1   **Modeling the photo-Fenton oxidation of the pharmaceutical paracetamol in**
2   **water including the effect of photon absorption (VRPA)**
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19 **Abstract**

20 A new model is proposed for the photo-Fenton oxidation of water contaminants

21 including the effect of photon absorption (volumetric rate of photon absorption, VRPA),

22 the effect of the geometry of the reactor and the illuminated volume to total volume

23 ratio (R_i) in the reaction system. Fe(III) was found to be the main species in the aqueous

24 solution responsible for photon absorption provided that hydrogen peroxide was not

25 totally consumed. Paracetamol was used as model pollutant at a concentration of 1 mM

26 to validate the model. The illuminated part of the raceway reactor configuration (total

27 length of 80 cm) was operated at two liquid depths (5.0 and 2.5 cm) equivalent to two

28 irradiated reactor volumes (2 and 1 L) and using R_i ratios in the range 0.30-0.65, which

29 changed the dark reactor volume. These values are commonly found in photo-Fenton

30 pilot plants for water treatment and purification. The model successfully fitted the

31 temporal evolution of the dissolved oxygen (O_2) and the hydrogen peroxide (H_2O_2)

32 concentrations and the evolution of the total organic carbon (TOC) in solution in both

33 reactor geometries and for different illuminated volume to total volume ratios. The

34 model can be easily extended to model other water contaminants and provides a robust

35 method for process design, process control and optimization.

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37 **Keywords:** *photo-Fenton, modeling, VRPA, paracetamol, photoreactor.*

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1. Introduction

Advanced oxidation processes (AOPs) which are based on the production of highly reactive hydroxyl radicals are effective methods for the degradation and mineralization of recalcitrant contaminants in water and wastewater [1]. Amongst these, AOPs driven by the absorption of photons such as heterogeneous photocatalysis with organic sensitizers and/or semiconductor oxides (mainly TiO_2) and the photo-Fenton process [3-5], can be powered by solar light irradiation. Obvious technological and environmental benefits [2] for these AOPs include a net cost reduction of the treatment process and the utilization of a green and sustainable source of energy.

The photo-Fenton process entails the reaction of iron salts and hydrogen peroxide in the presence of UV-vis radiation, which primarily produces hydroxyl radicals while photocatalytically regenerating Fe^{3+} to Fe^{2+}. The optimum pH is 2.8 [5] and to prevent the precipitation of the dissolved iron salts, the pH should be less than 4. Several scientific and technological aspects of the photo-Fenton process have been thoroughly studied at both laboratory and pilot-plant scale including: the type and nature of contaminants, the impact of the iron species, hydrogen peroxide and interfering species, methods for heterogenization and recovery of the catalyst and the economics of the process [6-9]. Despite this extensive body of knowledge on the photo-Fenton process, the mathematical modeling of the treatment process is still under development, which contrasts with other AOPs. Only a few models have been proposed using a simplified elementary reaction mechanisms or empirical approaches [10-14]. The complexity of the chemical reactions involved and the evolution of the organic matter present during the process are probably the most important reasons.

Photo-catalytically generated radicals can react with organic matter, with hydrogen peroxide or with other radicals. These parallel reactions in some cases generate oxygen, whilst others consume oxygen. Therefore, changes in the reaction dynamics of the photo-Fenton process are reflected by the evolution of the concentration of dissolved oxygen (O_2), becoming a robust and easily measurable indicator to follow the efficiency of the photo-Fenton process [15]. The modeling and monitoring of the evolution of dissolved oxygen during a photo-Fenton reaction is also important to design process control strategies based on reactant dosage [16-17].

The application of the photo-Fenton reaction process for industrial water treatment requires accurate modeling and scale-up considerations. In photo-Fenton reactor scale-up, remarkable differences often exist in the illuminated volume to total volume ratio (R_i) between laboratory, pilot and industrial plants, a parameter which has still not been fully investigated. Additionally, the effects of irradiance and photon absorption on process performance have not been widely studied. This analysis requires the use of detailed expressions regarding the relationship between reactor geometry and UV radiation distribution and the calculation of the local (LVRPA) and the volumetric rate (VRPA) of photon absorption [18].

In this study, we address the above deficiencies by proposing a new model for the photo-Fenton mineralization of water contaminants which includes the effect of the volumetric rate of photon absorption in the illuminated region of the reactor (VRPA) and the influence of the illuminated volume to total volume ratio (R_i) and liquid depth. These parameters are shown to have a significant impact on the global mineralization kinetics of the dissolved organic matter in an experimental raceway photoreactor.

2. Materials and methods

2.1 Photochemical reactor

The photoreactor, built in polyvinyl chloride (commonly abbreviated PVC), had flat raceway geometry. It was placed inside a SunTest CPS+ solar box and was irradiated from above by means of a Xenon lamp (300-800 nm). The distance from the lamp to the bottom of the reactor was 11 cm. The solar box included a photodiode and a control system which electronically controlled the irradiance to the set point. In addition, the UV irradiance reaching the surface of the liquid was monitored inside the solar box with a portable radiometer (PMA2100 – Solar Light Company) with a spectral response range from 320 to 400 nm. The power of the lamp was varied to provide different levels of irradiance to the water. The liquid depth and the liquid volume in the raceway photoreactor were either 5 cm and 2 L of liquid or 2.5 cm and 1 L of liquid. The other reactor dimensions were 20 x 20 cm (Figure 1). The reactor was operated in a total recirculation mode in which the liquid recirculated through an external well-mixed tank, which was kept in the dark. The irradiated volume to total (dark + irradiated) volume ratio (R_i) was varied by changing the volume of liquid in the recirculation system. The pH and dissolved oxygen were continuously monitored with CRISON 5335 and 6050

103   probes, respectively. The probes were placed inside two flow cells at the raceway

104   reactor exit, outside the solar box. The temperature of the liquid in the system was

105   measured with a CRISON 6050 probe and controlled at 30°C. The pH, dissolved

106   oxygen concentration and temperature probes were connected to a LabJack® U12 data

107   acquisition card which was interfaced by DAQfactory® software for continuous data

108   acquisition and monitoring. Aqueous samples from the reaction system were collected

109   from the well-mixed recirculation tank through a sampling port at the following times:

110   0, 5, 15, 30, 45, 60, 75, 90, 105 and 120 min.

111

2.2 Photochemical reactions and analytical methods

113   High purity acetaminophen (paracetamol) and hydrogen peroxide (30%) were supplied

114   by Sigma-Aldrich. Sulphuric acid (95-97%) was obtained from J. T. Baker and ferrous

115   sulphate (99%) from Fluka. The water matrix used was Milli-Q grade. Paracetamol,

116   often found in surface water and wastewater effluents [19], was chosen as the model

117   contaminant for the photo-oxidation experiments. The initial concentration of

118   paracetamol was 1 mM, which corresponds to 8.33 mM TOC. The other operating

119   conditions were: 17.7-26.5 mM H_2O_2, 0.36 mM Fe(II) and 32 W m^{-2} of irradiance. The

120   treatment was carried out under acidic pH (2.8). The effect of the irradiated volume to

121   total volume ratio, R_i, on the observed photoreaction kinetics was studied for values

122   equal to 0.30, 0.45 and 0.65. The liquid depth and the reactor volume were normally set

123   to 5 cm and 2 L respectively, except for selected experiments aimed at investigating the

124   effect of photon absorption in the reactor in which the irradiated reactor volume was

125   lowered to 1 L by changing the liquid depth to 2.5 cm.

126   The aqueous samples collected from the reactor at regular intervals were filtered

127   through 0.45 µm nylon filters (Millipore Millex-HN) prior to further analyses. The

128   decontamination process was followed by measuring the decrease in the total organic

129   carbon (TOC) for the samples using a Shimadzu-V_{CHP} TOC analyzer which was fitted

130   with an autosampler system. The residual hydrogen peroxide in solution was measured

131   with the ammonium metavanadate colorimetric method proposed by Nogueira et al.

132   2005 [20]. The concentration of iron species in the water was determined by the o-

133   phenanthroline standardized spectrometric procedure (ISO 6332). Absorbance

134   measurements were carried out with a Hach Lange DR 5000 spectrophotometer.

2.3 Radiation field model, LVRPA and VRPA

The radiation field incident to the liquid free surface was simulated as parallel rays normal to the reactor surface [21-22] to simplify the radiation field in the reactor in only one-dimension in space. As a consequence, the level of irradiance in the liquid could only vary with the depth from the surface [21]. The extent of absorption of radiation in the photo-Fenton reaction system investigated resulted from the combined effect of the concentration of the species in solution (Fe(III), Fe(II), H_2O_2, paracetamol and the transformation products) and the corresponding values of the molar absorption coefficients. Considering the concentrations of these species in the reaction system and their molar absortion coeffcients, Fe(III) in solution was dominant for the absorption of the incident radiation. Hydrogen peroxide and ferrous ion do not absorb radiation above 300 nm [18]. The absorption of paracetamol and of the transformation products during the photo-Fenton reaction was found to be negligible in comparison to the absorbance of Fe(III). The UV-vis absorption spectra of aqueous Fe(III) solutions at pH equal to 2.8 were, therefore, evaluated (Figure 2) and the spectral-averaged specific absorption coefficient k (mM^{-1} m^{-1}) of solution species was determined, Eq. 1.

$$\kappa = \frac{\int_{\lambda_{min}}^{\lambda_{max}} k_\lambda I_\lambda d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda d\lambda} \cong \frac{\sum_{\lambda min}^{\lambda max} k_\lambda I_\lambda}{\sum_{\lambda min}^{\lambda max} I_\lambda} \qquad\qquad (\text{Eq. 1})$$

where I_λ is the lamp power at the corresponding wavelength (W m^{-2}) which was supplied by the manufacturer, and k_λ is the specific absorption coefficient of the solution at the corresponding wavelength (mM^{-1} m^{-1}) determined from the results in Fig. 2 [18].

For the purpose of this study the wavelength limits in Eq. 1 were those corresponding to UV radiometer (320-400 nm) where the radiant energy was measured, although the integration should be extended to 320 nm, the absorption edge of Fe(III). The spectral-averaged specific absorption coefficient κ for Fe(III) acidic solutions in ultrapure water was 125 mM^{-1}m^{-1}.

The local volumetric rate of photon absorption (LVRPA) at a specific depth in the photochemical reactor was determined by a modified Beer-Lambert equation

$$\text{LVRPA} = \kappa \cdot C \cdot I_0 \cdot 10^{-k \cdot C \cdot x} \text{ , W m}^{-3} \qquad\qquad (\text{Eq. 2})$$

164   where C is the concentration of iron in solution (mM), I_0 is the irradiance (W m^{-2}) at the

165   reactor surface and x is the spatial coordinate (m) in the transversal direction from the

166   surface of the liquid to a specified liquid depth. The total radiant power absorbed in the

167   reactor was averaged over the liquid depth (VRPA) by integrating the LVRPA (Eq. 3)

168   and multiplying by the reactor free surface, $S_{reactor}$ (m^2):

169    $$VRPA = S_{reactor} \int_0^x \kappa \cdot C \cdot I_0 \cdot 10^{-k \cdot C \cdot x} dx, \text{W} \qquad \text{(Eq. 3)}$$

170   The photo-Fenton iron cycle is represented by the reaction of Fe(II) with hydrogen

171   peroxide generating the hydroxyl radical and Fe(III); and by the photochemical

172   reduction of Fe(III) with absorbed photons yielding another hydroxyl radical and Fe(II),

173   which completes the iron catalytic ideal cycle. The rate of hydroxyl radical and Fe(II)

174   formation varied with position in the reactor, however, the overall rate of formation of

175   these two species from the photochemical reaction is a function of the VRPA, the

176   radiant power absorbed in the reactor.

177

178   **2.4 Photo-Fenton Chemistry and Reaction Kinetic Model**

179   The elementary reactions of the photo-Fenton mechanism considered in the kinetic

180   model, the elementary rate laws and the mass balances for each of the participating

181   reacting species are shown in Table 1. The species included in the reaction mechanism

182   are: Fe(II), Fe(III), H_2O_2, R (all radicals are considered as a single type although

183   hydroxyl radical can be considered the predominant radical specie), dissolved oxygen

184   (O_2) and three different types of organic matter, M, MX and MX_2 (representing the

185   original compound and two groups of oxidized transformation products before

186   mineralization to CO_2). The lumping of the oxidized transformation products in groups

187   is related to the prediction capability of the model. The use of a lower number of

188   intermediate groups considerably diminishes the model prediction accuracy, while the

189   use of a higher number does not improve it.

190   The proposed photo-Fenton mechanism comprises three types of reactions: i) the photo-

191   Fenton catalytic cycle (Reactions 1 and 2) and radical formation, ii) Reactions 5-9 of

192   efficient radicals consumption (mineralization/oxidation reactions) and iii) Reaction 3

193   and 4, which represent the inefficient consumption of radicals to yield molecular

194   oxygen. Oxygen can be generated by the reaction between two radicals or between a

195 radical and hydrogen peroxide. Note that the Dorfman mechanism, responsible for

196 oxygen consumption during the first stages of mineralization, is reflected by the photo-

197 Fenton model (Reaction 5) [23]. Regarding the oxidation/mineralization reactions

198 (Reactions 5-9), only the partially oxidized organic matter can be completely

199 mineralized with the corresponding CO_2 release. TOC can be calculated as the sum of

200 M, MX_1 and MX_2. The use of TOC as a global contaminant concentration parameter

201 allows the model to be adapted to other contaminants or mixture of contaminants.

202 The dynamic model presented in this study is based on mass balances for the most

203 relevant components of the photo-Fenton reaction process operated in batch mode with

204 external recirculation through a well mixed vessel. However, the model can be extended

205 to other reactor operating conditions such as the continuous flow operation, by making

206 appropriate changes in the mass balances. The terms in the mass balances involving the

207 photochemical reaction (Reaction 2) include the illuminated volume to total volume

208 ratio R_i since this reaction can be carried out only under irradiation.

209 The dynamics of the dissolved oxygen uptake in the water is considered in the mass

210 balance (Eq. 20) through the overall volumetric gas-liquid mass transfer coefficient

211 ($K_L a$) which represents an additional model parameter [24]. Furthermore, another three

212 additional parameters are included in the oxygen mass balance, which can be considered

213 equivalent to the stoichiometric coefficients of the reaction mechanism.

214

215 **2.5 Numerical issues and assays**

216 The experiments carried out in this study were divided into two groups for parameter

217 identification (2/3 of the assays) and model validation (1/3 of the assays). The process

218 model parameters were obtained by implementing a Monte Carlo approach in

219 MATLAB$^{®}$ in which the objective was the minimization of the function of the squared

220 errors between experimental results and model prediction for the set monitored

221 variables.

222

223 **3. Results and discussion**

224 The photo-Fenton model developed in this study considers Fe(III) as the most
225 predominant photon absorbing species in solution. This is since H_2O_2 and Fe (II) do not
226 absorb above 300 nm, while the contaminant and the transformation products exhibited
227 negligible absorption compared with Fe(III). Figure 3 compares the absorbance of the
228 species in solution during the photo-Fenton reaction of paracetamol (8.33 mM TOC,
229 0.36 mM Fe(II), 35.3 mM H_2O_2 and 46 $W \cdot m^{-2}$ of UV irradiance) at different reaction
230 times and the absorbance of an acidified Fe(III) solution in pure water at equal
231 concentration (0.36 mM). The evolution of the absorption spectra during the reaction
232 was found to vary little, as long as the photo-Fenton cycle was operative and hydrogen
233 peroxide was present in the reaction system. During the first 30 min the absorption
234 spectra of the water resembled the absorption spectra of Fe(III) although the intensity
235 was lower. At around 45 min a greater fraction of Fe(III) was transformed to Fe(II)
236 while the contaminant was almost removed. Finally, when the decontamination process
237 was complete and the H_2O_2 had been consumed, the residual Fe(III) was
238 photochemically reduced to Fe(II) and the absorption spectra of the water changed to
239 reflect the absorption spectra of Fe(II) alone.

240 It was observed that the absorption spectra during this experiment were always lower
241 than those expected from a pure Fe(III) aqueous solution. This effect is related to the
242 transformation of a small fraction of Fe(III) to the non-absorbing Fe(II) during the
243 catalytic iron cycle. Thus, the results show that Fe(III) is the predominant absorbing
244 species during the photo-Fenton oxidation reaction and that other compounds in
245 solution are not interfering in the absortion of photons.

246 Figure 4 shows the results of oxidation of paracetamol as the model pollutant (8.33 mM
247 TOC), with 0.36 mM iron concentration, 32 $W\ m^{-2}$ irradiance and varying the R_i ratio at
248 0.30, 0.45 and 0.65. The initial hydrogen peroxide concentrations were 17.6 and 26.5
249 mM. This experimental conditions were selected in order to determine the effect of the
250 illuminated reactor volume fraction on the observed reaction kinetics and subsequently,
251 to check the correlation between model predictions and experimental results (TOC,
252 H_2O_2 and O_2). Higher irradiated reactor volumes, at fixed H_2O_2 concentration, resulted
253 in higher rates of TOC mineralization and H_2O_2 consumption, although the final
254 mineralization efficiency was similar in all cases. In contrast, when the R_i ratio was kept
255 constant, the final mineralization percentages were 65% and 70% respectively, when the
256 concentration of H_2O_2 was increased from 17.6 mM (the theoretical stoichiometric

257   requirement for complete oxidation of the initial TOC) to 26.5 mM (1.5 times the

258   stoichiometric requirement). Since hydrogen peroxide is also consumed in the

259   inefficient oxygen generating reaction (Reaction 3, Table 1) and considering that not all

260   the radicals produced are utilized to oxidize organic matter (see Reaction 4) [15], a

261   H_2O_2 requirement higher than the stoichiometric amount is needed for completing the

262   removal of the TOC, which explains the higher rates observed when 26.5 mM of

263   hydrogen peroxide was used. Regarding the temporal evolution of the dissolved oxygen,

264   initially, its concentration decreases to reach a minimum, which occurs when the

265   oxygen demand for the oxidation the organic matter (Dorfman mechanism) is higher

266   than either the oxygen generated by the Reactions 3 and 4 and the oxygen transferred

267   from the air/water interphase. Note that this stage may be more subdue if the rate of

268   generation of radicals is significant. However, after this stage, the oxygen concentration

269   reverse its trend and rises to reach a maximum, since the consumption of oxygen during

270   the early stages of mineralization halts and radicals generation provided by the photo-

271   Fenton cycle continues, while hydrogen peroxide is still present in the system. Once

272   hydrogen peroxide is totally consumed (halting also the photo-Fenton reaction) the

273   dissolved oxygen concentration tends to reach the equilibrium concentration with the

274   atmosphere [15].

275   The kinetic parameters obtained from the fitting of the model to the experimental results

276   of O_2, H_2O_2 and TOC concentration profiles at different R_i ratios are shown in Table 2.

277   The estimated model parameters are compatible with the fundamentals of the

278   elementary chemical reaction of the photo-Fenton mechanism. The monitoring of the

279   different reaction rates during model simulations pointed out the photochemical reaction

280   (Reaction 2) as the rate limiting step for the entire process. In contrast and as expected,

281   the highest kinetic constant was k_4 which involves radical-radical reactions. Other

282   kinetics constants are in agreement with the observed process phenomena. Organic

283   matter reactivity displays a decreasing trend during the treatment and this is reflected by

284   the corresponding kinetics constants values ($k_6>k_7>k_8>k_9$). At the beginning of the

285   process, a moderate decrease in the dissolved oxygen concentration is observed due to

286   the Dorfman reaction (Reaction 5), the kinetics constant, k_5, being considerably lower

287   than the other TOC mineralization constants.

288   The model was found to fit the temporal profiles of H_2O_2 and TOC at different R_i ratios

289   with a high degree of accuracy (Figure 5) also providing a good representation of the

290 increase and decrease in the concentration of oxygen. The model could accurately

291 predict the TOC mineralization and hydrogen peroxide consumption, although the

292 model under-predicted the consumption of H_2O_2 for short reaction times. The model

293 accurately predicted the final mineralization percentage and also the time required to

294 completely consume hydrogen peroxide. In addition, the O_2 profiles obtained by the

295 model were representative of the observed photo-Fenton behaviour.

296 Regarding the water treatment processes in which the photochemical reaction is the rate

297 limiting step, as occurs with the photo-Fenton reaction cycle, the variation of the

298 illuminated volume ratio (R_i) allows its influence on the overall reaction kinetics to be

299 evaluated. Usually, the R_i ratio in experimental reactor systems is high enough to

300 neglect the impact of the Fenton reaction in the dark volume. Indeed, interrupting the

301 UV irradiance during the photo-Fenton treatment dramatically slowed down the rate of

302 mineralization and the rate of oxygen generation even under an excess of hydrogen

303 peroxide [16]. Consequently, the accuracy of the model prediction slightly decreased

304 when using low R_i, although it still exhibited a typical trend of the photo-Fenton

305 reaction. The inclusion of the dark Fenton reaction (data not shown) did not improve the

306 capability of the model prediction to fit the experimental results and so, to follow the

307 parsimony principle, it was not taken into account.

308 The model was also investigated to predict the effect of varying the reactor geometry,

309 by halving the liquid depth to 2.5 cm in comparison with the depth of the liquid used

310 during the calibration of the model, which was 5 cm. The reactor volume also was

311 reduced by half to 1 L. The other experimental conditions were 8.33 mM TOC, 26.5

312 mM H_2O_2, 32 W m^{-2} of irradiance, R_i ratio of 0.45 and two iron concentrations, 0.14

313 and 0.36 mM (Figure 6).

314 One immediate consequence of changing the liquid depth and catalyst concentration is

315 the impact on the reactor optical thickness (Eq. 22):

316 $\tau = \kappa \cdot C \cdot x.$ (Eq. 22)

317 In the experiments performed at an initial catalyst concentration of 0.36 mM and 5 cm

318 of liquid depth the optical thickness was 2.25, a value situated into the theoretical

319 optimum range for photochemical reactors (1.8-3.4) [25]. In contrast, when the liquid

320 depth was diminished to 2.5 cm, the optical thickness decreased to 1.12 and to 0.43 for

321 0.36 mM and 0.14 mM of Fe, respectively. The later value is far from the optimal range

322 which points out to a loss of photon absorption efficiency and in consequence to slower

323 contaminant oxidation kinetics. However, the model estimations were in accordance

324 with the experimental results, even when the concentration of iron was lowered to 0.14

325 mM. Note that the model was calibrated for an iron concentration of 0.36 mM. As

326 anticipated, the assay with the lowest iron concentration resulted in a lower rate of

327 mineralization of paracetamol and the lower rate of consumption of hydrogen peroxide

328 was also reflected by the modified O_2 evolution profiles. In contrast, final TOC

329 concentrations achieved were the same in both assays suggesting that, under the range

330 studied, the iron concentration did not affect the final mineralization percentage but the

331 degradation rate.

332

333 **4. Conclusions**

334 A photo-Fenton model for organic matter mineralization based on general reactions has

335 been proposed. Although paracetamol has been chosen as the target pollutant for this

336 study, the model can be easily applied to other contaminants or mixtures of

337 contaminants because the oxidation/mineralization steps are based on a lumped

338 parameter represented by the TOC. The effect of the R_i ratio over the process kinetics

339 was successfully included in the model meaning that it is possible to use it for scaling-

340 up purposes, as noticeable differences regarding R_i ratio values normally exist between

341 laboratory, pilot and industrial scales. In addition, the effects of photo-reactor geometry

342 and light absorption were incorporated into the model by means of VRPA. After

343 evaluating the species responsible for photon absorption during the oxidation process -

344 mainly Fe(III), the use of VRPA in the model was validated by shortening the reactor

345 optical path length from 5 cm to 2.5 cm and varying the catalyst loading. In both cases,

346 the model successfully fitted the experimental data meaning that it would be possible to

347 optimize the process by selecting the most suitable reactor optical path length for a

348 given UV source based solely on model simulations. The dissolved oxygen

349 concentration was considered as a response variable and as an indicator of process

350 efficiency. The model can be used for controlling the Photo-Fenton process by

351 optimizing the dosing of hydrogen peroxide, ultimately leading to a reduction in the

352 operating costs of water treatment process.

353

5. Acknowledgements

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6. Bibliography

[1] V. Augugliaro, M. Litter, L. Palmisano, J. Soria, J. Photochem. Photobiol. C 7 (2006) 127-144.

[2] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Catal. Today 147 (2009) 1-59.

[3] M.L. Marín, L. Santos-Juanes, A. Arques, A.M. Amat, M.A. Miranda, Chem. Rev. 112 (2012) 1710-1750.

[4] A.G. Agrios, P.Pichat, J. Appl. Electrochem. 35 (2005) 655-663.

[5] J.J. Pignatello, E. Oliveros, A. MacKay, Crit. Rev. Env. Sci. Technol. 36 (2006) 1-84.

[6] J. Soler, A. García-Ripoll, N. Hayek, P. Miró, R. Vicente, A. Arques, A.M. Amat. Water Res. 43 (2009) 4441-4450.

[7] A. Zapata, I. Oller, E. Bizani, J.A. Sánchez-Pérez, M.I. Maldonado, S. Malato. Catal. Today 144 (2009) 94-99.

[8] S. Navalon, M. Alvaro, H. Garcia, Appl. Catal. B-Environ. 99 (2010) 1-26.

[9] L. Santos-Juanes Jordá, M.M. Ballesteros Martín, E. Ortega Gómez, A. Cabrera Reina, I.M. Román Sánchez, J.L. Casas López, J.A. Sánchez Pérez, J. Hazard. Mater. 186 (2011) 1924-1929.

[10] De Laat and Giang Le, Env. Sci. Technol. 39 (2005) 1811-1818.

380   [11] G.B. Ortiz de la Plata, O.M. Alfano, A.E. Cassano, Appl. Catal. B: Environ. 95
381   (2010) 14-25.

382   [12] M. Pérez-Moya, M. Graells, P. Buenestado, H.D. Mansilla, Appl. Catal. B:
383   Environ. 84 (2008) 313-323.

384   [13] S. Mohajeri, H.A. Aziz, M.A. Zahed, L. Mohajeri, M.J.K. Bashir, S.Q. Aziz, M. N.
385   Adlan, M.H. Isa, Water Sci. Technol. 64 (2011) 1652-1660.

386   [14] A. Cabrera Reina, L. Santos-Juanes Jordá, J.L. García Sánchez, J.L. Casas López,
387   J.A. Sánchez Pérez, Appl. Catal. B: Environ. 119-120 (2012) 132-138.

388   [15] L. Santos-Juanes, J.L.G. Sánchez, J.L.C. López, I. Oller, S. Malato, J.A. Sánchez
389   Pérez, Appl. Catal. B: Environ. 104 (2011) 316-323.

390   [16] E. Ortega-Gómez, J.C. Moreno Úbeda, J.D. Álvarez Hervás, J.L. Casas López, L.
391   Santos-Juanes Jordá, J.A. Sánchez Pérez, J. Hazard. Mater. 237-238 (2012) 223-230.

392   [17] L. Prieto-Rodríguez, I. Oller, A. Zapata, A. Agüera, S. Malato, Catal. Today 161
393   (2011) 247-254.

394   [18] J. Farias, E.D. Albizzati, O.M. Alfano, Catal. Today 144 (2009) 117-123.

395   [19] R. Moreno-González, S. Rodríguez-Mozaz, M. Gros, E. Pérez-Cánovas, D.
396   Barceló, V.M. León, Sci. Total Environ. 490 (2014) 59-72.

397   [20] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Talanta 66 (2005) 86-91.

398   [21] J. Colina-Maìrquez, F. Machuca-Martínez, G.L. Puma, Environ. Sci. Technol. 43
399   (2009) 8953-8960.

400   [22] O.M. Alfano, H.A. Irazoqui, A.E. Cassano, (2009) Photochem. Photobiol. Sci. 8
401   (2009) 1047-1058.

402   [23] L.M. Dorfman, I.A. Taub, R.E. Bühler, J. Chem. Phys. 36 (1962) 3051-3061.

403   [24] A. Cabrera Reina, J.L. Casas López, M.I. Maldonado Rubio, L. Santos-Juanes
404   Jordá, J.L. García Sánchez, J.A. Sánchez Pérez, Chem. Eng. J. 237 (2014) 469-477.

405   [25] G. Li Puma, Environ. Sci. Technol. 37 (2003) 5783-5791.

Table heads:

Table 1. Photo-Fenton reactions, kinetics rate laws and mass balances of the proposed model.

Table 2. Kinetics constants obtained after model calibration.

Figure captions:

Figure 1. Experimental setup

Figure 2. UV-Vis spectra of Fe(III) solutions at different concentrations

Figure 3. Comparison between the absorption spectra of a Fe(III) acidic solution and wastewater samples taken during a photo-Fenton assay

Figure 4. TOC mineralization and H_2O_2 consumption profiles for the experimental series in which the R_i ratio was varied between 0.30 and 0.65 and at two initial hydrogen peroxide concentrations, -left- 26.5 mM -right- 17.6 mM

Figure 5. Comparison between experimental TOC mineralization, H_2O_2 consumption and dissolved oxygen profiles and model predictions for the different values of R_i ratio (0.65 -left-, 0.45 -centre- and 0.30 -right-) when the initial H_2O_2 concentration chosen was 17.6 mM

Figure 6. Comparison between experimental and simulated profiles using a different solar reactor configuration (2.5 cm of liquid depth) and varying Fe concentration (0.14 mM -left- and 0.36 mM -right-)