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1 **Optimization of electrocatalytic H₂O₂ production at pilot plant scale**
2 **for solar-assisted water treatment**

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15 **Abstract**

16 This manuscript summarizes the successful start-up and operation of a hybrid eco-engineered
17 water treatment system, at pilot scale. The pilot unit, with 100-L capacity, has been devised
18 for the efficient electrocatalytic production of H₂O₂ at an air-diffusion cathode, triggering the
19 formation of •OH from Fenton's reaction with added Fe²⁺ catalyst. These radicals, in
20 combination with those formed at a powerful boron-doped diamond (BDD) anode in an
21 undivided cell, are used to degrade a mixture of model pesticides. The capability of the plant
22 to produce H₂O₂ on site was initially optimized using an experimental design based on central
23 composite design (CCD) coupled with response surface methodology (RSM). This aimed to
24 evaluate the effect of key process parameters like current density (*j*) and solution pH. The
25 influence of electrolyte concentration as well as liquid and air flow rates on H₂O₂
26 electrogeneration and current efficiency at optimized *j* and pH was also assessed. The best
27 operation conditions resulted in H₂O₂ mass production rate of 64.9 mg min⁻¹, 89.3% of
28 current efficiency and 0.4 kWh m⁻³ of energy consumption at short electrolysis time.
29 Performance tests at optimum conditions were carried out with 75 L of a mixture of pesticides
30 (pyrimethanil and methomyl) as a first step towards the elimination of organic contaminants
31 by solar photoelectro-Fenton (SPEF) process. The combined action of homogeneous (•OH)
32 and heterogeneous (BDD(•OH)) catalysis along with photocatalysis (UV photons collected at
33 a solar CPC photoreactor) allowed the removal of more than 50% of both pesticides in 5 min,
34 confirming the fast regeneration of Fe²⁺ catalyst through cathodic reduction and photo-Fenton
35 reaction.

36 *Keywords:* Boron-doped diamond; Gas-diffusion electrode; Hydrogen peroxide
37 electrogeneration; Solar photoelectro-Fenton; Wastewater treatment

38 **1. Introduction**

39 The extraordinary development of chemicals manufacturing and their widespread use in
40 all human activities is intimately associated with contamination of aquatic environment.
41 Water quality monitoring programs underline the seriousness of the problem worldwide and
42 highlight the potential hazards posed by mixtures of synthetic organic contaminants (SOCs)
43 and their metabolites in surface water and groundwater [1-4]. Typically, SOCs include
44 solvents, preservatives, pharmaceuticals and personal care products, lubricants, dyes or active
45 substances for plant protection [5]. Among the latter, methomyl (MET) and pyrimethanil
46 (PYR) are ubiquitous in intensive agriculture, which is worrisome since they are classified as
47 persistent organic pollutants (POPs) [6] and are considered extremely toxic [7,8]. This issue
48 has prompted the application of advanced oxidation processes (AOPs) for the fast and
49 complete removal of SOCs from polluted water streams [9], based on the in situ production of
50 hydroxyl radical ($\bullet\text{OH}$) as main reactive oxygen species (ROS).

51 Fenton's reaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), so-called
52 Fenton's reagent, is the most popular source of $\bullet\text{OH}$ for practical applications [10]. As an
53 upgraded approach, the electro-Fenton (EF) process allows overcoming two key limitations of
54 the conventional chemical method [11-13]: (i) it ensures the continuous regeneration of Fe^{2+}
55 through cathodic reduction of Fe^{3+} , thus requiring a much lower amount of catalyst to perform
56 the treatment, and (ii) it avoids the handling, storage and transportation of H_2O_2 produced
57 industrially, since this reagent can be electrosynthesized on site through Reaction (1) by using
58 appropriate cathode materials.

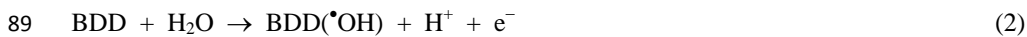


60 Electrocatalytic H_2O_2 generation is becoming a hot topic because the combination of
61 electrochemistry with new catalysts enables a more eco-friendly and less energy-intensive
62 production of this commodity [14,15]. Several prospective electrocatalysts have been

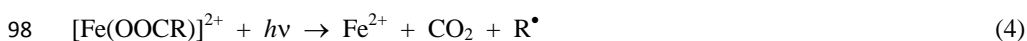
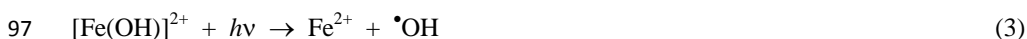
63 developed, with noble metals and metal alloys like Pd-Au, Pt-Hg and Pt/Pd-Hg as particularly
64 prominent options [14,16,17]. Non-precious Co-based particles are very active promoters of
65 Reaction (1) as well, at smaller cost [18]. Unfortunately, none of these catalysts is viable for
66 large-scale water treatment due to their high cost and toxicity, which has fostered the
67 investigation on inexpensive carbonaceous materials [14,19,20]. Unmodified carbon-based
68 catalysts exhibit appealing characteristics as cathodes, such as non-toxicity and high stability,
69 conductivity and durability. H₂O₂ production with such inexpensive materials is particularly
70 interesting for developing small- or medium-size decentralized units where the chemical is
71 generated on demand [21]. This can be achieved using graphite felt, reticulated vitreous
72 carbon, activated carbon fiber or carbon nanotubes as cathode, completely immersed into the
73 solution to generate H₂O₂ from dissolved O₂ [22-24]. However, much greater H₂O₂
74 concentrations are attained upon implementation of an air-chamber in the electrochemical
75 reactor, since it allows continuous air-feeding through a hydrophobized carbon-based gas-
76 diffusion electrode (GDE) [15,18,25-28]. Worth noting, the vast majority of studies on
77 Fenton-based electrochemical AOPs (EAOPs) reporting data on H₂O₂ production at GDE
78 have been carried out either at laboratory scale or in small pre-pilot plants of 2.5 L [29] and 5
79 L [30,31]. Only one work reported the use of a bigger plant with 25 L capacity, but it was
80 mainly focused on aniline degradation [32].

81 Undivided electrochemical cells are preferred to perform all these studies on water
82 treatment because the use of a separator would increase the cell voltage and hence, the energy
83 consumption. In addition, in such cells, the combination of carbonaceous cathodes with
84 electrocatalytic materials that promote the anodic production of heterogeneous hydroxyl
85 radical enhances the performance of EF process. Boron-doped diamond (BDD) thin film on Si
86 substrate is the best anode to oxidize H₂O to physisorbed •OH via Reaction (2) [11,13,33],

87 owing to its large overpotential for O₂ evolution. However, Ti and Nb are more suitable for
88 plant-scale applications due to their much higher mechanical and chemical resistance.



90 The best performance among Fenton-based EAOPs for SOCs degradation is attained
91 upon continuous irradiation of the treated solution with UV/Vis light. This is feasible
92 employing a UVA lamp in photoelectro-Fenton (PEF) process [11,13], since it promotes: (i) a
93 high regeneration rate of Fe²⁺, with concomitant production of homogeneous [•]OH, from
94 photoreduction of the main Fe(III) species at pH ~ 3.0 (Reaction (3)), (ii) the
95 photodegradation of Fe(III)-carboxylate complexes formed as intermediates (Reaction (4)),
96 and (iii) the direct photolysis of some pollutants and/or their oxidation by-products [11,34].



99 In order to achieve the synergy between electrocatalytic and photolytic reactions at an
100 affordable cost, UVA lamps have been lately replaced by direct sunlight irradiation, yielding
101 the promising solar PEF (SPEF) process. Its great oxidation capability arises from: (i) the
102 higher UV photon flux from sun if the solar collector design is adapted to the photoreactor,
103 which upgrades the [•]OH production, along with (ii) the additional illumination within the
104 visible range ($\lambda > 400$ nm), promoting Reaction (3) (also active in the visible range) and
105 accelerating the photolysis of refractory Fe(III)-carboxylate complexes (Reaction (4)) [34].
106 Very good degradation results by SPEF with GDE were obtained using a recirculation small
107 pilot plant of 2.5-L capacity equipped with a flat-plate photoreactor [35-37], also employed to
108 treat pesticides like mecoprop [35], diuron [38] or tebuthiuron and ametryn [39]. Replacement
109 by a more efficient photoreactor based on compound parabolic collectors (CPC) could
110 increase the efficiency of SPEF due to the greater photon flux supply to the solution. At

111 present, CPC is the most popular photoreactor, as confirmed by its integration in most of the
112 SPEF units for treating 2.2 L [40], 6 L [41], 8 L [42] and up to 10 L [43-48], which is the
113 largest volume investigated so far.

114 Based on the excellent performance of SPEF at limited scale, a larger pilot plant has been
115 developed for the treatment of SOC_s by EAOPs with H₂O₂ electrogeneration. The system,
116 with capacity to treat up to 100 L, consists of four undivided Nb-BDD/GDE filter-press cells
117 coupled with a solar CPC, and has been installed and tested at Plataforma Solar de Almería
118 (PSA), the largest European facility to test solar technologies. As a first step toward the
119 treatment of real wastewater, this work is focused on the optimization of pilot plant main
120 operation variables for the electrocatalytic H₂O₂ production, including current density (*j*),
121 solution pH, liquid flow rate, air flow rate and electrolyte concentration. This was made with
122 the aid of central composite design (CCD) coupled to response surface methodology (RSM).
123 The plant was further validated by performing degradation trials under optimum conditions
124 using a mixture of fungicide PYR and insecticide MET spiked into conductive water at high
125 concentrations to simulate real agricultural wastewater. Note that these pesticides have only
126 been studied before by AOPs like solar TiO₂ photocatalysis and solar photo-Fenton at pilot
127 scale [6] and EF at lab scale [8].

128 **2. Materials and methods**

129 *2.1. Chemicals*

130 Heptahydrated ferrous sulfate (Sigma-Aldrich) used as catalyst and anhydrous sodium
131 sulfate (Fluka) employed as background electrolyte were of analytical grade. PYR (IQV,
132 AgroEvo, 98% purity) and MET (Aragonesas Agro, 99.5% purity) were of reagent grade and
133 used without further purification. Mixtures of the two pesticides were prepared with deionized
134 water (conductivity < 10 μS cm⁻¹, dissolved organic carbon (DOC) < 0.5 mg L⁻¹) and the

135 electrolyte, and their pH was adjusted with analytical grade sulfuric acid (J.T. Baker). Organic
136 solvents and other chemicals employed for HPLC analysis of the pesticides were of analytical
137 grade from Sigma-Aldrich.

138 2.2. Pilot plant

139 Images of the filter-press type electrochemical cells and the CPC photoreactor, along with
140 a schematic diagram of the pilot plant, are shown in Fig. 1. The plant consisted of four plate-
141 and-frame electrochemical reactors (Electro MP-Cells from ElectroCell) coupled to a
142 purpose-made solar CPC. Each cell contained an anode made of BDD thin film deposited on a
143 niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode,
144 both with 0.01 m² effective area. The CPC photoreactor had a total illuminated area of 2 m²,
145 corresponding to an irradiated volume of 23 L. It was comprised of 10 borosilicate glass tubes
146 (150 cm length × 4.5 cm inner diameter) mounted in an aluminum frame on a platform tilted
147 37° (PSA, 37°N, 2.4°W). The working volume was 25 L to carry out the optimization of H₂O₂
148 electrogeneration, and 75 L to perform the degradation experiments. The unit was equipped
149 with two magnetic drive pumps (PAN World, 0.75 kW), one for pumping the solution from
150 the feed tank (maximum capacity of 100 L) to the electrochemical cells, and the other for the
151 liquid recirculation to and from the CPC. The GDE was fed with compressed air (ABAC air
152 compressor, 1.5 kW) at a pressure and flow rate regulated with a back-pressure gauge and a
153 flowmeter, respectively, in order to avoid the flooding of the air chamber. The experiments
154 were made at constant j using a Delta Electronika power supply (limited to 70 V and 22 A).

155 Global ultraviolet solar radiation (UV_G) was measured using a radiometer (Kipp &
156 Zonen, model CUV 3) mounted on a platform tilted 37°, the same angle as the photoreactor,
157 which provided data in terms of incident irradiance ($W_{UV} m^{-2}$). This informs about the energy
158 reaching any surface in the same position with regard to the sun. Eq. (5) allows combining the

159 data from trials performed in different days, thus enabling comparison with results obtained in
160 other photocatalytic experiments [49].

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot \overline{UV}_{G,n} \cdot A_r \cdot V_T \quad (5)$$

161 where Q_{UV} is the accumulated UV energy per unit of volume (kJ L^{-1}), $\overline{UV}_{G,n}$ (in W m^{-2}) is the
162 average UV radiation measured during $\Delta t_n (= t_n - t_{n-1})$, A_r is the irradiated surface area (2 m^2)
163 and V_T is the total volume treated in the pilot plant.

164 2.3. Experimental design

165 Experimental design by RSM was employed to optimize the in situ electrogeneration of
166 H_2O_2 . Trials were performed with one of the four identical electrochemical cells of the pilot,
167 assuming that the resulting optimum conditions would be also valid for the other three cells.
168 Two optimization criteria were considered: (a) maximization of the concentration of the
169 produced H_2O_2 , and (b) maximization of the current efficiency (CE, in percentage), defined as
170 the ratio between the electricity consumed by the electrode reaction of interest and the total
171 electricity supplied. CE can be calculated via Eq. (6), where n represents the stoichiometric
172 number of electrons transferred in Reaction (1), F is the Faraday constant ($96,487 \text{ C mol}^{-1}$),
173 $[\text{H}_2\text{O}_2]$ the concentration of H_2O_2 accumulated in bulk solution (mg L^{-1}), V_T the volume of the
174 treated solution (L), $M(\text{H}_2\text{O}_2)$ the molecular weight of H_2O_2 (34 g mol^{-1}), and Q the charge
175 consumed during the electrolysis (C).

$$176 \% CE = \frac{nF[\text{H}_2\text{O}_2]V_T}{1000 M(\text{H}_2\text{O}_2)Q} \times 100 \quad (6)$$

177 RSM was first used to assess the relationship between response (H_2O_2 concentration or %
178 CE) and two independent variables, namely the solution pH (factor A) and j (factor B), as
179 well as to optimize the relevant conditions in order to predict the best value of responses.
180 CCD, the most widely used approach of RSM and, more specifically, a face centered
181 composite (FCC) design, was employed to determine the effect of the two variables. Design

182 Expert[®] v.7.0.0 software (Stat-Ease Inc., USA) was used. Three levels between -1 and +1
183 were established for the two independent variables (Table 1). Ranges were chosen based on
184 preliminary experiments (data not shown here), background knowledge, and some constraints
185 arising from the cathodic H₂O₂ electrogeneration and the nature of the electrode materials. For
186 example, the production of H₂O₂ is favored at acidic pH (Reaction (2)), whereas the use of
187 GDE and BDD anode limits the operation cell voltage to less than 25 V to prevent surface
188 damage, which would cause the loss of electrocatalytic properties, and keep a reasonable CE
189 [50]. This means that maximum current that can be applied is 10 A ($j = 100 \text{ mA cm}^{-2}$).

190 For the CCD, a 2³ full factorial design with 3 replicates at the center point (resulting in 19
191 experiments) was used to determine the optimum values of independent variables. These
192 experiments were carried out by recirculating synthetic solutions of 50 mM Na₂SO₄ at a liquid
193 flow rate of 4.4 L min⁻¹, and they were randomly performed to minimize the effect of
194 systematic errors. Analysis of variance (ANOVA) of the data was performed to identify
195 significant values ($p\text{-value} < 0.05$). The quality of the fit of polynomial model was expressed
196 by the value of correlation coefficient (R^2). The main indicators demonstrating the
197 significance and adequacy of the used model include the model F-value (Fisher variation
198 ratio), probability value (Prob > F), and adequate precision. The optimal region of the
199 independent variables was determined by plotting three-dimensional response surfaces of the
200 independent and dependent variables. Additionally, numerical optimization of the
201 independent variables was carried out using the same software.

202 A second set of experiments was carried out aiming to assess the effect of electrolyte
203 concentration as well as liquid and air flow rates, under the optimum pH and j conditions. The
204 best operation conditions were finally applied to degrade mixtures of pesticides, in the
205 absence or presence of iron catalyst. In SPEF, the pesticide solution was irradiated when
206 circulating through the CPC photoreactor.

207 *2.4. Instruments and analytical methods*

208 The concentration of H₂O₂ accumulated during the electrolysis was determined by adding
209 Ti(IV) oxysulfate to the sample and measuring the absorbance at 410 nm, according to DIN
210 38409 H15. Iron concentration was measured by using 1,10-phenanthroline, following ISO
211 6332. In both cases, a Unicam UV/Vis UV2 spectrophotometer was employed. Dissolved
212 organic carbon (DOC) was measured after sample filtration through a 0.22 µm Nylon filter,
213 on a Shimadzu TOC-VCSN analyzer. The degradation rate of the two pesticides was
214 monitored on a UPLC/UV Agilent Technologies Series 1200, equipped with a C-18
215 ZORBAX XDB C-18 analytical column. The column was kept at 30 °C and the injection
216 volume was 50 µL. A linear gradient profile with water and acetonitrile (ACN) eluted at a
217 flow rate of 1 mL min⁻¹ was established as follows: 0-4 min, isocratic at 85/15 (v/v)
218 H₂O/ACN; 4-8 min, gradient from 85/15 to 20/80 (v/v); 8-15 min, isocratic at 85/15 (v/v). Re-
219 equilibration time was 3 min. The UV signals for MET and PYR were monitored at the
220 wavelength of their maximum absorption, 230 nm and 270 nm, respectively. For UPLC
221 analyses, 9 mL of sample were filtered through a 0.22 µm PTFE syringe filter. Then, it was
222 washed with 1 mL of UPLC grade ACN to extract any compound adsorbed on the filter. The
223 pH of the treated solution was monitored by means of a Crison 25 pH-meter.

224 **3. Results and discussion**

225 *3.1. Influence of independent experimental variables on the in situ H₂O₂ electrogeneration*

226 The results obtained from the experimental design matrix including the two independent
227 variables (pH, *j*) are shown in Table 2. The responses (H₂O₂ concentration and % CE) are
228 presented at two electrolysis times, 5 and 30 min, corresponding to approximately one and
229 five circulations of the initial feed solution volume (25 L) through the electrochemical cell,
230 respectively. The average values of the two responses at 30 min are illustrated in Fig. 2a,

231 whereas the changes in H₂O₂ mass production rate over the electrolysis time are depicted at
232 constant pH = 3.0 (Fig. 2b) or $j = 100 \text{ mA cm}^{-2}$ (Fig. 2c).

233 As expected, a higher accumulation of H₂O₂ was found as the electrolyses were
234 prolonged, although this occurred in concomitance with current efficiency decrease (Table 2).
235 This is also confirmed from the profiles of the H₂O₂ production rates with time, since the
236 highest values were attained at the beginning of the electrolyses until quasi-steady values
237 were observed at longer times, regardless of the j (Fig. 2b) or the pH (Fig. 2c) studied.
238 According to Eq. (6), the gradual lower efficiency with electrolysis time is related to the
239 reduced [H₂O₂]/ Q ratio as a result of nonlinear increase of the accumulated H₂O₂. This kind of
240 behavior can be partly explained by the use of batch operation mode, since the H₂O₂
241 production rate at the air-diffusion cathode from Reaction (1) becomes equal to its
242 decomposition rate by parasitic reactions that can take place in the cell. For example, the
243 continuous recirculation of H₂O₂ accumulated in the solution may promote its electrochemical
244 reduction at the cathode surface (Reaction (8)) and, to much lesser extent, its spontaneous
245 disproportion in the bulk (Reaction (9)) [11].



248 Furthermore, considering that an undivided electrochemical reactor is employed, other
249 additional parasitic reactions occur, as for example the oxidation of H₂O₂ to O₂ at the Nb-
250 BDD anode surface via HO₂[•] as an intermediate, according to the following reactions:



253 In addition, it is worth mentioning that H₂O₂ decomposition is promoted as the solution
254 pH becomes more alkaline, according to the following reaction:



256 As a consequence of these undesired reactions, the accumulated H_2O_2 concentration is
257 always below the theoretical maximum. As explained in the Introduction, undivided reactors
258 are the best choice for water treatment, but divided ones should be employed for industrial
259 electrochemical H_2O_2 production. Note that similar trends for H_2O_2 accumulation have been
260 reported by Brillas and co-workers, as shown during the electrolysis of Na_2SO_4 solutions in a
261 similar batch filter-press BDD/GDE reactor at j values between 50 and 150 mA cm^{-2} [29].

262 In addition, Fig. 2b and 2c show that the maximum H_2O_2 production was achieved at 100
263 mA cm^{-2} and pH 3.0. This agrees with the fact that a higher electron and proton supply
264 promotes a faster O_2 reduction from Reaction (1).

265 3.2. Validation of the correlation models

266 With the aid of Design Expert software, the models that best correlated the responses and
267 the independent variables shown in Table 2 were:

268 (i) Quadratic model:

$$269 [\text{H}_2\text{O}_2] = 2.19 - 0.31 \cdot \text{pH} + 0.81 \cdot j - 0.05 \cdot \text{pH} \cdot j + 0.15 \cdot \text{pH}^2 - 2.42 \times 10^{-3} \cdot j^2 \quad (12)$$

270 (ii) Two-factor interaction model (2FI):

$$271 \% \text{ CE} = 61.68 - 0.43 \cdot \text{pH} - 0.18 \cdot j - 0.0275 \cdot \text{pH} \cdot j \quad (13)$$

272 Both models were validated by the analysis of variances (ANOVA), and the results are
273 summarized in Table 3. The statistical significance was assessed by means of Fisher's test.
274 The F-values calculated for the lack of fit of the quadratic and the 2FI models were 30.44 and
275 60.89, respectively, suggesting that they are satisfactory. Similar conclusions can be drawn
276 from the low probability values (p-value) at a 95% confidence level (< 0.0001) for both
277 models. The statistical significance of the two models is also verified from Fig. 3, since the
278 actual values of the accumulated H_2O_2 concentration and current efficiency are randomly
279 distributed around the mean of predicted values. Moreover, good linear correlations between

280 the predicted and observed values for H₂O₂ concentration and % CE, with corresponding R²
281 values of 0.932 and 0.924, were obtained.

282 According to the ANOVA analysis (Table 3), the effects of the independent variables (A-
283 pH, B-*j*) were obvious and the effective order was *j* > initial pH, whereas the interaction of the
284 two variables (AB) was not obvious (p-value > 0.1). This can also be deduced from Fig. 2b
285 and 2c, which show that the H₂O₂ production is more substantially affected by *j* (Fig. 2b)
286 rather than by solution pH, with the latter showing only a slight superiority at pH 3.0 as
287 compared to neutral pH (Fig. 2c). This is important, since the adjustment of pH when treating
288 wastewater complicates the process and increases the water salinity and the operation cost (for
289 acidification and subsequent neutralization).

290 3.3. Optimization by response surface methodology

291 To better assess the effect of pH and *j* on H₂O₂ production and current efficiency and
292 identify their optimum values, 3D response surfaces and contour maps were developed with
293 the aid of Design Expert software. The response surface plot shown in Fig. 4 implies that the
294 generation of H₂O₂ increases with *j* at acidic pH values. On the other hand, the current
295 efficiency (Fig. 5) decreases as *j* is raised, regardless of the initial pH of the electrolyte
296 solution. As explained above, this is attributed to the batch operation mode in an undivided
297 cell configuration, which promotes the activation of detrimental side reactions. Four sets of
298 optimum pH and *j* values were proposed by the statistical software (Table 4), yielding
299 maximum H₂O₂ production and current efficiency. Among the four solutions proposed,
300 solution number 1, requiring electrolyte pH = 3.0 and *j* = 73.66 mA cm⁻² (~74.0), was selected
301 as the optimum one. Under these conditions, a set of experiments was conducted aiming to
302 validate the two correlation models (Eq. (12) and (13)) and to investigate the effect of other
303 operation conditions like liquid and air flow rates, as well as electrolyte concentration. The
304 main goal was to fully optimize the electrocatalytic H₂O₂ production at plant scale, eventually

305 yielding the most effective (highest H₂O₂ production rate), efficient (maximum CE
306 percentage) and profitable (lowest energy consumption) process at large scale.

307 The results of two replicate experiments under the aforementioned optimum conditions
308 are summarized in Table 5. The relative errors were below 5% for both, H₂O₂ generation and
309 % CE (3.69% and 4.38%, respectively), demonstrating the excellent fitting of the
310 experimental results (actual values) with those predicted by the two models.

311 3.3.1. *Effect of liquid flow rate*

312 The feed flow rate is closely related to the hydraulic residence time (HRT) of the treated
313 solution within the electrochemical cell. This is of great significance under continuous
314 operation mode, where the feed solution is continuously treated and discharged. For batch
315 operation, as is the case of the experiments carried out in this work, the recirculation flow rate
316 does not necessarily match the HRT, but it rather affects the mixing and may create turbulent
317 flow within the electrochemical cell. This, in turn, may intensify the mass transport induced
318 by the higher local concentration of molecular oxygen dissolved in the aqueous phase. Indeed,
319 when the flow rate was doubled (from 2.8 to 5.6 L min⁻¹), H₂O₂ production was gradually
320 greater at each given time (Fig. 6b), finally increasing by 28.8% at 30 min (Fig. 6a, [H₂O₂] in
321 mg min⁻¹). Current efficiency also increased in the same proportion, as a result of the higher
322 H₂O₂ generation at similar charge consumption (note that energy consumption varied between
323 1.97 and 2.00 kWh m⁻³ for all pilot runs) (Fig. 6a).

324 3.3.2. *Effect of air flow rate*

325 Large feeding of air or pure O₂ to the air chamber is often needed to counterbalance the
326 existing pressure on the wet face of the GDE, thereby avoiding flooding that would stop the
327 H₂O₂ production. If correctly adjusted, an increase in air flow rate may upgrade the H₂O₂
328 accumulation. As found for the pilot plant studied in this work, a rise in the air flow rate from
329 2.5 and 5 L min⁻¹ to 10 L min⁻¹, resulted in an enhanced H₂O₂ production by 23.1% and

330 15.6% at 30 min, respectively (Fig. 7a and 7b). Moreover, the kinetics of H₂O₂ production
331 was faster at the maximum air flow rate of 10 L min⁻¹ (Fig. 7b), with no negative effect on the
332 corresponding energy consumption, which was similar at all air flow rates examined. This is
333 interesting, since one might presume that an excessive air feeding could generate too many
334 bubbles within the electrochemical reactor, thereby increasing the ohmic drop and also
335 affecting the stability of the liquid flow rate, which did not occur.

336 Based on these results, as well as on the better performance of the plant at high
337 electrolyte flow rates, it can be concluded that the combined increase of air and liquid flow
338 rates may effectively enhance the fraction of oxygen consumed for H₂O₂ production
339 (Reaction (1)) over the total amount of air fed. Indeed, under the optimum operation
340 conditions, namely 50 mM Na₂SO₄ solution at pH 3.0 treated at 74 mA cm⁻², with liquid flow
341 rate of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹, the highest H₂O₂ mass production rate and
342 current efficiency were obtained. In the first 5 min of electrolysis, these conditions led to
343 H₂O₂ production with a mass rate of 64.9 mg min⁻¹, 89.3% current efficiency and energy
344 consumption of 0.4 kWh m⁻³. These values are among the best achieved with similar system
345 configurations. For example, Flox et al. [29] reported a production rate of ca. 23 mg min⁻¹ at
346 30 min in 50 mM Na₂SO₄ at pH 3.0, 100 mA cm⁻² and liquid flow rate of 3 L min⁻¹, whereas
347 Fig. 7a shows a higher H₂O₂ electrogeneration rate of 32 mg min⁻¹ at that time.

348 3.3.3. *Effect of electrolyte concentration*

349 Considering the rather small electrode gap (6 mm) between the anode and cathode in the
350 electrochemical cell, it was assumed that the solution conductivity would not significantly
351 affect the production of H₂O₂. Therefore, a set of experiments was made to determine the
352 possible influence of electrolyte concentration. It was observed that, within the range of 25-75
353 mM of Na₂SO₄, which is equal to a solution conductivity range of 4.6 to 12.3 mS cm⁻¹, the
354 accumulation of H₂O₂ was quite analogous, being only slightly higher in the case of 50 mM

355 (Fig. 8). However, a rather substantial effect is observed regarding the energy consumption,
356 since a higher conductivity led to a gradually lower consumption; i.e. 3.24, 2.00 and 1.61
357 kWh m⁻³ at 25, 50 and 75 mM Na₂SO₄, respectively. This was expected, since the increase of
358 electrolyte concentration causes a reduction of the ohmic resistance in the bulk solution, and
359 accelerates the electron transfer, thus decreasing the overall charge consumption. From these
360 findings, it can be concluded that the system would be more efficient at higher water
361 conductivity. Therefore, future industrial application of this technology should focus on high
362 conductivity wastewater or be coupled with membrane technologies for treating membrane
363 concentrates.

364 *3.4. Treatment of a mixture of pesticides*

365 After the optimum operation conditions were determined for attaining the best balance
366 between H₂O₂ production and current efficiency, the plant performance was validated by
367 carrying out several tests to assess its capability to degrade a mixture of two model SOCs,
368 namely PYR and MET, which were treated by sun-assisted AOPs like solar photo-Fenton
369 [6,51]. All the assays were made with 75 L of mixtures of both pesticides in water with 50
370 mM Na₂SO₄ under optimized conditions: pH 3.0, 74 mA cm⁻² and air flow rate of 10 L min⁻¹.

371 First, a mixture containing 50 mg L⁻¹ PYR and 90 mg L⁻¹ MET (i.e., 71 mg L⁻¹ DOC) was
372 treated by EO with electrogenerated H₂O₂. The influence of liquid flow rate (2.8, 4.4 and 5.6
373 L min⁻¹) was investigated, aiming to promote a larger oxidation of both organic contaminants
374 either by increasing the HRT (at a lower flow rate) or by enhancing the mass transport of
375 pollutants to the anode surface (at a higher flow rate). However, no significant effect of this
376 parameter was found, which suggests that the amount of BDD([•]OH) produced via Reaction
377 (2) at 74 mA cm⁻² was high enough to react with both pesticides regardless of the
378 hydrodynamic conditions (within the studied range). Fig. 9a and 9b depict the normalized
379 decays of PYR and MET concentrations at a liquid flow rate of 5.6 L min⁻¹, respectively. As

380 can be seen, the degradation by EO-H₂O₂ was very slow, only attaining 20% and 30% of PYR
381 and MET removal after 120 min. The larger degradation of MET could be explained by the
382 greater electrocatalytic behavior of BDD with this pesticide as a result of a more favorable
383 adsorption on its surface, thus reacting more quickly with physisorbed BDD([•]OH). At the end
384 of the electrolysis, almost no mineralization was achieved in EO process, in agreement with
385 the refractory nature of typical reaction by-products like carboxylic acids [10-13]. In all these
386 trials, the energy consumption was around 10 kWh m⁻³.

387 The same pesticides mixture was treated by EF, using the optimized parameters with
388 liquid flow rate of 5.6 L min⁻¹, in the presence of different amounts of Fe²⁺ as catalyst (not
389 shown). After 120 min, a higher degradation percentage was reached for both pesticides, with
390 up to 35% and 40% for PYR and MET, respectively. This demonstrates that the H₂O₂
391 produced under optimized conditions reacted with added Fe²⁺ according to Fenton's reaction,
392 yielding homogeneous [•]OH that enhanced the degradation because this radical acted
393 concomitantly with BDD([•]OH). The former was confined into the reactor, whereas the latter
394 radical was transported throughout the whole volume. In contrast, DOC abatement only
395 attained 8% as maximum, which agrees with the high stability of Fe(III)-carboxylate
396 complexes formed as intermediates [11]. Worth mentioning, a much larger mineralization was
397 achieved working with a pesticide mixture that accounted for 20 mg L⁻¹ DOC, using 1.0 mM
398 Fe²⁺. In this case, 32% DOC removal was attained at 120 min. It is also important to note that
399 the Fe²⁺ concentration remained almost constant during all these EF trials, which confirms the
400 capability of the cathode to regenerate it from Fe(III) reduction.

401 Finally, the mixtures with 71 mg L⁻¹ DOC were comparatively treated by SPEF using the
402 best Fe²⁺ concentration (i.e., 0.5mM). In these experiments, required accumulated UV energy,
403 Q_{UV} , was 7.1 kJ L⁻¹. As it can be observed in Fig. 9, 55% and 50% removal of PYR and MET
404 was reached in only 5 min, which confirms the fast Fe²⁺ photoregeneration with additional

405 •OH production from Reaction (3). At longer time, the degradation was much slower, but
406 ended in 77% and 70% removal, respectively, at 120 min. This is a much better performance
407 as compared to EO and EF, which was further confirmed by DOC abatements higher than
408 15%, in agreement with the powerful action of UV/Vis photons on Fe(III)-carboxylate
409 complexes according to Reaction (4).

410 **4. Conclusions**

411 The successful performance of the largest SPEF pilot plant existing to date has been
412 demonstrated in this work. The core of the plant, the filter-press electrochemical reactor, is
413 comprised of a Nb-BDD anode and a GDE as cathode. Optimization of main operation
414 parameters has been carried out according to a thorough experimental design, in order to
415 maximize the electrocatalytic H₂O₂ production with a high current efficiency. Optimum
416 values obtained for the key parameters were: pH 3.0, 74 mA cm⁻², liquid flow rate of 5.6 L
417 min⁻¹ and air flow rate of 10 L min⁻¹. Their application yielded a mass rate of up to 64.9 mg
418 H₂O₂ min⁻¹, current efficiency of 89.3% and energy consumption of 0.4 kWh m⁻³ during the
419 first minutes. The SPEF treatment of 75 L of pesticides mixtures allowed the removal of more
420 than 50% of each pesticide in only 5 min, where upon further degradation as well as
421 mineralization of by-products and their Fe(III) complexes became much slower but always
422 superior to EO and EF treatments. Further optimization of the SPEF process for treating
423 different kind of wastewater in the integrated pilot system is in progress.

424 **Acknowledgments**

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429 acknowledged.

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518 **Figure captions**

519 **Fig. 1.** Front view of (a) the four filter-press type electrochemical cells of the pilot unit, and
520 (b) the CPC photoreactor. In (c), schematic diagram of the pilot unit equipped with one cell
521 (examined in this work), showing: (1) CPC photoreactor, (2) valve, (3) feed tank, (4) power
522 supply, (5) electrochemical reactor, (6) liquid flowmeter, (7) air compressor, (8) magnetic
523 pump.

524 **Fig. 2.** (a) Accumulated H_2O_2 concentration and current efficiency (% CE) at different pH
525 values and current densities (j). The values were obtained after 30 min of continuous
526 recirculation of a 50 mM Na_2SO_4 solution at a liquid flow rate of 4.4 L min^{-1} and air flow rate
527 of 5 L min^{-1} . (b) H_2O_2 production rate as function of electrolysis time, at constant pH = 3.0
528 and various j values. (c) H_2O_2 production rate as function of electrolysis time, at constant $j =$
529 100 mA cm^{-2} and varying pH.

530 **Fig. 3.** Comparison of the actual results obtained experimentally regarding (a) H_2O_2
531 production and (b) current efficiency (in %), with those predicted via central composite
532 design equations (12) and (13), respectively.

533 **Fig. 4.** (a) 3D surface plot and (b) contour plot for the H_2O_2 production as function of the
534 initial pH (A) and current density (B). Experimental data correspond to 30-min electrolyses
535 under continuous recirculation of a 50 mM Na_2SO_4 solution at liquid flow rate of 4.4 L min^{-1}
536 and air flow rate of 5 L min^{-1} .

537 **Fig. 5.** (a) 3D surface plot and (b) contour plot for current efficiency (in %), as in Fig. 4.

538 **Fig. 6.** (a) Effect of liquid flow rate on various process efficiency parameters, corresponding
539 to 30-min electrolyses; (b) accumulated H_2O_2 as a function of electrolysis time, at three

540 different liquid flow rates. Fixed parameters: 50 mM Na₂SO₄ at pH 3.0, $j = 74 \text{ mA cm}^{-2}$, air
541 flow rate of 5 L min⁻¹.

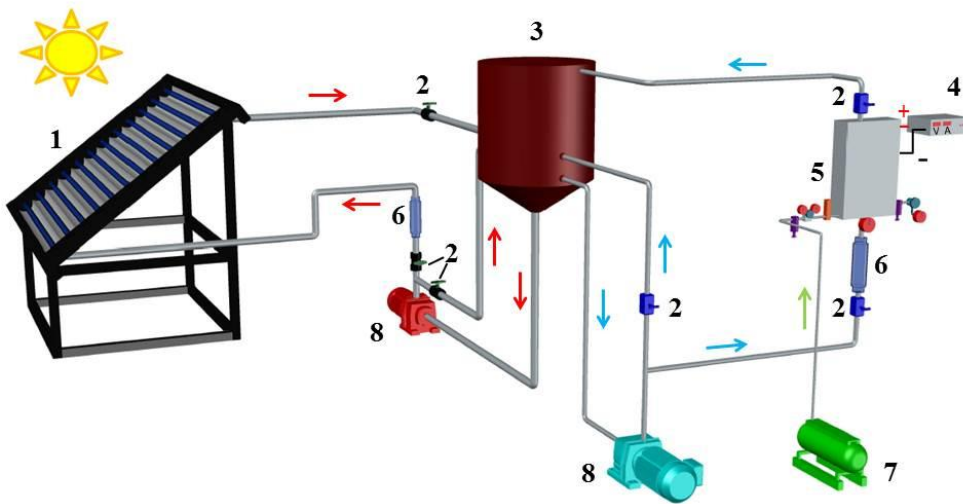
542 **Fig. 7.** (a) Effect of air flow rate on various process efficiency parameters, corresponding to
543 30-min electrolyses; (b) accumulated H₂O₂ as function of electrolysis time, at different air
544 flow rates. Fixed parameters: 50 mM Na₂SO₄ at pH 3.0, $j = 74 \text{ mA cm}^{-2}$, liquid flow rate of
545 4.4 L min⁻¹. The optimum trial corresponds to the same conditions but using a liquid flow rate
546 of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹.

547 **Fig. 8.** (a) Effect of Na₂SO₄ molar concentration on various process efficiency parameters,
548 corresponding to 30-min electrolyses; (b) accumulated H₂O₂ as a function of electrolysis time,
549 at three different electrolyte concentrations. Fixed parameters: electrolyte solution at pH 3.0, j
550 = 74 mA cm⁻², liquid flow rate of 4.4 L min⁻¹ and air flow rate of 5 L min⁻¹.

551 **Fig. 9.** Normalized concentration decays of pesticides (a) pyrimethanil (PYR) and (b)
552 methomyl (MET) versus electrolysis time during the (○, □) electro-oxidation (EO) and
553 (●, ■) solar photoelectro-Fenton (SPEF) treatment of 75 L of mixtures of both pesticides (71
554 mg L⁻¹ DOC) in deionized water with 50 mM Na₂SO₄ at pH 3.0 using the pilot plant at $j = 74$
555 mA cm⁻², liquid flow rate of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹. SPEF treatment was
556 performed in the presence of 0.5 mM Fe²⁺ as catalyst.

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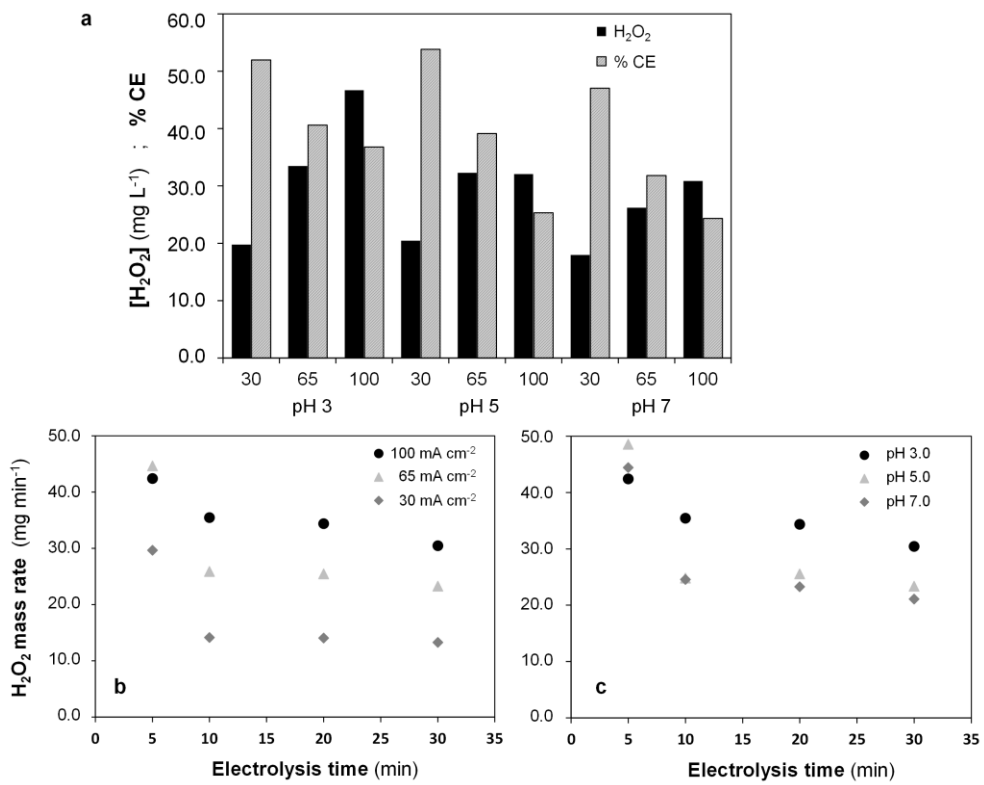
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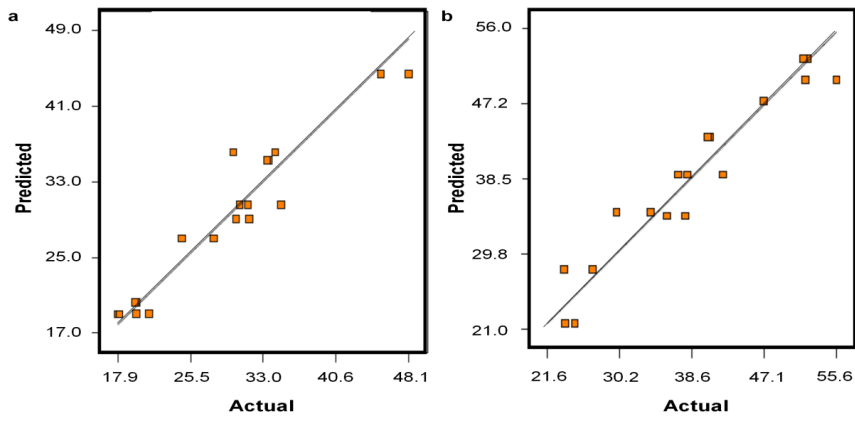
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Fig. 1



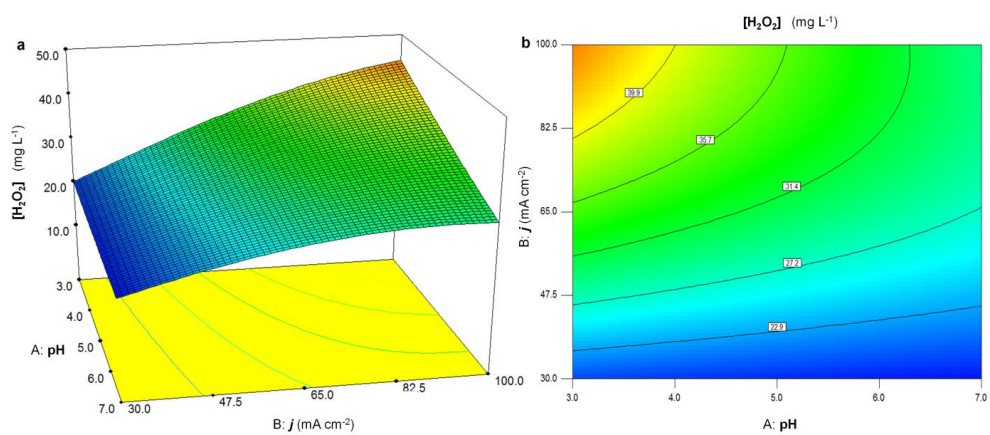
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Fig. 2



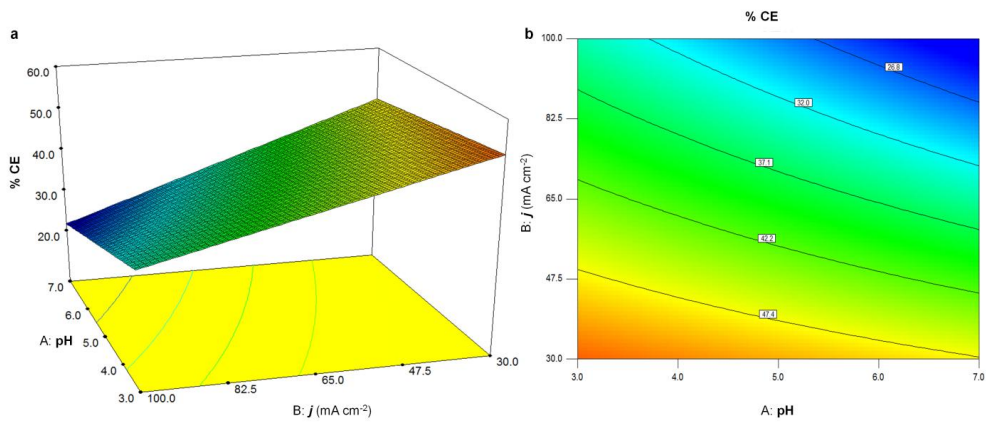
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Fig. 3



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Fig. 4



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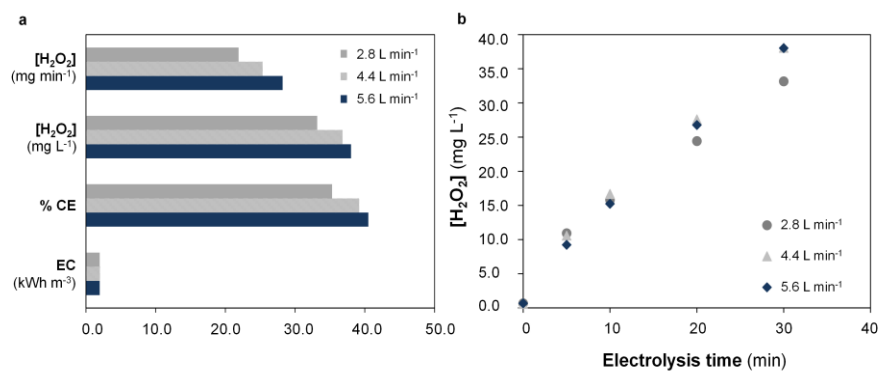
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Fig. 5



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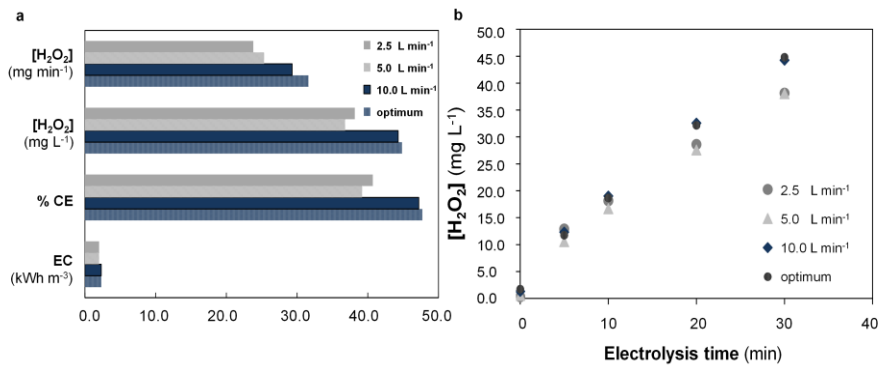
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Fig. 6



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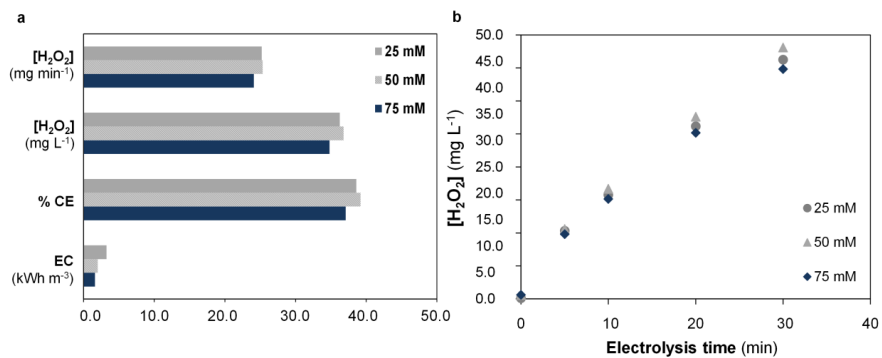
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Fig. 7



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Fig. 8

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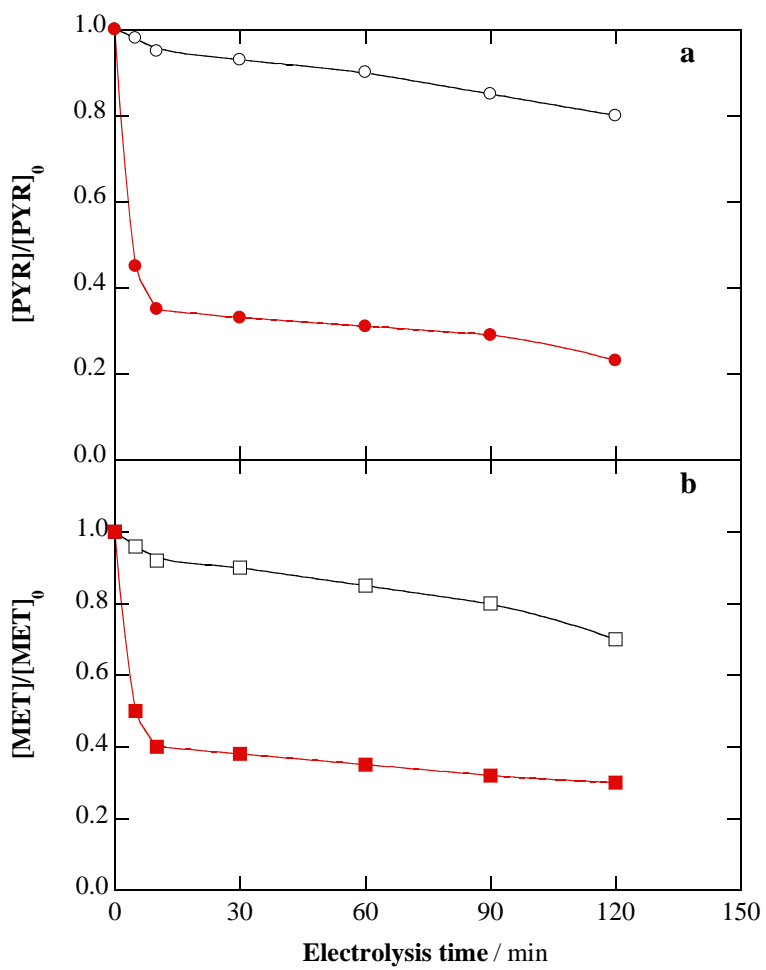


Fig. 9

634 **Table 1**

635 Experimental range and levels of independent variables

Variable	Factor	Units	Level and Range		
			Low (-1)	Central (0)	High (+1)
pH	A	-	3	5	7
<i>j</i>	B	mA cm ⁻²	30	65	100

636

637

638 **Table 2**

639 Design of experiments and results

Run	Independent variables		Responses ($t = 5\text{min}$)		Responses ($t = 30\text{min}$)	
	pH	j (mA cm^{-2})	$[\text{H}_2\text{O}_2]$ (mg L^{-1})	% CE	$[\text{H}_2\text{O}_2]$ (mg L^{-1})	% CE
1	3	100	15.11	71.40	48.12	37.90
2	7	30	4.97	78.30	18.06	47.05
3	5	65	10.41	75.70	34.85	42.30
4	7	100	8.88	42.00	31.55	24.90
5	3	30	5.93	93.40	19.67	51.70
6	3	100	13.41	63.40	45.25	35.70
7	5	65	9.23	67.20	31.42	38.10
8	5	100	9.71	45.90	34.25	27.00
9	3	65	8.93	65.00	33.59	40.70
10	7	100	8.45	40.00	30.16	23.80
11	5	100	8.36	39.60	29.90	23.60
12	5	30	6.23	98.20	21.15	55.60
13	5	65	8.67	63.10	30.55	37.00
14	5	30	5.49	86.60	19.80	52.00
15	3	30	5.75	90.70	19.85	52.20
16	7	65	7.71	56.10	27.85	33.80
17	3	65	9.67	70.30	33.38	40.50
18	7	65	6.58	47.90	24.54	29.80
19	7	30	4.84	76.30	17.89	47.00

640

641 **Table 3**

642 ANOVA results for response surface of the Quadratic and 2FI models

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
<i>Quadratic model</i>	1225.26	5	245.05	30.44	<0.0001	significant
A-pH	206.75	1	206.75	25.68	0.0002	
B-j	880.82	1	880.82	109.41	<0.0001	
AB	98.63	1	98.63	12.25	0.0039	
A ²	1.56	1	1.56	0.19	0.6673	
B ²	38.61	1	38.61	4.80	0.0474	
Residual	104.66	13	8.05			
Lack of fit	73.34	3	24.45	7.80	0.0056	not significant
Pure error	31.33	10	3.13			
<i>2FI model</i>	1723.02	3	574.34	60.89	<0.0001	significant
A-pH	228.38	1	228.38	24.21	0.0002	
B-j	1466.34	1	1466.34	155.45	<0.0001	
AB	28.31	1	28.31	3.00	0.1037	
Residual	141.49	15	9.43			
Lack of fit	102.41	5	20.48	5.24	0.0127	not significant
Pure error	39.08	10	3.91			

643

644

645 **Table 4**

646 Optimum operation conditions proposed by Design Expert 7.0.0 software to attain maximum

647 H₂O₂ concentration and current efficiency at 30 min of electrolysis.

Test number	pH	j (mA cm ⁻²)	[H ₂ O ₂] (mg L ⁻¹)	% CE	Desirability	
1	3.00	73.66	38.0961	41.0744	0.604	Selected
2	3.00	74.16	38.2467	40.9437	0.604	
3	3.00	72.82	37.8392	41.2949	0.604	
4	3.00	70.00	36.9532	42.0343	0.603	

648

649

650 **Table 5**

651 Models validation under optimum conditions, with experimental data obtained after 30 min of
652 electrolysis under continuous recirculation of 50 mM Na₂SO₄ solution at pH 3.0, 74 mA cm⁻²,
653 liquid flow rate of 3.3 L min⁻¹ and air flow rate of 5 L min⁻¹. Two independent runs were
654 performed

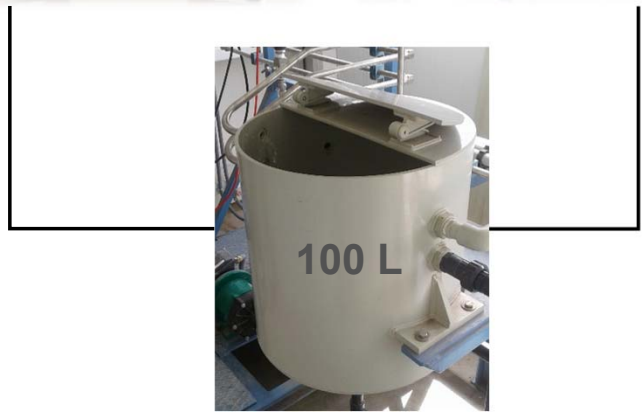
	Run		Average actual values	Predicted values	Relative error (%)
	a	b			
H ₂ O ₂ (mg L ⁻¹)	35.51	38.07	36.79	38.20	3.69
% CE	37.80	40.60	39.20	40.99	4.38

655



BDD($\cdot\text{OH}$)

Pesticides degradation

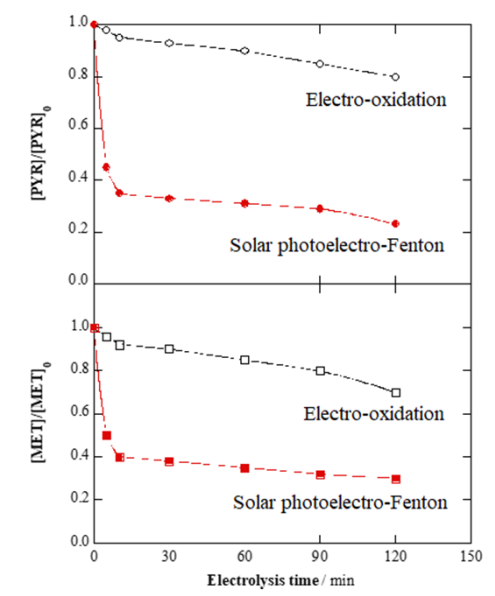


Fe^{2+} solar regeneration

Optimization

pH 3.0
73.6 mA cm⁻²

64.9 mg H₂O₂ min⁻¹
Current Efficiency 89.3%



Highlights

- The first known solar photo-assisted electro-catalytic pilot plant (100 L) has been optimized and started-up.
- Synergy between homogeneous ($\bullet\text{OH}$), heterogeneous (BDD($\bullet\text{OH}$)) and solar photocatalysis was evaluated.
- Solar photoelectro-~~n~~-Fenton process removed more than 50% of a pesticides mixture in only 5 minutes.

1 **Optimization of electrocatalytic H₂O₂ production at pilot plant scale**
2 **for solar-assisted water treatment**

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14

Field Code Changed

15 **Abstract**

16 This manuscript summarizes the successful start-up and operation of a hybrid eco-engineered
17 water treatment system, at pilot scale. The pilot unit, with 100-L capacity, has been devised
18 for the efficient electrocatalytic production of H₂O₂ at an air-diffusion cathode, triggering the
19 formation of •OH from Fenton's reaction with added Fe²⁺ catalyst. These radicals, in
20 combination with those formed at a powerful boron-doped diamond (BDD) anode in an
21 undivided cell, are used to degrade a mixture of model pesticides. The capability of the plant
22 to produce H₂O₂ on site was initially optimized using an experimental design based on central
23 composite design (CCD) coupled with response surface methodology (RSM). This aimed to
24 evaluate the effect of key process parameters like current density (*j*) and solution pH. The
25 influence of electrolyte concentration as well as liquid and air flow rates on H₂O₂
26 electrogeneration and current efficiency at optimized *j* and pH was also assessed. The best
27 operation conditions resulted in H₂O₂ mass production rate of 64.9 mg min⁻¹, 89.3% of
28 current efficiency and 0.4 kWh m⁻³ of energy consumption at short electrolysis time.
29 Performance tests at optimum conditions were carried out with 75 L of a mixture of pesticides
30 (pyrimethanil and methomyl) as a first step towards the elimination of organic contaminants
31 by solar photoelectro-Fenton (SPEF) process. The **combined action of** homogeneous (•OH)
32 and heterogeneous (BDD(•OH)) catalysis along with photocatalysis (UV photons collected at
33 a solar CPC photoreactor) allowed the removal of more than 50% of both pesticides in 5 min,
34 confirming the fast regeneration of Fe²⁺ catalyst through cathodic reduction and photo-Fenton
35 reaction.

36 *Keywords:* Boron-doped diamond; Gas-diffusion electrode; Hydrogen peroxide
37 electrogeneration; Solar photoelectro-Fenton; Wastewater treatment

38 **1. Introduction**

39 The extraordinary development of chemicals manufacturing and their widespread use in
40 all human activities is intimately associated with contamination of aquatic environment.
41 Water quality monitoring programs underline the seriousness of the problem worldwide and
42 highlight the potential hazards posed by mixtures of synthetic organic contaminants (SOCs)
43 and their metabolites in surface water and groundwater [1-4]. Typically, SOC include
44 solvents, preservatives, pharmaceuticals and personal care products, lubricants, dyes or active
45 substances for plant protection [5]. Among the latter, methomyl (MET) and pyrimethanil
46 (PYR) are ubiquitous in intensive agriculture, which is worrisome since they are classified as
47 persistent organic pollutants (POPs) [6] and are considered extremely toxic [7,8]. This issue
48 has prompted the application of advanced oxidation processes (AOPs) for the fast and
49 complete removal of SOC from polluted water streams [9], based on the in situ production of
50 hydroxyl radical ($\bullet\text{OH}$) as main reactive oxygen species (ROS).

51 Fenton's reaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), so-called
52 Fenton's reagent, is the most popular source of $\bullet\text{OH}$ for practical applications [10]. As an
53 upgraded approach, the electro-Fenton (EF) process allows overcoming two key limitations of
54 the conventional chemical method [11-13]: (i) it ensures the continuous regeneration of Fe^{2+}
55 through cathodic reduction of Fe^{3+} , thus requiring a much lower amount of catalyst to perform
56 the treatment, and (ii) it avoids the handling, storage and transportation of H_2O_2 produced
57 industrially, since this reagent can be electrosynthesized on site through Reaction (1) by using
58 appropriate cathode materials.

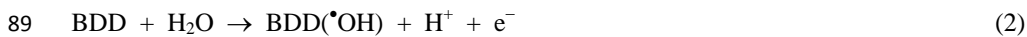


60 Electrocatalytic H_2O_2 generation is becoming a hot topic because the combination of
61 electrochemistry with new catalysts enables a more eco-friendly and less energy-intensive
62 production of this commodity [14,15]. Several prospective electrocatalysts have been

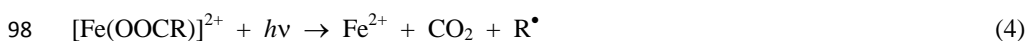
63 developed, with noble metals and metal alloys like Pd-Au, Pt-Hg and Pt/Pd-Hg as particularly
64 prominent options [14,16,17]. Non-precious Co-based particles are very active promoters of
65 Reaction (1) as well, at smaller cost [18]. Unfortunately, none of these catalysts is viable for
66 large-scale water treatment due to their high cost and toxicity, which has fostered the
67 investigation on inexpensive carbonaceous materials [14,19,20]. Unmodified carbon-based
68 catalysts exhibit appealing characteristics as cathodes, such as non-toxicity and high stability,
69 conductivity and durability. H₂O₂ production with such inexpensive materials is particularly
70 interesting for developing small- or medium-size decentralized units where the chemical is
71 generated on demand [21]. This can be achieved using graphite felt, reticulated vitreous
72 carbon, activated carbon fiber or carbon nanotubes as cathode, completely immersed into the
73 solution to generate H₂O₂ from dissolved O₂ [22-24]. However, much greater H₂O₂
74 concentrations are attained upon implementation of an air-chamber in the electrochemical
75 reactor, since it allows continuous air-feeding through a hydrophobized carbon-based gas-
76 diffusion electrode (GDE) [15,18,25-28]. Worth noting, the vast majority of studies on
77 Fenton-based electrochemical AOPs (EAOPs) reporting data on H₂O₂ production at GDE
78 have been carried out either at laboratory scale or in small pre-pilot plants of 2.5 L [29] and 5
79 L [30,31]. Only one work reported the use of a bigger plant with 25 L capacity, but it was
80 mainly focused on aniline degradation [32].

81 Undivided electrochemical cells are preferred to perform all these studies on water
82 treatment because the use of a separator would increase the cell voltage and hence, the energy
83 consumption. In addition, in such cells, the combination of carbonaceous cathodes with
84 electrocatalytic materials that promote the anodic production of heterogeneous hydroxyl
85 radical enhances the performance of EF process. Boron-doped diamond (BDD) thin film on Si
86 substrate is the best anode to oxidize H₂O to physisorbed •OH via Reaction (2) [11,13,33],

87 owing to its large overpotential for O₂ evolution. However, Ti and Nb are more suitable for
88 plant-scale applications due to their much higher mechanical and chemical resistance.



90 The best performance among Fenton-based EAOPs for SOCs degradation is attained
91 upon continuous irradiation of the treated solution with UV/Vis light. This is feasible
92 employing a UVA lamp in photoelectro-Fenton (PEF) process [11,13], since it promotes: (i) a
93 high regeneration rate of Fe²⁺, with concomitant production of homogeneous [•]OH, from
94 photoreduction of the main Fe(III) species at pH ~ 3.0 (Reaction (3)), (ii) the
95 photodegradation of Fe(III)-carboxylate complexes formed as intermediates (Reaction (4)),
96 and (iii) the direct photolysis of some pollutants and/or their oxidation by-products [11,34].



99 In order to achieve the synergy between electrocatalytic and photolytic reactions at an
100 affordable cost, UVA lamps have been lately replaced by direct sunlight irradiation, yielding
101 the promising solar PEF (SPEF) process. Its great oxidation capability arises from: (i) the
102 higher UV photon flux from sun if the solar collector design is adapted to the photoreactor,
103 which upgrades the [•]OH production, along with (ii) the additional illumination within the
104 visible range ($\lambda > 400$ nm), promoting Reaction (3) (also active in the visible range) and
105 accelerating the photolysis of refractory Fe(III)-carboxylate complexes (Reaction (4)) [34].
106 Very good degradation results by SPEF with GDE were obtained using a recirculation small
107 pilot plant of 2.5-L capacity equipped with a flat-plate photoreactor [35-37], also employed to
108 treat pesticides like mecoprop [35], diuron [38] or tebuthiuron and ametryn [39]. Replacement
109 by a more efficient photoreactor based on compound parabolic collectors (CPC) could
110 increase the efficiency of SPEF due to the greater photon flux supply to the solution. At

111 present, CPC is the most popular photoreactor, as confirmed by its integration in most of the
112 SPEF units for treating 2.2 L [40], 6 L [41], 8 L [42] and up to 10 L [43-48], which is the
113 largest volume investigated so far.

114 Based on the excellent performance of SPEF at limited scale, a larger pilot plant has been
115 developed for the treatment of SOC_s by EAOPs with H₂O₂ electrogeneration. The system,
116 with capacity to treat up to 100 L, consists of four undivided Nb-BDD/GDE filter-press cells
117 coupled with a solar CPC, and has been installed and tested at Plataforma Solar de Almería
118 (PSA), the largest European facility to test solar technologies. As a first step toward the
119 treatment of real wastewater, this work is focused on the optimization of pilot plant main
120 operation variables for the electrocatalytic H₂O₂ production, including current density (*j*),
121 solution pH, liquid flow rate, air flow rate and electrolyte concentration. This was made with
122 the aid of central composite design (CCD) coupled to response surface methodology (RSM).
123 The plant was further validated by performing degradation trials under optimum conditions
124 using a mixture of fungicide PYR and insecticide MET spiked into conductive water at high
125 concentrations to simulate real agricultural wastewater. Note that these pesticides have only
126 been studied before by AOPs like solar TiO₂ photocatalysis and solar photo-Fenton at pilot
127 scale [6] and EF at lab scale [8].

128 **2. Materials and methods**

129 *2.1. Chemicals*

130 Heptahydrated ferrous sulfate (Sigma-Aldrich) used as catalyst and anhydrous sodium
131 sulfate (Fluka) employed as background electrolyte were of analytical grade. PYR (IQV,
132 AgroEvo, 98% purity) and MET (Aragonesas Agro, 99.5% purity) were of reagent grade and
133 used without further purification. Mixtures of the two pesticides were prepared with deionized
134 water (conductivity < 10 μS cm⁻¹, dissolved organic carbon (DOC) < 0.5 mg L⁻¹) and the

135 electrolyte, and their pH was adjusted with analytical grade sulfuric acid (J.T. Baker). Organic
136 solvents and other chemicals employed for HPLC analysis of the pesticides were of analytical
137 grade from Sigma-Aldrich.

138 2.2. Pilot plant

139 Images of the filter-press type electrochemical cells and the CPC photoreactor, along with
140 a schematic diagram of the pilot plant, are shown in Fig. 1. The plant consisted of four plate-
141 and-frame electrochemical reactors (Electro MP-Cells from ElectroCell) coupled to a
142 purpose-made solar CPC. Each cell contained an anode made of BDD thin film deposited on a
143 niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the cathode,
144 both with 0.01 m² effective area. The CPC photoreactor had a total illuminated area of 2 m²,
145 corresponding to an irradiated volume of 23 L. It was comprised of 10 borosilicate glass tubes
146 (150 cm length × 4.5 cm inner diameter) mounted in an aluminum frame on a platform tilted
147 37° (PSA, 37°N, 2.4°W). The working volume was 25 L to carry out the optimization of H₂O₂
148 electrogeneration, and 75 L to perform the degradation experiments. The unit was equipped
149 with two magnetic drive pumps (PAN World, 0.75 kW), one for pumping the solution from
150 the feed tank (maximum capacity of 100 L) to the electrochemical cells, and the other for the
151 liquid recirculation to and from the CPC. The GDE was fed with compressed air (ABAC air
152 compressor, 1.5 kW) at a pressure and flow rate regulated with a back-pressure gauge and a
153 flowmeter, respectively, in order to avoid the flooding of the air chamber. The experiments
154 were made at constant j using a Delta Electronika power supply (limited to 70 V and 22 A).

155 Global ultraviolet solar radiation (UV_G) was measured using a radiometer (Kipp &
156 Zonen, model CUV 3) mounted on a platform tilted 37°, the same angle as the photoreactor,
157 which provided data in terms of incident irradiance ($W_{UV} m^{-2}$). This informs about the energy
158 reaching any surface in the same position with regard to the sun. Eq. (5) allows combining the

159 data from trials performed in different days, thus enabling comparison with results obtained in
160 other photocatalytic experiments [49].

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot \overline{UV}_{G,n} \cdot A_r \cdot V_T \quad (5)$$

161 where Q_{UV} is the accumulated UV energy per unit of volume (kJ L^{-1}), $\overline{UV}_{G,n}$ (in W m^{-2}) is the
162 average UV radiation measured during $\Delta t_n (= t_n - t_{n-1})$, A_r is the irradiated surface area (2 m^2)
163 and V_T is the total volume treated in the pilot plant.

164 2.3. Experimental design

165 Experimental design by RSM was employed to optimize the in situ electrogeneration of
166 H_2O_2 . Trials were performed with one of the four identical electrochemical cells of the pilot,
167 assuming that the resulting optimum conditions would be also valid for the other three cells.
168 Two optimization criteria were considered: (a) maximization of the concentration of the
169 produced H_2O_2 , and (b) maximization of the current efficiency (CE, in percentage), defined as
170 the ratio between the electricity consumed by the electrode reaction of interest and the total
171 electricity supplied. CE can be calculated via Eq. (6), where n represents the stoichiometric
172 number of electrons transferred in Reaction (1), F is the Faraday constant ($96,487 \text{ C mol}^{-1}$),
173 $[\text{H}_2\text{O}_2]$ the concentration of H_2O_2 accumulated in bulk solution (mg L^{-1}), V_T the volume of the
174 treated solution (L), $M(\text{H}_2\text{O}_2)$ the molecular weight of H_2O_2 (34 g mol^{-1}), and Q the charge
175 consumed during the electrolysis (C).

$$176 \quad \% CE = \frac{nF[\text{H}_2\text{O}_2]V_T}{1000 M(\text{H}_2\text{O}_2)Q} \times 100 \quad (6)$$

177 RSM was first used to assess the relationship between response (H_2O_2 concentration or %
178 CE) and two independent variables, namely the solution pH (factor A) and j (factor B), as
179 well as to optimize the relevant conditions in order to predict the best value of responses.
180 CCD, the most widely used approach of RSM and, more specifically, a face centered
181 composite (FCC) design, was employed to determine the effect of the two variables. Design

182 Expert[®] v.7.0.0 software (Stat-Ease Inc., USA) was used. Three levels between -1 and +1
183 were established for the two independent variables (Table 1). Ranges were chosen based on
184 preliminary experiments (data not shown here), background knowledge, and some constraints
185 arising from the cathodic H₂O₂ electrogeneration and the nature of the electrode materials. For
186 example, the production of H₂O₂ is favored at acidic pH (Reaction (2)), whereas the use of
187 GDE and BDD anode limits the operation cell voltage to less than 25 V to prevent surface
188 damage, which would cause the loss of electrocatalytic properties, and keep a reasonable CE
189 [50]. This means that maximum current that can be applied is 10 A ($j = 100 \text{ mA cm}^{-2}$).

190 For the CCD, a 2³ full factorial design with 3 replicates at the center point (resulting in 19
191 experiments) was used to determine the optimum values of independent variables. These
192 experiments were carried out by recirculating synthetic solutions of 50 mM Na₂SO₄ at a liquid
193 flow rate of 4.4 L min⁻¹, and they were randomly performed to minimize the effect of
194 systematic errors. Analysis of variance (ANOVA) of the data was performed to identify
195 significant values ($p\text{-value} < 0.05$). The quality of the fit of polynomial model was expressed
196 by the value of correlation coefficient (R^2). The main indicators demonstrating the
197 significance and adequacy of the used model include the model F-value (Fisher variation
198 ratio), probability value (Prob > F), and adequate precision. The optimal region of the
199 independent variables was determined by plotting three-dimensional response surfaces of the
200 independent and dependent variables. Additionally, numerical optimization of the
201 independent variables was carried out using the same software.

202 A second set of experiments was carried out aiming to assess the effect of electrolyte
203 concentration as well as liquid and air flow rates, under the optimum pH and j conditions. The
204 best operation conditions were finally applied to degrade mixtures of pesticides, in the
205 absence or presence of iron catalyst. In SPEF, the pesticide solution was irradiated when
206 circulating through the CPC photoreactor.

207 *2.4. Instruments and analytical methods*

208 The concentration of H₂O₂ accumulated during the electrolysis was determined by adding
209 Ti(IV) oxysulfate to the sample and measuring the absorbance at 410 nm, according to DIN
210 38409 H15. Iron concentration was measured by using 1,10-phenanthroline, following ISO
211 6332. In both cases, a Unicam UV/Vis UV2 spectrophotometer was employed. Dissolved
212 organic carbon (DOC) was measured after sample filtration through a 0.22 µm Nylon filter,
213 on a Shimadzu TOC-VCSN analyzer. The degradation rate of the two pesticides was
214 monitored on a UPLC/UV Agilent Technologies Series 1200, equipped with a C-18
215 ZORBAX XDB C-18 analytical column. The column was kept at 30 °C and the injection
216 volume was 50 µL. A linear gradient profile with water and acetonitrile (ACN) eluted at a
217 flow rate of 1 mL min⁻¹ was established as follows: 0-4 min, isocratic at 85/15 (v/v)
218 H₂O/ACN; 4-8 min, gradient from 85/15 to 20/80 (v/v); 8-15 min, isocratic at 85/15 (v/v). Re-
219 equilibration time was 3 min. The UV signals for MET and PYR were monitored at the
220 wavelength of their maximum absorption, 230 nm and 270 nm, respectively. For UPLC
221 analyses, 9 mL of sample were filtered through a 0.22 µm PTFE syringe filter. Then, it was
222 washed with 1 mL of UPLC grade ACN to extract any compound adsorbed on the filter. The
223 pH of the treated solution was monitored by means of a Crison 25 pH-meter.

224 **3. Results and discussion**

225 *3.1. Influence of independent experimental variables on the in situ H₂O₂ electrogeneration*

226 The results obtained from the experimental design matrix including the two independent
227 variables (pH, *j*) are shown in Table 2. The responses (H₂O₂ concentration and % CE) are
228 presented at two electrolysis times, 5 and 30 min, corresponding to approximately one and
229 five circulations of the initial feed solution volume (25 L) through the electrochemical cell,
230 respectively. The average values of the two responses at 30 min are illustrated in Fig. 2a,

231 whereas the changes in H₂O₂ mass production rate over the electrolysis time are depicted at
232 constant pH = 3.0 (Fig. 2b) or $j = 100 \text{ mA cm}^{-2}$ (Fig. 2c).

233 As expected, a higher accumulation of H₂O₂ was found as the electrolyses were
234 prolonged, although this occurred in concomitance with current efficiency decrease (Table 2).
235 This is also confirmed from the profiles of the H₂O₂ production rates with time, since the
236 highest values were attained at the beginning of the electrolyses until quasi-steady values
237 were observed at longer times, regardless of the j (Fig. 2b) or the pH (Fig. 2c) studied.
238 According to Eq. (6), the gradual lower efficiency with electrolysis time is related to the
239 reduced [H₂O₂]/ Q ratio as a result of nonlinear increase of the accumulated H₂O₂. This kind of
240 behavior can be partly explained by the use of batch operation mode, since the H₂O₂
241 production rate at the air-diffusion cathode from Reaction (1) becomes equal to its
242 decomposition rate by parasitic reactions that can take place in the cell. For example, the
243 continuous recirculation of H₂O₂ accumulated in the solution may promote its electrochemical
244 reduction at the cathode surface (Reaction (8)) and, to much lesser extent, its spontaneous
245 disproportion in the bulk (Reaction (9)) [11].



248 Furthermore, considering that an undivided electrochemical reactor is employed, other
249 additional parasitic reactions occur, as for example the oxidation of H₂O₂ to O₂ at the Nb-
250 BDD anode surface via HO₂[•] as an intermediate, according to the following reactions:



253 In addition, it is worth mentioning that H₂O₂ decomposition is promoted as the solution
254 pH becomes more alkaline, according to the following reaction:



256 | As a consequence of these undesired reactions, the accumulated H₂O₂ concentration is
257 always below the theoretical maximum. As explained in the Introduction, undivided reactors
258 are the best choice for water treatment, but divided ones should be employed for industrial
259 electrochemical H₂O₂ production. Note that similar trends for H₂O₂ accumulation have been
260 reported by Brillas and co-workers, as shown during the electrolysis of Na₂SO₄ solutions in a
261 similar batch filter-press BDD/GDE reactor at *j* values between 50 and 150 mA cm⁻² [29].

262 In addition, Fig. 2b and 2c show that the maximum H₂O₂ production was achieved at 100
263 mA cm⁻² and pH 3.0. This agrees with the fact that a higher electron and proton supply
264 promotes a faster O₂ reduction from Reaction (1).

265 3.2. Validation of the correlation models

266 With the aid of Design Expert software, the models that best correlated the responses and
267 the independent variables shown in Table 2 were:

268 (i) Quadratic model:

$$269 \quad [H_2O_2] = 2.19 - 0.31 \cdot \text{pH} + 0.81 \cdot j - 0.05 \cdot \text{pH} \cdot j + 0.15 \cdot \text{pH}^2 - 2.42 \times 10^{-3} \cdot j^2 \quad (12)$$

270 (ii) Two-factor interaction model (2FI):

$$271 \quad \% \text{ CE} = 61.68 - 0.43 \cdot \text{pH} - 0.18 \cdot j - 0.0275 \cdot \text{pH} \cdot j \quad (13)$$

272 Both models were validated by the analysis of variances (ANOVA), and the results are
273 summarized in Table 3. The statistical significance was assessed by means of Fisher's test.
274 The F-values calculated for the lack of fit of the quadratic and the 2FI models were 30.44 and
275 60.89, respectively, suggesting that they are satisfactory. Similar conclusions can be drawn
276 from the low probability values (p-value) at a 95% confidence level (< 0.0001) for both
277 models. The statistical significance of the two models is also verified from Fig. 3, since the
278 actual values of the accumulated H₂O₂ concentration and current efficiency are randomly
279 distributed around the mean of predicted values. Moreover, good linear correlations between

280 the predicted and observed values for H₂O₂ concentration and % CE, with corresponding R²
281 values of 0.932 and 0.924, were obtained.

282 According to the ANOVA analysis (Table 3), the effects of the independent variables (A-
283 pH, B-*j*) were obvious and the effective order was *j* > initial pH, whereas the interaction of the
284 two variables (AB) was not obvious (p-value > 0.1). This can also be deduced from Fig. 2b
285 and 2c, which show that the H₂O₂ production is more substantially affected by *j* (Fig. 2b)
286 rather than by solution pH, with the latter showing only a slight superiority at pH 3.0 as
287 compared to neutral pH (Fig. 2c). This is important, since the adjustment of pH when treating
288 wastewater complicates the process and increases the water salinity and the operation cost (for
289 acidification and subsequent neutralization).

290 3.3. Optimization by response surface methodology

291 To better assess the effect of pH and *j* on H₂O₂ production and current efficiency and
292 identify their optimum values, 3D response surfaces and contour maps were developed with
293 the aid of Design Expert software. The response surface plot shown in Fig. 4 implies that the
294 generation of H₂O₂ increases with *j* at acidic pH values. On the other hand, the current
295 efficiency (Fig. 5) decreases as *j* is raised, regardless of the initial pH of the electrolyte
296 solution. As explained above, this is attributed to the batch operation mode in an undivided
297 cell configuration, which promotes the activation of detrimental side reactions. Four sets of
298 optimum pH and *j* values were proposed by the statistical software (Table 4), yielding
299 maximum H₂O₂ production and current efficiency. Among the four solutions proposed,
300 solution number 1, requiring electrolyte pH = 3.0 and *j* = 73.66 mA cm⁻² (~74.0), was selected
301 as the optimum one. Under these conditions, a set of experiments was conducted aiming to
302 validate the two correlation models (Eq. (12) and (13)) and to investigate the effect of other
303 operation conditions like liquid and air flow rates, as well as electrolyte concentration. The
304 main goal was to fully optimize the electrocatalytic H₂O₂ production at plant scale, eventually

305 yielding the most effective (highest H₂O₂ production rate), efficient (maximum CE
306 percentage) and profitable (lowest energy consumption) process at large scale.

307 The results of two replicate experiments under the aforementioned optimum conditions
308 are summarized in Table 5. The relative errors were below 5% for both, H₂O₂ generation and
309 % CE (3.69% and 4.38%, respectively), demonstrating the excellent fitting of the
310 experimental results (actual values) with those predicted by the two models.

311 3.3.1. Effect of liquid flow rate

312 The feed flow rate is closely related to the hydraulic residence time (HRT) of the treated
313 solution within the electrochemical cell. This is of great significance under continuous
314 operation mode, where the feed solution is continuously treated and discharged. For batch
315 operation, as is the case of the experiments carried out in this work, the recirculation flow rate
316 does not necessarily match the HRT, but it rather affects the mixing and may create turbulent
317 flow within the electrochemical cell. This, in turn, may intensify the mass transport induced
318 by the higher local concentration of molecular oxygen dissolved in the aqueous phase. Indeed,
319 when the flow rate was doubled (from 2.8 to 5.6 L min⁻¹), H₂O₂ production was gradually
320 greater at each given time (Fig. 6b), finally increasing by 28.8% at 30 min (Fig. 6a, [H₂O₂] in
321 mg min⁻¹). Current efficiency also increased in the same proportion, as a result of the higher
322 H₂O₂ generation at similar charge consumption (note that energy consumption varied between
323 1.97 and 2.00 kWh m⁻³ for all pilot runs) (Fig. 6a).

324 3.3.2. Effect of air flow rate

325 Large feeding of air or pure O₂ to the air chamber is often needed to counterbalance the
326 existing pressure on the wet face of the GDE, thereby avoiding flooding that would stop the
327 H₂O₂ production. If correctly adjusted, an increase in air flow rate may upgrade the H₂O₂
328 accumulation. As found for the pilot plant studied in this work, a rise in the air flow rate from
329 2.5 and 5 L min⁻¹ to 10 L min⁻¹, resulted in an enhanced H₂O₂ production by 23.1% and

330 15.6% at 30 min, respectively (Fig. 7a and 7b). Moreover, the kinetics of H₂O₂ production
331 was faster at the maximum air flow rate of 10 L min⁻¹ (Fig. 7b), with no negative effect on the
332 corresponding energy consumption, which was similar at all air flow rates examined. This is
333 interesting, since one might presume that an excessive air feeding could generate too many
334 bubbles within the electrochemical reactor, thereby increasing the ohmic drop and also
335 affecting the stability of the liquid flow rate, which did not occur.

336 Based on these results, as well as on the better performance of the plant at high
337 electrolyte flow rates, it can be concluded that the combined increase of air and liquid flow
338 rates may effectively enhance the fraction of oxygen consumed for H₂O₂ production
339 (Reaction (1)) over the total amount of air fed. Indeed, under the optimum operation
340 conditions, namely 50 mM Na₂SO₄ solution at pH 3.0 treated at 74 mA cm⁻², with liquid flow
341 rate of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹, the highest H₂O₂ mass production rate and
342 current efficiency were obtained. In the first 5 min of electrolysis, these conditions led to
343 H₂O₂ production with a mass rate of 64.9 mg min⁻¹, 89.3% current efficiency and energy
344 consumption of 0.4 kWh m⁻³. These values are among the best achieved with similar system
345 configurations. For example, Flox et al. [29] reported a production rate of ca. 23 mg min⁻¹ at
346 30 min in 50 mM Na₂SO₄ at pH 3.0, 100 mA cm⁻² and liquid flow rate of 3 L min⁻¹, whereas
347 Fig. 7a shows a higher H₂O₂ electrogeneration rate of 32 mg min⁻¹ at that time.

348 3.3.3. *Effect of electrolyte concentration*

349 Considering the rather small electrode gap (6 mm) between the anode and cathode in the
350 electrochemical cell, it was assumed that the solution conductivity would not significantly
351 affect the production of H₂O₂. Therefore, a set of experiments was made to determine the
352 possible influence of electrolyte concentration. It was observed that, within the range of 25-75
353 mM of Na₂SO₄, which is equal to a solution conductivity range of 4.6 to 12.3 mS cm⁻¹, the
354 accumulation of H₂O₂ was quite analogous, being only slightly higher in the case of 50 mM

355 (Fig. 8). However, a rather substantial effect is observed regarding the energy consumption,
356 since a higher conductivity led to a gradually lower consumption; i.e. 3.24, 2.00 and 1.61
357 kWh m⁻³ at 25, 50 and 75 mM Na₂SO₄, respectively. This was expected, since the increase of
358 electrolyte concentration causes a reduction of the ohmic resistance in the bulk solution, and
359 accelerates the electron transfer, thus decreasing the overall charge consumption. From these
360 findings, it can be concluded that the system would be more efficient at higher water
361 conductivity. Therefore, future industrial application of this technology should focus on high
362 conductivity wastewater or be coupled with membrane technologies for treating membrane
363 concentrates.

364 *3.4. Treatment of a mixture of pesticides*

365 After the optimum operation conditions were determined for attaining the best balance
366 between H₂O₂ production and current efficiency, the plant performance was validated by
367 carrying out several tests to assess its capability to degrade a mixture of two model SOCs,
368 namely PYR and MET, which were treated by sun-assisted AOPs like solar photo-Fenton
369 [6,51]. All the assays were made with 75 L of mixtures of both pesticides in water with 50
370 mM Na₂SO₄ under optimized conditions: pH 3.0, 74 mA cm⁻² and air flow rate of 10 L min⁻¹.

371 First, a mixture containing 50 mg L⁻¹ PYR and 90 mg L⁻¹ MET (i.e., 71 mg L⁻¹ DOC) was
372 treated by EO with electrogenerated H₂O₂. The influence of liquid flow rate (2.8, 4.4 and 5.6
373 L min⁻¹) was investigated, aiming to promote a larger oxidation of both organic contaminants
374 either by increasing the HRT (at a lower flow rate) or by enhancing the mass transport of
375 pollutants to the anode surface (at a higher flow rate). However, no significant effect of this
376 parameter was found, which suggests that the amount of BDD([•]OH) produced via Reaction
377 (2) at 74 mA cm⁻² was high enough to react with both pesticides regardless of the
378 hydrodynamic conditions (within the studied range). Fig. 9a and 9b depict the normalized
379 decays of PYR and MET concentrations at a liquid flow rate of 5.6 L min⁻¹, respectively. As

380 can be seen, the degradation by EO-H₂O₂ was very slow, only attaining 20% and 30% of PYR
381 and MET removal after 120 min. The larger degradation of MET could be explained by the
382 greater electrocatalytic behavior of BDD with this pesticide as a result of a more favorable
383 adsorption on its surface, thus reacting more quickly with physisorbed BDD([•]OH). At the end
384 of the electrolysis, almost no mineralization was achieved in EO process, in agreement with
385 the refractory nature of typical reaction by-products like carboxylic acids [10-13]. In all these
386 trials, the energy consumption was around 10 kWh m⁻³.

387 The same pesticides mixture was treated by EF, using the optimized parameters with
388 liquid flow rate of 5.6 L min⁻¹, in the presence of different amounts of Fe²⁺ as catalyst (not
389 shown). After 120 min, a higher degradation percentage was reached for both pesticides, with
390 up to 35% and 40% for PYR and MET, respectively. This demonstrates that the H₂O₂
391 produced under optimized conditions reacted with added Fe²⁺ according to Fenton's reaction,
392 yielding homogeneous [•]OH that enhanced the degradation because this radical acted
393 concomitantly with BDD([•]OH). The former was confined into the reactor, whereas the latter
394 radical was transported throughout the whole volume. In contrast, DOC abatement only
395 attained 8% as maximum, which agrees with the high stability of Fe(III)-carboxylate
396 complexes formed as intermediates [11]. Worth mentioning, a much larger mineralization was
397 achieved working with a pesticide mixture that accounted for 20 mg L⁻¹ DOC, using 1.0 mM
398 Fe²⁺. In this case, 32% DOC removal was attained at 120 min. It is also important to note that
399 the Fe²⁺ concentration remained almost constant during all these EF trials, which confirms the
400 capability of the cathode to regenerate it from Fe(III) reduction.

401 Finally, the mixtures with 71 mg L⁻¹ DOC were comparatively treated by SPEF using the
402 best Fe²⁺ concentration (i.e., 0.5mM). In these experiments, required accumulated UV energy,
403 Q_{UV}, was 7.1 kJ L⁻¹. As it can be observed in Fig. 9, 55% and 50% removal of PYR and MET
404 was reached in only 5 min, which confirms the fast Fe²⁺ photoregeneration with additional

405 •OH production from Reaction (3). At longer time, the degradation was much slower, but
406 ended in 77% and 70% removal, respectively, at 120 min. This is a much better performance
407 as compared to EO and EF, which was further confirmed by DOC abatements higher than
408 15%, in agreement with the powerful action of UV/Vis photons on Fe(III)-carboxylate
409 complexes according to Reaction (4).

410 **4. Conclusions**

411 The successful performance of the largest SPEF pilot plant existing to date has been
412 demonstrated in this work. The core of the plant, the filter-press electrochemical reactor, is
413 comprised of a Nb-BDD anode and a GDE as cathode. Optimization of main operation
414 parameters has been carried out according to a thorough experimental design, in order to
415 maximize the electrocatalytic H₂O₂ production with a high current efficiency. Optimum
416 values obtained for the key parameters were: pH 3.0, 74 mA cm⁻², liquid flow rate of 5.6 L
417 min⁻¹ and air flow rate of 10 L min⁻¹. Their application yielded a mass rate of up to 64.9 mg
418 H₂O₂ min⁻¹, current efficiency of 89.3% and energy consumption of 0.4 kWh m⁻³ during the
419 first minutes. The SPEF treatment of 75 L of pesticides mixtures allowed the removal of more
420 than 50% of each pesticide in only 5 min, where upon further degradation as well as
421 mineralization of by-products and their Fe(III) complexes became much slower but always
422 superior to EO and EF treatments. Further optimization of the SPEF process for treating
423 different kind of wastewater in the integrated pilot system is in progress.

424 **Acknowledgments**

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- 517

518 **Figure captions**

519 **Fig. 1.** Front view of (a) the four filter-press type electrochemical cells of the pilot unit, and
520 (b) the CPC photoreactor. In (c), schematic diagram of the pilot unit equipped with one cell
521 (examined in this work), showing: (1) CPC photoreactor, (2) valve, (3) feed tank, (4) power
522 supply, (5) electrochemical reactor, (6) liquid flowmeter, (7) air compressor, (8) magnetic
523 pump.

524 **Fig. 2.** (a) Accumulated H_2O_2 concentration and current efficiency (% CE) at different pH
525 values and current densities (j). The values were obtained after 30 min of continuous
526 recirculation of a 50 mM Na_2SO_4 solution at a liquid flow rate of 4.4 L min^{-1} and air flow rate
527 of 5 L min^{-1} . (b) H_2O_2 production rate as function of electrolysis time, at constant pH = 3.0
528 and various j values. (c) H_2O_2 production rate as function of electrolysis time, at constant $j =$
529 100 mA cm^{-2} and varying pH.

530 **Fig. 3.** Comparison of the actual results obtained experimentally regarding (a) H_2O_2
531 production and (b) current efficiency (in %), with those predicted via central composite
532 design equations (12) and (13), respectively.

533 **Fig. 4.** (a) 3D surface plot and (b) contour plot for the H_2O_2 production as function of the
534 initial pH (A) and current density (B). Experimental data correspond to 30-min electrolyses
535 under continuous recirculation of a 50 mM Na_2SO_4 solution at liquid flow rate of 4.4 L min^{-1}
536 and air flow rate of 5 L min^{-1} .

537 **Fig. 5.** (a) 3D surface plot and (b) contour plot for current efficiency (in %), as in Fig. 4.

538 **Fig. 6.** (a) Effect of liquid flow rate on various process efficiency parameters, corresponding
539 to 30-min electrolyses; (b) accumulated H_2O_2 as a function of electrolysis time, at three

540 different liquid flow rates. Fixed parameters: 50 mM Na₂SO₄ at pH 3.0, $j = 74 \text{ mA cm}^{-2}$, air
541 flow rate of 5 L min⁻¹.

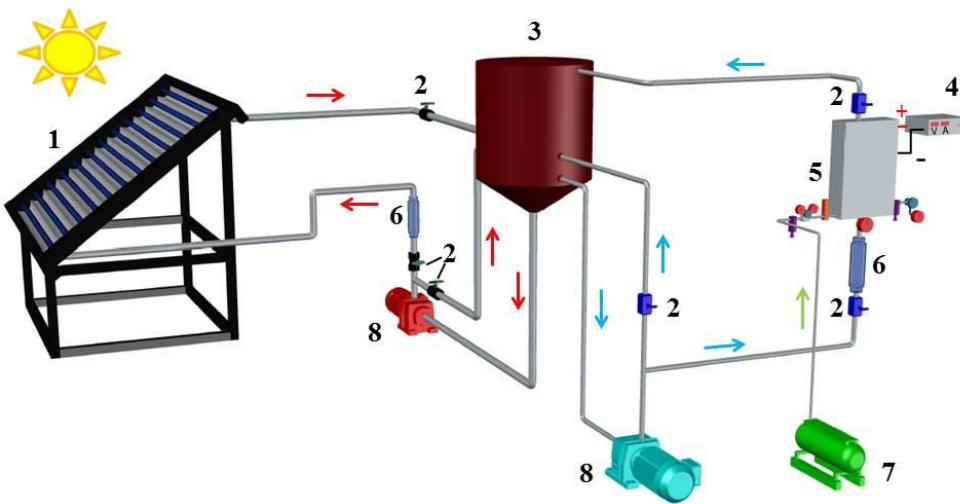
542 **Fig. 7.** (a) Effect of air flow rate on various process efficiency parameters, corresponding to
543 30-min electrolyses; (b) accumulated H₂O₂ as function of electrolysis time, at different air
544 flow rates. Fixed parameters: 50 mM Na₂SO₄ at pH 3.0, $j = 74 \text{ mA cm}^{-2}$, liquid flow rate of
545 4.4 L min⁻¹. The optimum trial corresponds to the same conditions but using a liquid flow rate
546 of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹.

547 **Fig. 8.** (a) Effect of Na₂SO₄ molar concentration on various process efficiency parameters,
548 corresponding to 30-min electrolyses; (b) accumulated H₂O₂ as a function of electrolysis time,
549 at three different electrolyte concentrations. Fixed parameters: electrolyte solution at pH 3.0, j
550 = 74 mA cm⁻², liquid flow rate of 4.4 L min⁻¹ and air flow rate of 5 L min⁻¹.

551 **Fig. 9.** Normalized concentration decays of pesticides (a) pyrimethanil (PYR) and (b)
552 methomyl (MET) versus electrolysis time during the (○, □) electro-oxidation (EO) and
553 (●, ■) solar photoelectro-Fenton (SPEF) treatment of 75 L of mixtures of both pesticides (71
554 mg L⁻¹ DOC) in deionized water with 50 mM Na₂SO₄ at pH 3.0 using the pilot plant at $j = 74$
555 mA cm⁻², liquid flow rate of 5.6 L min⁻¹ and air flow rate of 10 L min⁻¹. SPEF treatment was
556 performed in the presence of 0.5 mM Fe²⁺ as catalyst.

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Fig. 1

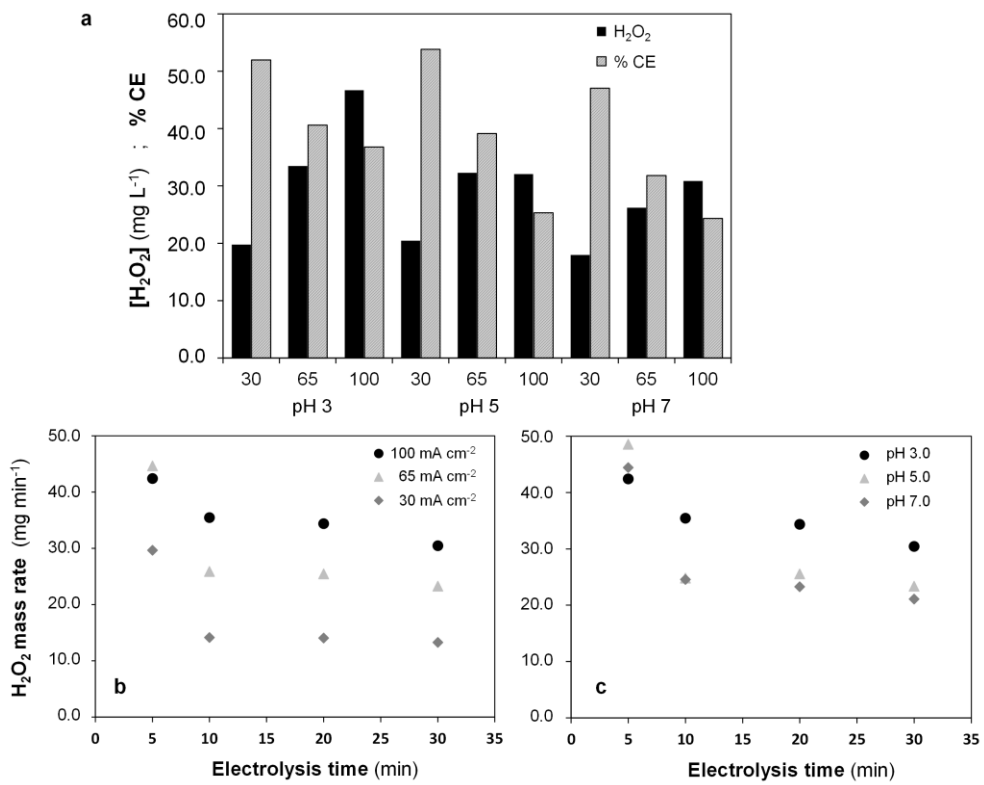
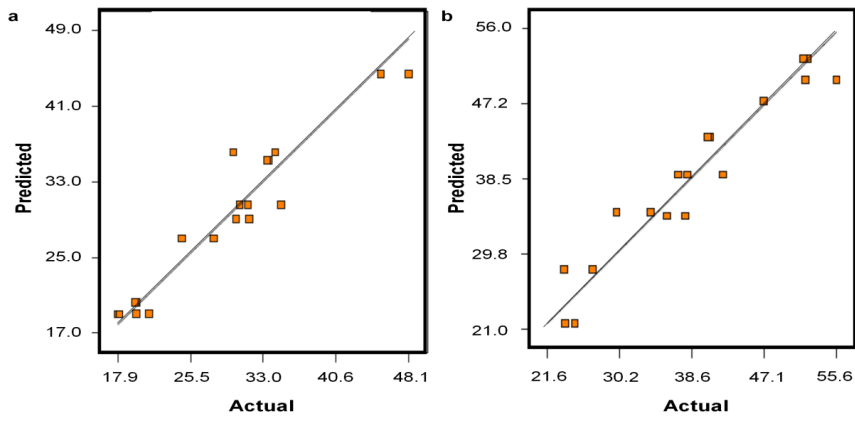


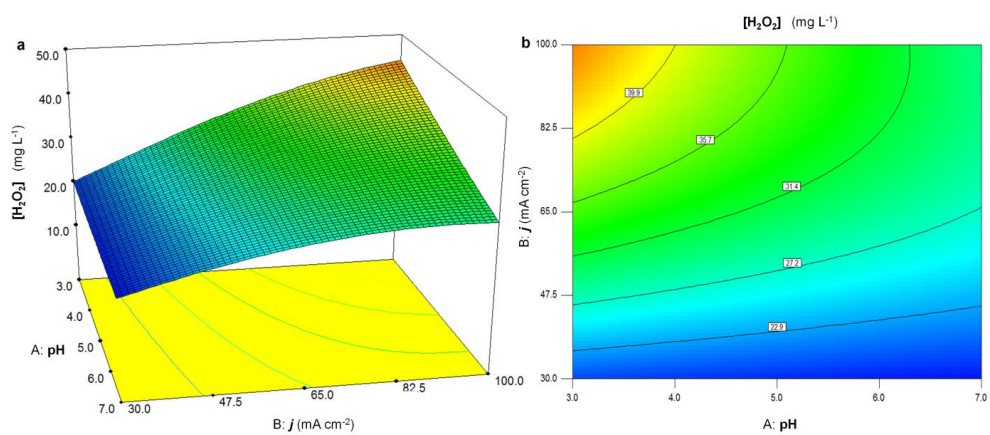
Fig. 2

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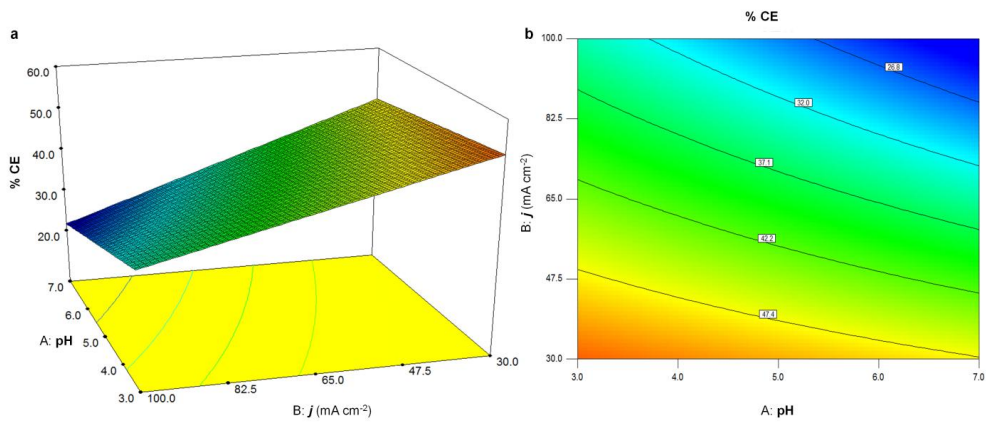
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Fig. 3



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Fig. 4



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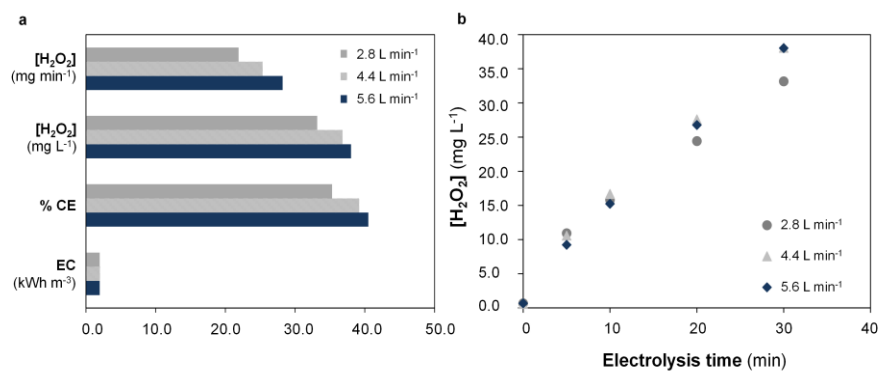
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Fig. 5



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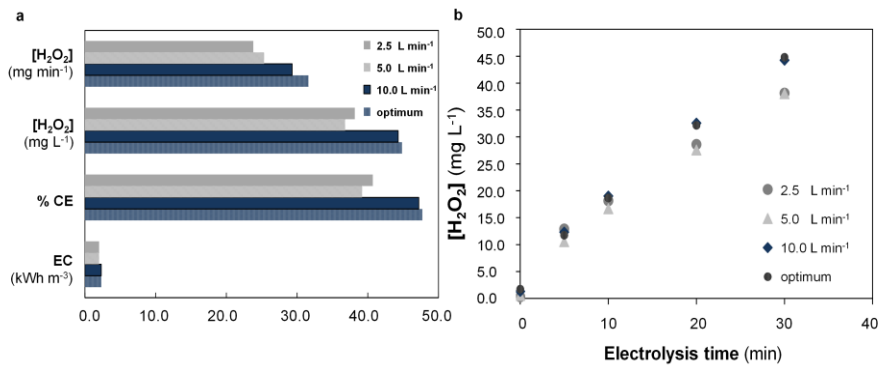
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Fig. 6



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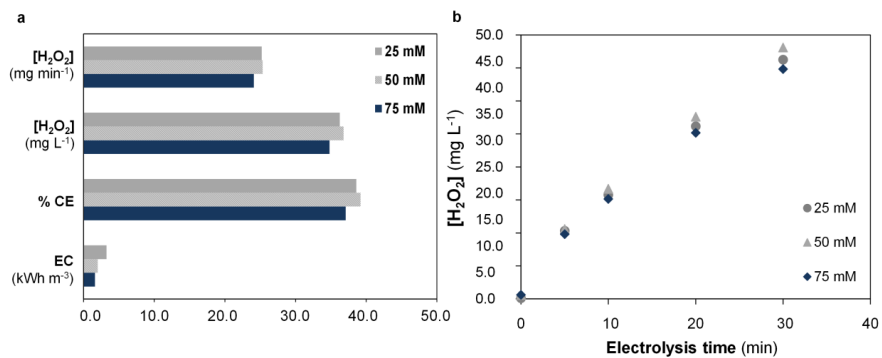
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Fig. 7



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Fig. 8

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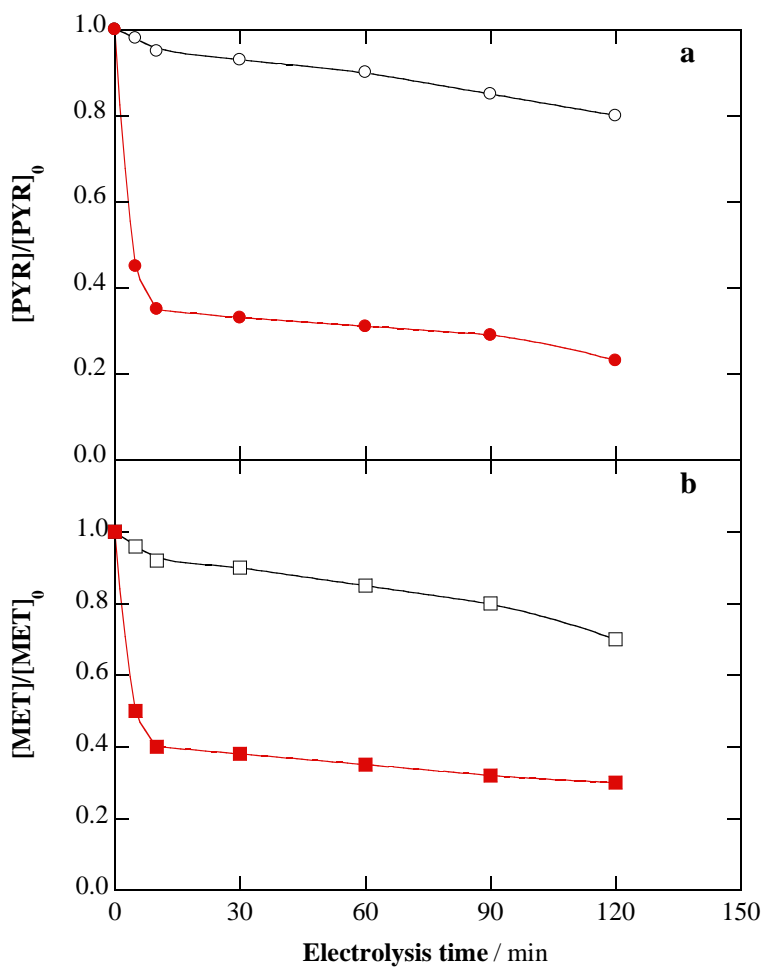


Fig. 9

634 **Table 1**

635 Experimental range and levels of independent variables

Variable	Factor	Units	Level and Range		
			Low (-1)	Central (0)	High (+1)
pH	A	-	3	5	7
<i>j</i>	B	mA cm ⁻²	30	65	100

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637

638 **Table 2**

639 Design of experiments and results

Run	Independent variables		Responses ($t = 5\text{min}$)		Responses ($t = 30\text{min}$)	
	pH	j (mA cm^{-2})	$[\text{H}_2\text{O}_2]$ (mg L^{-1})	% CE	$[\text{H}_2\text{O}_2]$ (mg L^{-1})	% CE
1	3	100	15.11	71.40	48.12	37.90
2	7	30	4.97	78.30	18.06	47.05
3	5	65	10.41	75.70	34.85	42.30
4	7	100	8.88	42.00	31.55	24.90
5	3	30	5.93	93.40	19.67	51.70
6	3	100	13.41	63.40	45.25	35.70
7	5	65	9.23	67.20	31.42	38.10
8	5	100	9.71	45.90	34.25	27.00
9	3	65	8.93	65.00	33.59	40.70
10	7	100	8.45	40.00	30.16	23.80
11	5	100	8.36	39.60	29.90	23.60
12	5	30	6.23	98.20	21.15	55.60
13	5	65	8.67	63.10	30.55	37.00
14	5	30	5.49	86.60	19.80	52.00
15	3	30	5.75	90.70	19.85	52.20
16	7	65	7.71	56.10	27.85	33.80
17	3	65	9.67	70.30	33.38	40.50
18	7	65	6.58	47.90	24.54	29.80
19	7	30	4.84	76.30	17.89	47.00

640

641 **Table 3**

642 ANOVA results for response surface of the Quadratic and 2FI models

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	
<i>Quadratic model</i>	1225.26	5	245.05	30.44	<0.0001	significant
A-pH	206.75	1	206.75	25.68	0.0002	
B-j	880.82	1	880.82	109.41	<0.0001	
AB	98.63	1	98.63	12.25	0.0039	
A ²	1.56	1	1.56	0.19	0.6673	
B ²	38.61	1	38.61	4.80	0.0474	
Residual	104.66	13	8.05			
Lack of fit	73.34	3	24.45	7.80	0.0056	not significant
Pure error	31.33	10	3.13			
<i>2FI model</i>	1723.02	3	574.34	60.89	<0.0001	significant
A-pH	228.38	1	228.38	24.21	0.0002	
B-j	1466.34	1	1466.34	155.45	<0.0001	
AB	28.31	1	28.31	3.00	0.1037	
Residual	141.49	15	9.43			
Lack of fit	102.41	5	20.48	5.24	0.0127	not significant
Pure error	39.08	10	3.91			

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645 **Table 4**

646 Optimum operation conditions proposed by Design Expert 7.0.0 software to attain maximum

647 H₂O₂ concentration and current efficiency at 30 min of electrolysis.

Test number	pH	j (mA cm ⁻²)	[H ₂ O ₂] (mg L ⁻¹)	% CE	Desirability	
1	3.00	73.66	38.0961	41.0744	0.604	Selected
2	3.00	74.16	38.2467	40.9437	0.604	
3	3.00	72.82	37.8392	41.2949	0.604	
4	3.00	70.00	36.9532	42.0343	0.603	

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650 **Table 5**

651 Models validation under optimum conditions, with experimental data obtained after 30 min of
652 electrolysis under continuous recirculation of 50 mM Na₂SO₄ solution at pH 3.0, 74 mA cm⁻²,
653 liquid flow rate of 3.3 L min⁻¹ and air flow rate of 5 L min⁻¹. Two independent runs were
654 performed

	Run		Average actual values	Predicted values	Relative error (%)
	a	b			
H ₂ O ₂ (mg L ⁻¹)	35.51	38.07	36.79	38.20	3.69
% CE	37.80	40.60	39.20	40.99	4.38

655