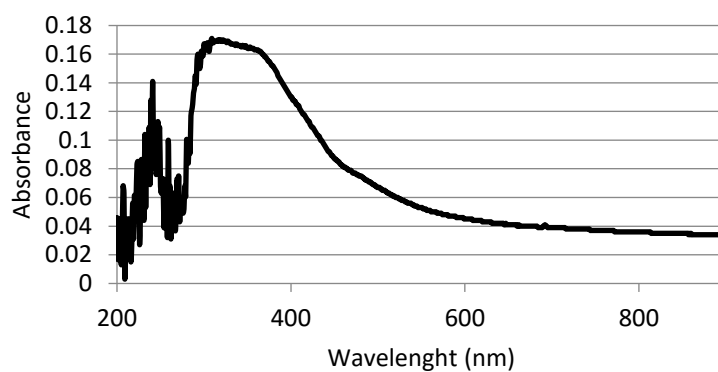
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724 Table S1. Preliminary study of degradation of an Antipyrine aqueous solution by UV-
725 LED photo-Fenton intensified by ferrioxalate with addition of persulfate. $[\text{TOC}]_0 = 35$
726 mg L^{-1} ; pH: 2.8; UV-A LED lamp (11 W; $\lambda = 365 \text{ nm}$).

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<i>Preliminary study</i>					
Experiment	$[\text{H}_2\text{O}_2]_0,$ mg L^{-1}	$[\text{Fe (II)}]_0,$ mg L^{-1}	$[\text{H}_2\text{C}_2\text{O}_4]_0,$ mg L^{-1}	$[\text{S}_2\text{O}_8^{2-}]_0,$ mg L^{-1}	$k_{\text{AP}}, \text{min}^{-1}$
P-1	100	12.5	50	500	0.346
P-2	90	12.5	50	500	0.302
P-3	70	12.5	50	500	0.248
P-4	50	12.5	50	500	0.113
P-5	20	12.5	50	500	0.014

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Figure S2: Absorption spectra of ferrioxalate solution

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