

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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40 **1. Introduction**

41 Advanced oxidation processes (AOPs) which are based on the production of highly
42 reactive hydroxyl radicals are effective methods for the degradation and mineralization
43 of recalcitrant contaminants in water and wastewater [1]. Amongst these, AOPs driven
44 by the absorption of photons such as heterogeneous photocatalysis with organic
45 sensitizers and/or semiconductor oxides (mainly TiO₂) and the photo-Fenton process [3-
46 5], can be powered by solar light irradiation. Obvious technological and environmental
47 benefits [2] for these AOPs include a net cost reduction of the treatment process and the
48 utilization of a green and sustainable source of energy.

49 The photo-Fenton process entails the reaction of iron salts and hydrogen peroxide in the
50 presence of UV-vis radiation, which primarily produces hydroxyl radicals while
51 photocatalytically regenerating Fe³⁺ to Fe²⁺. The optimum pH is 2.8 [5] and to prevent
52 the precipitation of the dissolved iron salts, the pH should be less than 4. Several
53 scientific and technological aspects of the photo-Fenton process have been thoroughly
54 studied at both laboratory and pilot-plant scale including: the type and nature of
55 contaminants, the impact of the iron species, hydrogen peroxide and interfering species,
56 methods for heterogenization and recovery of the catalyst and the economics of the
57 process [6-9]. Despite this extensive body of knowledge on the photo-Fenton process,
58 the mathematical modeling of the treatment process is still under development, which
59 contrasts with other AOPs. Only a few models have been proposed using a simplified
60 elementary reaction mechanisms or empirical approaches [10-14]. The complexity of
61 the chemical reactions involved and the evolution of the organic matter present during
62 the process are probably the most important reasons.

63 Photo-catalytically generated radicals can react with organic matter, with hydrogen
64 peroxide or with other radicals. These parallel reactions in some cases generate oxygen,
65 whilst others consume oxygen. Therefore, changes in the reaction dynamics of the
66 photo-Fenton process are reflected by the evolution of the concentration of dissolved
67 oxygen (O₂), becoming a robust and easily measurable indicator to follow the efficiency
68 of the photo-Fenton process [15]. The modeling and monitoring of the evolution of
69 dissolved oxygen during a photo-Fenton reaction is also important to design process
70 control strategies based on reactant dosage [16-17].

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

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

86 **2. Materials and methods**

87 **2.1 Photochemical reactor**

88 The photoreactor, built in polyvinyl chloride (commonly abbreviated PVC), had flat
89 raceway geometry. It was placed inside a SunTest CPS+ solar box and was irradiated
90 from above by means of a Xenon lamp (300-800 nm). The distance from the lamp to the
91 bottom of the reactor was 11 cm. The solar box included a photodiode and a control
92 system which electronically controlled the irradiance to the set point. In addition, the
93 UV irradiance reaching the surface of the liquid was monitored inside the solar box with
94 a portable radiometer (PMA2100 – Solar Light Company) with a spectral response
95 range from 320 to 400 nm. The power of the lamp was varied to provide different levels
96 of irradiance to the water. The liquid depth and the liquid volume in the raceway
97 photoreactor were either 5 cm and 2 L of liquid or 2.5 cm and 1 L of liquid. The other
98 reactor dimensions were 20 x 20 cm (Figure 1). The reactor was operated in a total
99 recirculation mode in which the liquid recirculated through an external well-mixed tank,
100 which was kept in the dark. The irradiated volume to total (dark + irradiated) volume
101 ratio (R_i) was varied by changing the volume of liquid in the recirculation system. The
102 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

112 **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 H₂O₂, 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.

135 **2.3 Radiation field model, LVRPA and VRPA**

136 The radiation field incident to the liquid free surface was simulated as parallel rays
137 normal to the reactor surface [21-22] to simplify the radiation field in the reactor in only
138 one-dimension in space. As a consequence, the level of irradiance in the liquid could
139 only vary with the depth from the surface [21]. The extent of absorption of radiation in
140 the photo-Fenton reaction system investigated resulted from the combined effect of the
141 concentration of the species in solution (Fe(III), Fe(II), H₂O₂, paracetamol and the
142 transformation products) and the corresponding values of the molar absorption
143 coefficients. Considering the concentrations of these species in the reaction system and
144 their molar absorption coefficients, Fe(III) in solution was dominant for the absorption of
145 the incident radiation. Hydrogen peroxide and ferrous ion do not absorb radiation above
146 300 nm [18]. The absorption of paracetamol and of the transformation products during
147 the photo-Fenton reaction was found to be negligible in comparison to the absorbance
148 of Fe(III). The UV-vis absorption spectra of aqueous Fe(III) solutions at pH equal to 2.8
149 were, therefore, evaluated (Figure 2) and the spectral-averaged specific absorption
150 coefficient k (mM⁻¹ m⁻¹) of solution species was determined, Eq. 1.

$$151 \quad \kappa = \frac{\int_{\lambda_{min}}^{\lambda_{max}} k_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_{\lambda} d\lambda} \cong \frac{\sum_{\lambda_{min}}^{\lambda_{max}} k_{\lambda} I_{\lambda}}{\sum_{\lambda_{min}}^{\lambda_{max}} I_{\lambda}} \quad (\text{Eq. 1})$$

152

153 where I_{λ} is the lamp power at the corresponding wavelength (W m⁻²) which was
154 supplied by the manufacturer, and k_{λ} is the specific absorption coefficient of the solution
155 at the corresponding wavelength (mM⁻¹ m⁻¹) determined from the results in Fig. 2 [18].

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

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

$$163 \quad \text{LVRPA} = \kappa \cdot C \cdot I_0 \cdot 10^{-k \cdot C \cdot x}, \text{ W m}^{-3} \quad (\text{Eq. 2})$$

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):

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

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 CO₂ release. TOC can be calculated as the sum of
200 M, MX₁ and MX₂. 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_{La}) 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 H₂O₂ 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 H₂O₂ and 46 W·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 H₂O₂ 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 absorption 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 H₂O₂ and O₂). Higher irradiated reactor volumes, at fixed H₂O₂ concentration, resulted
253 in higher rates of TOC mineralization and H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 O₂, H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 O₂ 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 H₂O₂, 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):

$$316 \quad \tau = \kappa \cdot C \cdot x. \quad (\text{Eq. 22})$$

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 O₂ 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

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406 **Table heads:**

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

409 Table 2. Kinetics constants obtained after model calibration.

410

411 **Figure captions:**

412 Figure 1. Experimental setup

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

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

416 Figure 4. TOC mineralization and H₂O₂ consumption profiles for the experimental
417 series in which the R_i ratio was varied between 0.30 and 0.65 and at two initial
418 hydrogen peroxide concentrations, -left- 26.5 mM -right- 17.6 mM

419 Figure 5. Comparison between experimental TOC mineralization, H₂O₂ consumption
420 and dissolved oxygen profiles and model predictions for the different values of R_i ratio
421 (0.65 -left-, 0.45 -centre- and 0.30 -right-) when the initial H₂O₂ concentration chosen
422 was 17.6 mM

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