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1 **Optimal degradation of organophosphorus pesticide at low levels in water using Fenton**
2 **and photo-Fenton processes and identification of by-products by GC-MS/MS**

3

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26 **Abstract**

27 This study aiming to determine the optimal conditions to degrade an organophosphate
28 pesticide diazinon (DZN) at low levels concentrations ($\mu\text{g.mL}^{-1}$) and to identify the by-
29 products generated. The degradation processes utilized were the Fenton and photo-Fenton.
30 The iron concentration $[\text{Fe}^{2+}]$, the hydrogen peroxide concentrations $[\text{H}_2\text{O}_2]$, and the solution
31 pH are the investigated parameters. The Doehlert three-parameter experimental design was
32 applied to model and optimize both degradation processes. The mathematical models
33 suggested were assessed and validated by application of analysis of variances ANOVA. In the
34 case of Fenton process, the greatest yield of degradation (79%) was obtained at
35 $[\text{Fe}^{2+}] = 35 \text{ mg.L}^{-1}$ (0.63 mmol.L^{-1}), $[\text{H}_2\text{O}_2] = 423 \text{ mg.L}^{-1}$ ($12.44 \text{ mmol.L}^{-1}$), and $\text{pH} = 5.0$.
36 In photo-Fenton process, the maximum yield of degradation (96%) was obtained under the
37 conditions of $[\text{Fe}^{2+}] = 29 \text{ mg.L}^{-1}$ (0.52 mmol.L^{-1}), $[\text{H}_2\text{O}_2] = 258 \text{ mg.L}^{-1}$ (7.59 mmol.L^{-1}) and
38 $\text{pH} = 4.6$. QuEChERS (quick, easy, cheap, effective, rugged, and safe), as extraction
39 technique, and GC-MS/MS (gas chromatography coupled with triple quadrupole mass
40 spectrometry) were used to identify the by-products degradation of DZN. The identified
41 compounds are diazoxon, triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-
42 methylpyrimidine-4-ol, 2-isopropyl-6-methylpyrimidine-4-ol (IMP) and hydroxydiazinon.
43 Three possible pathways for diazinon degradation have been suggested and the hydroxylation,
44 oxidation and hydrolysis are likely probable degradation mechanisms.

45

46 **Keywords:** degradation; diazinon; water; detection of by-products; advanced oxidation
47 process

48

49 1. Introduction

50 Population growth and human survival require ever-increasing food production, which
51 is largely supported by vital agricultural activities (Sadowski and Baer-Nawrocka, 2018). One
52 group of chemicals used to improve agricultural yield (Malakootian et al., 2020) are
53 pesticides, employed to control pests and weeds and to enhance food production (de Souza et
54 al., 2020). Some of these compounds are known as persistent organic pollutants and thus
55 remain in water for a long time, accumulate in sediments and travel long distances. They exert
56 toxic effects on the environment, human health, and living organisms, even at low
57 concentrations (Katsikantami et al., 2019; Vasseghian et al., 2021; Vasseghian, et al., 2020).

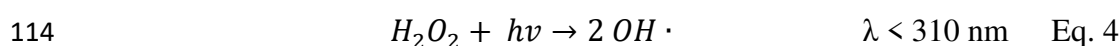
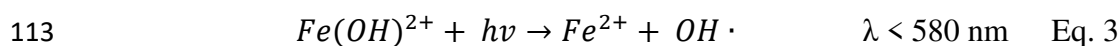
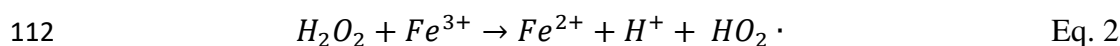
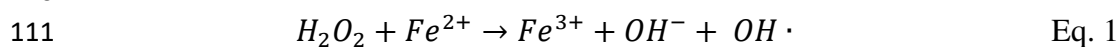
58 Globally, pesticides are classified into four main families, depending on their use,
59 chemical composition, and nature of active ingredients (Kaur et al., 2019). Herbicides are a
60 class of pesticide used to control or prevent the growth of weeds (Fernanda Pereira Barbosa,
61 2019). Insecticides are used against insect eggs, larvae, and adult insects, and fungicides are
62 designed to eliminate or limit the development of parasitic plant fungi. Diazinon (DZN), an
63 insecticide and highly toxic organophosphate pesticide (Čolović et al., 2010), is used to
64 control insects in residential, agricultural and livestock areas (Acero et al., 2008). Its presence
65 in surface waters is widespread due to extensive use (Real et al., 2007). For example, in the
66 USA, 6 million kg of DZN are applied annually (Real et al., 2007). Under favorable
67 environmental conditions, it can accumulate in groundwater due to its limited
68 biodegradability (Molla et al., 2019; Raeisi et al., 2016). Several pesticides are usually
69 detected in waters at the concentration range of 1–1000 $\mu\text{g.L}^{-1}$ (Jones et al., 2017). DZN has
70 been detected in surface waters at concentrations of 80 ng.L^{-1} to 25 $\mu\text{g.L}^{-1}$ in countries such as
71 the USA, Spain, and Canada (Glinski et al., 2018; Metcalfe et al., 2019; Proia et al., 2013).
72 This compound is toxic to humans, inhibiting the enzyme acetylcholinesterase, which is
73 essential for nervous system function (Shirzad-Siboni et al., 2015; Zhang et al., 2010). Fatal
74 human doses were found to be in the range of 90–444 mg.kg^{-1} (Molla et al., 2019). Aquatic
75 system toxicity is 350 ng.L^{-1} with a 48 h LC_{50} of 4.4 mg.L^{-1} in killifish (Daneshvar et al.,
76 2007; Kazemizad et al., 2016). DZN is categorized as a WHO class II compound, considered
77 moderately hazardous (World Health Organization, 2010).

78 The toxicity of DZN, its resistance to natural decomposition and its persistence in the
79 environment compel us to find methods that eliminate and/or degrade this molecule (Molla et
80 al., 2019). In recent years, several studies have focused on the degradation of pesticides in

81 aqueous solution by different processes (Al Momani et al., 2004a; Al Momani et al., 2004b;
 82 Al Momani et al., 2009, 2007; Contreras et al., 2003). Gar Alalm et al. (2015) attempted to
 83 degrade DZN by two processes and found photocatalysis degraded DZN by 40% and photo-
 84 Fenton by approximately 50%. Activated carbon prepared from flamboyant pods modified
 85 with Fe^{2+} has also been used as a TiO_2 support, and the photocatalytic degradation using this
 86 combination was approximately 80% (Hassan et al., 2017). Similarly, using tungsten-doped
 87 zinc oxide nanoparticles as a catalyst, Maleki et al. (2020) observed 89% of DZN degradation.
 88 Nasrollahi et al. (2020) used a biological approach involving bacterial endophytes in rice
 89 plants to degrade DZN (50% degradation). Membrane techniques have also been investigated
 90 to eliminate DZN, and nanofibrous membranes eliminated 84% of DZN (Pordel et al., 2019).

91 Advanced oxidation processes (AOPs) have proven to be particularly effective
 92 technologies for the degradation of organophosphate pesticides (Vasseghian et al., 2020;
 93 Wang and Shih, 2015). AOPs are based on the intrinsic ability of hydroxyl radicals ($OH\cdot$)
 94 (Moradi et al., 2020a) generated in the case of the Fenton and Photo Fenton processes, by
 95 specific chemical reactions in aqueous solution, to promote rapid and non-selective oxidation
 96 of organic molecules, thereby promoting their degradation (Kanakaraju et al., 2018; Moradi et
 97 al., 2021; Moradi et al., 2020b; Vasseghian et al., 2020). In the others AOPs, the active
 98 species may be O_3 (ozonation), O_2 (persulfate-based oxidation), etc. The photo-Fenton
 99 process combines the Fenton reagents hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in the
 100 presence of UV-visible radiation to produce more $OH\cdot$ radicals *via* four reactions: i) a catalytic
 101 reaction of H_2O_2 with Fe^{2+} ions, a Fenton reaction (Eq. 1) (Nichela et al., 2013); ii) a Fenton
 102 process initiated by Fe^{3+} (Eq. 2); iii) a photo-reduction of Fe^{3+} to Fe^{2+} ions (Eq. 3); and iv) a
 103 peroxide photolysis *via* shorter wavelengths (Eq. 4) (Rahim Pouran et al., 2015). Ferrous ions
 104 generated in the reaction represented by Eq. 3 allow producing additional hydroxyl radicals.
 105 These radicals have a high oxidation potential (E_0) ranging between 2.72 V (Han et al., 2020)
 106 and 2.80 V (Singh et al., 2019) and can break down organic compounds such as pesticides
 107 (Moradi et al., 2020). In addition, the photo-Fenton reactions cause faster mineralization of
 108 organic compounds than the dark reaction due to the presence of UV irradiation or sunlight
 109 (Audino et al., 2017).

110



115 In recent years, statistical methods have been extensively applied for experimental
116 design in many science fields (Hanrahan and Lu, 2006; Doufene et al., 2018; Smaali et al.,
117 2021). Most of experimental designs commonly use parameter screening (Dragoi and
118 Vasseghian, 2020), response modeling and optimization (Callao, 2014). Central Composite,
119 Box-Behnken, and Doehlert, experimental designs employed in Responses Surfaces
120 Methodology (RSM) (Heydari et al., 2018; Moradi et al., 2018), are relevant in modeling
121 and/or optimization (Ferreira et al., 2007). Doehlert design is one of the most commonly used
122 designs because it provides more advantages than Central Composite and Box-Behnken
123 (Callao, 2014; Ferreira et al., 2007).

124 To date, no study has evaluated the degradation of DZN at trace levels ($\mu\text{g.L}^{-1}$) and
125 identified DZN degradation by-products at ultra-trace levels (ng.L^{-1}), likely due to the lack of
126 advanced analytical methods and an efficient and rapid extraction protocol. Our study is novel
127 in combining simple and efficient degradation processes, the application of an experimental
128 design to determine the optimal degradation conditions, and the use of efficient extraction and
129 analysis techniques to monitor DZN degradation and to determine degradation by-products at
130 ultra-trace concentrations (ng.L^{-1}) in aqueous matrices. We applied advanced oxidation
131 processes (Fenton and photo-Fenton) and a Doehlert design to optimize and model each
132 process. Hydrogen peroxide (H_2O_2), ferrous ions (Fe^{2+}) concentrations and pH were
133 optimized to eliminate efficiently DZN. In the present work, extremely sensitive and reliable
134 techniques based on a QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction
135 approach and gas chromatography coupled with triple quadrupole mass spectrometry
136 (GC-MS/MS) were used to identify intermediate products in water. The possible pathways of
137 the degradation of DZN were also proposed. We believe our study will inform future
138 experimental studies of organophosphate pesticide pollutant degradation in wastewater,
139 especially DZN.

140

141 **2. Materials and methods**

142 **2.1. Materials and reagents**

143 Diazinon was purchased from Sigma-Aldrich (99%, purity). Its chemical formula is
144 $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_3\text{PS}$ and the International Union of Pure and Applied Chemistry (IUPAC) name is
145 O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate (CAS: 333-41-5). The
146 molecular weight, the solubility in water at 20°C and the pK_a of DZN are $304.35 \text{ g.mol}^{-1}$,
147 60 mg.L^{-1} and 2.6, respectively. Hydrogen peroxide (33%, w/w) and Fe^{2+} ions were produced
148

149 from ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as a source of Fe^{2+} . Sodium hydroxide
150 (NaOH) and hydrochloric acid (HCl) solutions were used to adjust the solution pH in each
151 experiment. All chemicals were of analytical reagents grade and purchased from Sigma-
152 Aldrich, France. The ultrapure water (18.2 $\text{M}\Omega\cdot\text{cm}$ of resistivity) was used in this work.

153

154 **2.2. Diazinon degradation via Fenton and photo-Fenton experiments**

155 All Fenton process experiments were conducted in a 250 mL capacity Pyrex batch
156 reactor with 100 mL of ultrapure water at room temperature in the dark (25 °C). The
157 concentration of the effluent was 1 $\mu\text{g}\cdot\text{mL}^{-1}$, prepared by dissolving DZN in ultrapure water.
158 For Fenton reagents, the added of the DZN concentration was depended on the conditions of
159 each experiment. The photo-Fenton experiments were carried out in a cubical photo-reactor
160 equipped with a cooler to maintain a constant temperature. A Pyrex crystallizer batch reactor
161 with a capacity of 250 mL was used to ensure consistent and direct exposure of the solution to
162 the lamplight supplied by Philips lamp (11 W, UVA).

163 **2.3. Analytical methods**

164 **2.3.1. UHPLC/DAD analysis**

165 Diazinon concentration in aqueous solutions was measured using an ultra-high-
166 performance liquid chromatography coupled with a diode array detector (UHPLC/DAD)
167 (Agilent Technology, Model 1260, France). Chromatographic separation was performed with
168 a C18 column (150 mm \times 4.6 mm, 2.7 μm) (Agilent Technology, France). The auto-sampler
169 was maintained at 5 °C. Acetonitrile and ultrapure water were used as mobile phases.
170 Isocratic elution mode was applied for chromatographic separation. The eluent used was a
171 mixed solvent of acetonitrile and ultrapure water (60/40, v/v). The mobile phase flow rate was
172 0.4 $\text{mL}\cdot\text{min}^{-1}$ and the retention time of DZN was 17.8 min. DZN was quantified at
173 $\lambda_{\text{max}} = 210$ nm. The UHPLC/DAD was used to evaluate the amount of DZN in the aqueous
174 solution. The degradation yield Y_i of DZN was calculated using equation 5.

$$175 \quad Y_i = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (\text{Eq. 5})$$

176 in which C_0 and C_t are the DZN initial concentration and DZN concentration at a given time t
177 in $\text{mg}\cdot\text{L}^{-1}$, respectively.

178

179 **2.3.2. GC-MS/MS analysis**

180 The standard solution and sample extracts were analyzed by gas chromatography
181 coupled with triple quadrupole mass spectrometry (GC-MS/MS) (Agilent Technology,
182 7890B-7000D, France). GC separation was performed using a Phenomenex capillary column
183 ZB-XLB-HT Inferno™ (30 m × 0.25 mm × 0.25 μm). The injection volume was 3 μL. The
184 column temperature program was as follows: the initial temperature was maintained at 75 °C
185 for 2.57 min, increased to 150 °C at a rate of 50 °C/min, increased to 200 °C at 6 °C/min, then
186 to 280 °C at 16 °C/min, and held there for 15 min. The mass spectrometer (MS/MS) was
187 operated with an electron impact (EI) source for detection. The electron energy was 70 eV,
188 and the transfer line temperature was set at 280 °C. The total duration of the analysis was
189 32.40 min. The mass-to-charge ratio (m/z) of DZN is 304 uma.

190 **2.3.3. QuEChERS extraction method**

191
192
193 Before analysis by GC-MS/MS, a QuEChERS (quick, easy, cheap, effective, rugged,
194 and safe) dispersive solid phase extraction (d-SPE) was performed. The extraction followed
195 is based on the principle of d-SPE extraction with an organic solvent in the presence of salts
196 to ensure the transformation of the molecules in the effluent to the organic phase
197 (Drożdżyński and Kowalska, 2009; Iqbal et al., 2020). This recently developed technique can
198 be employed to recover many targets, including highly polar pesticides and highly acidic
199 molecules. The QuEChERS technique can be carried out in two steps. The first one is an
200 extraction using organic solvents (acetonitrile or hexane) and inorganic salts (MgSO₄ and
201 NaCl) to separate the water-organic phase, followed by a purification step, utilized to
202 eliminate all interfering components. The proposed technique, based on several studies (Abdel
203 Ghani and Hanafi, 2016; Iqbal et al., 2020; Zaidon et al., 2019), was modified for the present
204 work. The QuEChERS (Interchim, France) extraction technique consists of combining 10 mL
205 of the sample with 10 mL of acetonitrile in an extraction tube containing a mixture of salts.
206 The tube is passed through the vortex for 1 min to mix the two phases. Subsequent
207 centrifugation (3000 rpm) for 5 min ensures sufficient separation of the two phases. In the
208 purification step, 6 mL of the organic phase from the tube used in the first step was
209 transferred to a second tube (clean up tube), vortexed for 30 s, and centrifuged (3000 rpm) for
210 5 min to provide the final organic solution.

211 After extraction, the eluate was collected in a 14 mL, conical graduated glass Pyrex tube
212 (VWR, Fontenay-sous-Bois, France). The extract was evaporated to a final volume of 10 μ L
213 using a PuriVap-6 system (Interchim, France), under a high-purity nitrogen stream and
214 transferred to a vial for GC-MS/MS analysis.

215 **2.4. Doehlert design methodology**

216 One of the best experimental designs for second-order models is the Doehlert design
217 proposed by D.H Doehlert in 1970 (Ferreira, 2004). It is often preferred over the Central
218 Composite design and Box-Behnken designs as it is easily expanded in experimental and
219 variable space (Ferreira et al., 2007). These experimental designs are types of response
220 surface methodologies (RSM). The number of tests (“n”) in the Doehlert design depends on
221 multiple factors (“k”) according to the equation $n = k(k + 1)$, and one or more central points
222 can be added. Another advantage of this plan is that the number of levels is not the same for
223 each variable, allowing for a free choice of the variables with a small or large number of
224 levels (Ferreira, 2004). In the case of three variables, the first one was studied at five levels,
225 the second one at seven levels, and the last one at three levels, so the variables’ position can
226 be chosen according to their importance (Ferreira, 2004).

227 For modeling and optimization purposes, the experimental data have been explored
228 through a quadratic polynomial model (Eq. 6).

$$229 \hat{Y} = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (\text{Eq. 6})$$

230 in which \hat{Y} is the predicted response, b_0 is a constant, b_i is a linear constant, b_{ij} are the
231 interaction coefficients, b_{ii} are quadratic coefficients, and x_i , x_j are the coded values of the
232 variables. The Doehlert matrix with coded and actual values of variables for each Fenton and
233 photo-Fenton experiment are shown in Table 1.

234
235

Table 1

236 **3. Results and discussion**

237 **3.1. Development and validation of the predictive regression models**

238 The yields of DZN degradation estimated from the application of Doehlert design are
239 given in Table 1 for each Fenton and photo-Fenton experiment. Two regression models are

240 suggested, the responses considered are the degradation yield of DZN by Fenton (\hat{Y}_F) and
241 photo-Fenton (\hat{Y}_{Ph-F}) processes.
242

243 The modeling objective is to determine the best regression relationship linking the
244 dependent variables (responses) and the independent variables (factors). Modeling is an
245 important step in the optimization process. It could not be considered reliable if the final
246 model did not provide a significant level of correlation between input and output data. All
247 factors included in the final model must be statistically significant. The level of significance
248 model factor (b of Eq. 6) is determined by estimation of the student parameter value (t_i),
249 which is compared to the critical student value (t_{crit}), determined from Student statistical table
250 (not given in the main text), depending on the model degree of freedom (df) and the
251 significance level (α). Generally, (α) is taken to be equal to 0.05 (5%), it represents the
252 probability value (p-value). A coefficient of model is considered significant if its $|t_i| < p$ -value
253 (Benredouane et al., 2016).

254 The estimation of model factors shows that in the case of Fenton process, five factors
255 (including the b_0 (see Eq. 6)) are statistically significant, namely $[Fe^{2+}]$, $[H_2O_2]$, $(pH * [H_2O_2])$
256 and pH^2 , and in the case of photo-Fenton process, six factors (including the b_0) are
257 statistically significant, namely $[Fe^{2+}]$, pH , $[Fe^{2+}]^2$, $[H_2O_2]$ and pH^2 . All these factors have
258 a p-value < 0.05 . The analysis of variance (ANOVA) is used systematically as the main
259 method to validate regression models in design of experiments methodology approach. To
260 validate the suggested models (including only the significant factors), a Fisher test is carried
261 out. The Fisher-value (F-value) of the model (estimated on basis of the ratio between model
262 and residual mean square) and compared to Fisher-Value critical (F_{crit}) were determined from
263 Fisher-Snedecor table with two degrees of freedom (df_1 and df_2) and ($\alpha = 5\%$). For Fenton
264 process model, F-value ($df_1= 5$, $df_2= 7$) = 10.80 and for photo-Fenton process model, F-value
265 ($df_1= 4$, $df_2= 8$) = 14.46. The F_{crit} are respectively equal to 3.97 and 3.84, then in both cases,
266 F-value $> F_{crit}$, which means that the suggested models are validated at the fixed level of
267 significance. Based on these considerations, final models retained for both processes are given
268 by equations 7 and 8.

$$269 \quad \hat{Y}_{Ph-F} = 94.0 + 7.9[Fe^{2+}] + 5.1 pH - 20.0[Fe^{2+}]^2 - 31.4[H_2O_2] - 12.3pH^2 \quad (\text{Eq. 7})$$

$$270 \quad \hat{Y}_F = 69.9 + 6.1[Fe^{2+}] + 4.9[H_2O_2] - 10.8 pH \cdot [H_2O_2] - 11.4pH^2 \quad (\text{Eq. 8})$$

271 The predicted values of the DZN degradation yield are estimated for each process and
272 compared with the experimental values; the corresponding plots are shown in Figure 1(a) and
273 (b). The R^2 and adjusted R^2 values obtained were 0.911 and 0.849 for the photo-Fenton and
274 0.844 and 0.766 for the Fenton process.

275

276 **3.2. Determination of optimal conditions of degradation**

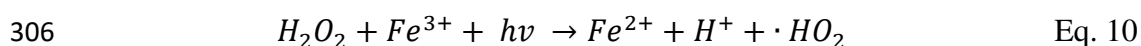
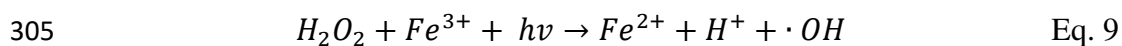
277 Modde software was used to determine the optimum points for each degradation
278 process. Results show that equation 7 describes a critical point corresponding to a maximum
279 degradation yield (96%); this is shown in Figure 1(c), plotted using the 3D graph. The factor
280 values in this case were $[\text{Fe}^{2+}] = 29 \text{ mg.L}^{-1}$ (0.52 mmol.L^{-1}); $[\text{H}_2\text{O}_2] = 258 \text{ mg.L}^{-1}$
281 (7.59 mmol.L^{-1}) and $\text{pH} = 4.6$. So, equation 8 does not present a critical point; in this case, the
282 extreme value theorem (Weierstrass) was applied to resolve this problem (Martínez-Legaz,
283 2014), this is confirmed by plots in 3D graph (Fig 1 (d) and (e)). The highest value
284 corresponding to the optimal value was obtained at the boundary of the study range. As seen
285 in Table 1, the greatest degradation (79%) was obtained under the conditions of run 3,
286 indicating that the optimal conditions were $[\text{Fe}^{2+}] = 35 \text{ mg.L}^{-1}$ (0.63 mmol.L^{-1});
287 $[\text{H}_2\text{O}_2] = 423 \text{ mg.L}^{-1}$ ($12.44 \text{ mmol.L}^{-1}$) and $\text{pH} = 5.0$. Furthermore, the 3D response surface
288 plot shows the highest yield corresponding to optimal values cited previously. However, on
289 the basis of experimental design results and in the case of Fenton process, pH is not a
290 significant parameter. The optimal conditions do not vary therefore greatly when the pH
291 changes but to take in account the conditions of iron precipitation, the pH has been fixed to
292 3.4 (the low level value).

293

Figure 1

294

295 These results show that the optimal concentrations of Fe^{2+} and H_2O_2 for the photo-
296 Fenton process were lower than those of the Fenton process, and the yield of the degradation
297 was greater using the photo-Fenton process. These results highlight the significant effect of
298 UV-irradiation. When the reaction medium was exposed to artificial light, degradation yield
299 significantly improved with a lower reagent consumption than in the Fenton process: only
300 29 mg.L^{-1} (0.52 mmol.L^{-1}) of Fe^{2+} and 258 mg.L^{-1} (7.59 mmol.L^{-1}) of H_2O_2 were used instead
301 of 35 mg.L^{-1} (0.63 mmol.L^{-1}) and 423 mg.L^{-1} ($12.44 \text{ mmol.L}^{-1}$) of H_2O_2 to obtain 96% instead
302 of 79% for the photo-Fenton and Fenton process, respectively. These findings can be
303 explained by the fact that the ferric ions resulting from photodegradation (Eq. 1) have been
304 photochemically regenerated into ferrous ions according to equations 9 and 10.



307

308 These ions further react with H₂O₂ to produce radical hydroxyl and ferric ions, and in
309 this manner, the cycle continues, as confirmed by other studies (Ameta et al., 2018; Audino et
310 al., 2017; Marchetti and Bessa Azevedo, 2020).

311 Notably, the ratio of the reagent concentrations (H₂O₂/Fe²⁺) under the optimal
312 conditions for both processes are different: 20 for the Fenton process and 15 for the photo-
313 Fenton process. These results indicate that the implementation of the process requires the
314 lowest reagent ratio with a maximum of degradation.

315

316 **3.3. Validation of optimal conditions**

317 An experiment for each process was conducted under the corresponding optimal
318 conditions by following DZN degradation over time. The results are shown in Figure 2.

319

Figure 2

320 Our findings displayed that the degradation of DZN was complete after just 15 min for
321 the photo-Fenton process. In contrast, degradation using the Fenton process reached a yield of
322 85% after one hour of the experiment. The degradation using the photo-Fenton process was
323 faster and more efficient than in the Fenton process, which implies that the light from the UV
324 radiation accelerated the degradation process and improved the performance to achieve
325 complete DZN degradation. From a technical-economic point of view, it should be noted that
326 the use of a lamp in the photo-Fenton process results in slightly higher energy consumption
327 than in the Fenton process.

328

329 **3.4. Determination of by-products using QuEChERS and GC-MS/MS methods**

330

331 GC-MS/MS was employed to identify the generated degradation by-products of DZN.
332 In this purpose, three samples were taken to determine the by-products: the 1st one before the
333 process launch (starting point), the 2nd one after 5 min, and the last one at 60 min.
334 A dispersive solid phase extraction using acetonitrile in the QuEChERS protocol (section
335 2.3.3) was used to analyze these samples. The results of the analysis of each sample are
336 presented with the chromatograms obtained from the GC-MS/MS (Figure 3).

337

338
339

Figure 3

340 As observed in the chromatograms, the DZN retention time was 17 min, and the
341 molecular weight usually obtained was 304 uma (Fig. 3.a). Several by-products were detected
342 (Fig. 3.b), grouped in Table 2 by their retention time. By comparing Figs. 3.a and 3.b, we
343 notice the disappearance of the DZN peak, implying the total degradation of DZN after 5 min.
344 We can also notice in Figure 3.c that no by-products were detected after 60 min of
345 degradation confirming the total mineralization of DZN (Figure 3.c). These results confirm
346 the results obtained previously. In addition, the by-products found in this work correspond to
347 the results found in previously published studies. In their study of photocatalytic DZN
348 degradation under sunlight irradiation, Molla et al. (2019) revealed eight by-products:
349 diazoxon, triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-methylpyrimidine-
350 4-ol, 2-isopropyl-4-ethyl-6-methylpyrimidine-5-ol, 2-isopropyl-6-methylpyrimidine-4-ol and
351 hydroxydiazinon. The six of them are the same as those in our study, which are: diazoxon,
352 triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-methylpyrimidine-4-ol, 2-
353 isopropyl-6-methylpyrimidine-4-ol (IMP) and hydroxydiazinon.

354 In another study, Wang and Shih (2015) degraded DZN using a sono-Fenton process
355 and found four by-products: diazoxon, triethyl phosphate, 2-isopropyl-6-methylpyrimidine-4-
356 ol, and hydroxydiazinon, compounds also found in this work. Wang and Shih (2015) and
357 Molla et al. (2019) performed their experiments with initial DZN concentrations of 50 and
358 10 mg.L⁻¹, respectively, much greater than the concentration used in the present study
359 (1 mg.L⁻¹). This lower concentration represents a more logical approximation of realistic
360 wastewater concentrations. Furthermore, while we observed complete mineralization within
361 30 min, Molla et al. (2019) observed complete mineralization in 20 hours while Wang and
362 Shih (2015) achieved only 30% of mineralization.

363 In the present study, the GC-MS/MS analysis method combined with the QuEChERS
364 extraction approach and the pre-concentration method showed excellent performance in
365 detecting by-products even at concentrations on the order of ng.L⁻¹. This methodology could
366 be used to detect pesticides (at trace levels) and their by-products in waters at ultra-trace
367 levels. Furthermore, as already mentioned, our concentrations of DZN, and associated by
368 products during our degradation process approximate more closely realistic concentrations
369 than the earlier investigations.
370

371 **Table 2**

372

373 **3.5. Pathways for degradation of diazinon**

374

375 Several previous studies have suggested a DZN degradation pathway (Molla et al.,
376 2019; Wang and Shih, 2015; Lee et al., 2020). The degradation mechanism of DZN is quite a
377 complex process. Indeed, the number of intermediates and their nature let think that the
378 degradation may be carried out according to several mechanisms, involving several oxidizing
379 species. Hydroxylation, oxidation and hydrolysis are the more probable mechanisms of the
380 DZN degradation. In the Figure 4, an overall scheme includes different routes of by-products
381 formation and their disappearance on basis of the present work and previous reports. Due to
382 the action of the hydroxyl radicals the degradation of DZN involved mainly hydroxylation
383 (Wang and Wang, 2020). In this first step, the hydroxylation of DZN produces
384 hydroxydiazinon, which degrades into other by-products along three different paths.

385 In the path A, the degradation of hydroxydiazinon involves the cleavage of the C-O
386 bond, producing 2-isopropyl-6-methyl-pyrimidine-4-ol (IMP), which is the most detected by-
387 product in the present study. This compound later degrades to 2-isopropyl-5-ethyl-6-
388 methylpyrimidine-4-ol. The second route (B) proceeds in parallel with the first (A), and the
389 hydroxydiazinon degrades into triethyl thiophosphate (TTP). It must be noted that the
390 formation of IMP and TTP may occur by hydrolysis mechanism. After this step, TTP releases
391 the sulfate ion and produces triethyl phosphate (TP). The last path proposed (C) is a
392 degradation based on the C–O bond's cleavage combined with conversion of the
393 thiophosphate ester into phosphate ester, whereby the hydroxydiazinon degrades by forming
394 diazoxon. This is due probably to an oxidative mechanism providing diazoxon which
395 undergoes hydrolyze to provide TP and IMP (Lee et al., 2020). Triethyl phosphate is then
396 produced via IMP or another route, which also degrades into 2-isopropyl-5-ethyl-6-
397 methylpyrimidine-4-ol (Fig. 4).

398

399 **Figure 4**

400

401 In Table 3 the effectiveness of degradation/elimination of DZN are compared from
402 several studies including our work. All the cited references were performed at initial DZN
403 concentrations between 10 to 50 mg.L⁻¹. The present work targeted depollution of water

404 containing very low amounts of DZN, on the order of $1 \mu\text{g.mL}^{-1}$. Table 3 provides several
405 techniques used to treat water polluted by DZN. Hassan et al. (2017) used a coupling process
406 of adsorption and photocatalysis, and after 80 min of contact time, the yield of elimination
407 achieved was 95%. Maleki et al. (2020) synthesized a new catalyst for photocatalysis that
408 degraded 99% of DZN in 180 min. The biological treatment employed by Nasrollahi et al.
409 (2020) degraded 55% of DZN but, like other previous studies, requiring greater time. The
410 membrane technique as an elimination process was developed by Pordel et al. (2019), in
411 which they removed 84% of DZN. A few investigations have used advanced oxidation
412 processes. Wang and Shih (2015) coupled the Fenton and sonolysis processes and 98% of
413 DZN degradation was obtained after 60 min with 30% of total mineralization. In contrast, Gar
414 Alalm et al. (2015) utilized photodegradation by applying the photo-Fenton and
415 photocatalysis processes under solar irradiation. They achieved a DZN degradation yield of
416 50% and 39% after 120 min and 150 min for photo-Fenton and photocatalysis, respectively.
417 Invariably, these works focused on DZN at a relatively high initial concentration, the
418 elimination of which generally exceeded 60 min (Table 3).

419

Table 3

420 In this work, both the Fenton and the photo-Fenton processes showed excellent
421 performance, 80% of DZN was degraded using Fenton process after 30 min, and total
422 degradation and mineralization (diazinon and by-products) were obtained by the photo-Fenton
423 after 5 min and 15 min, respectively. Comparing the previous results obtained in the cases of
424 different processes applied to treat contaminated water by DZN, it is obvious that the kinetics
425 of degradation is faster at low concentration of pollutant; this result was already reported in
426 the literature (Lee et al., 2020). These results also reveal a high efficiency of the Fenton and
427 photo-Fenton as degradation techniques for the aqueous solution containing DZN at low level
428 of concentrations.

429 4. Conclusion

430 This study investigated the degradation of DZN in water by two types of advanced
431 oxidation processes: Fenton and photo-Fenton. The application of the Doehlert design as an
432 experimental methodology for the optimization of the experimental parameters of the two
433 processes allowed us to develop two mathematical regression models for each process and
434 then determine the corresponding optimal points. Under these conditions, complete
435 degradation of diazinon and by-products was obtained after only 5 min using the photo-

436 Fenton process. Utilization of the Fenton process allowed for 85% degradation yield after
437 60 min. All experiments included an initial DZN concentration of 1 mg.L⁻¹, a realistic
438 wastewater concentration. By-product identification was carried out using a new method
439 based on the QuEChERS extraction, pre-concentration, and GC-MS/MS analysis. This
440 methodology allowed us to determine the photodegradation by-products even at very low
441 concentrations (ng.L⁻¹). DZN degradation using the photo-Fenton process generated six
442 different by-products and 3 degradation paths have been proposed.

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451

452 **Credit author's statement**

453

454 **Chemseddine Zekkaoui**: Data curation, Formal analysis, Methodology, Software, Writing-
455 original draft; **Tarek Berrama**: Supervision, Conceptualization, Formal analysis,
456 Methodology, Software, Validation, Writing-original draft, Writing-review & editing; **David**
457 **Dumoulin**: Writing-review & editing; **Gabriel Billon**: Writing – review & editing; **Yassine**
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459 Software, Validation, Writing-review & editing.

460 **Declaration of competing interest**

461 The authors declare that they have no known competing financial interests or personal
462 relationships that could have appeared to influence the work reported in this paper.

463

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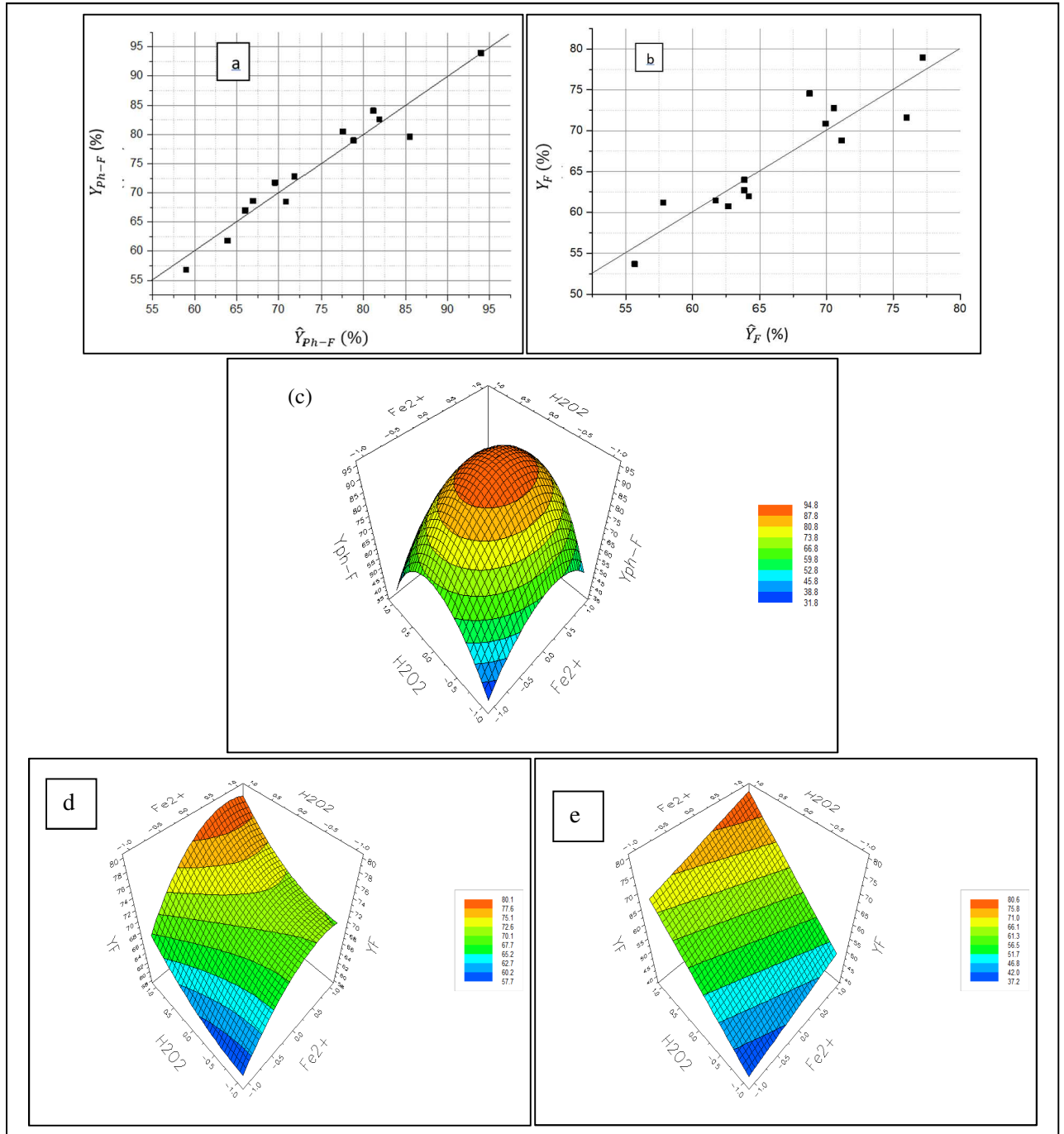


Figure 1. Experimental versus predicted values for (a) Photo-Fenton process, (b) Fenton process, and 3D response surface plots for (c) Photo-Fenton process, (d) and (e) Fenton process.

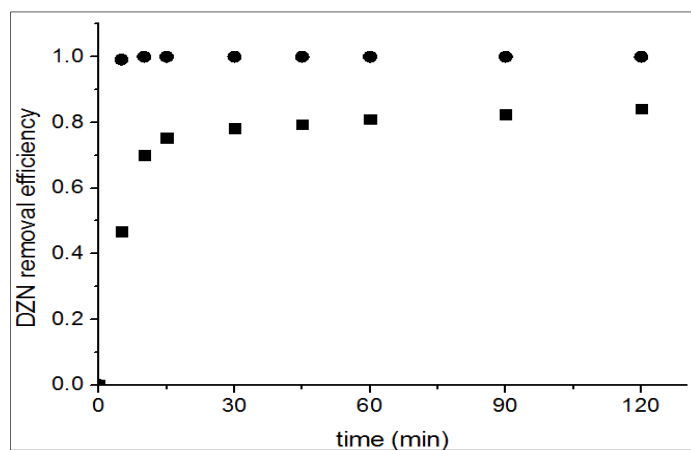


Figure 2. Kinetics of diazinon degradation under optimal conditions for: ■ Fenton and ● Photo-Fenton.

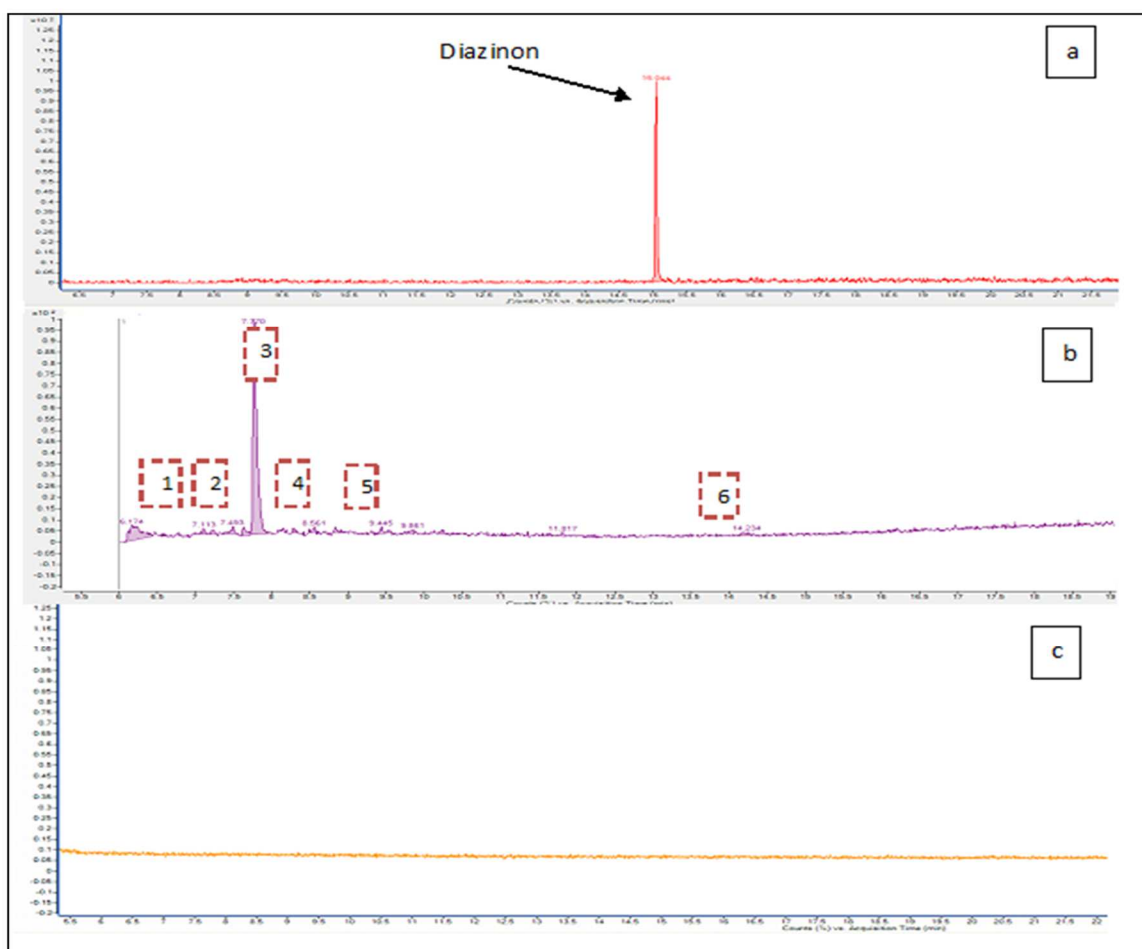


Figure 3. Chromatograms obtained by GC-MS/MS, (a). before Photo-Fenton degradation, (b). after 5 min of Photo-Fenton process and (c) after 60 min of Photo-Fenton degradation.

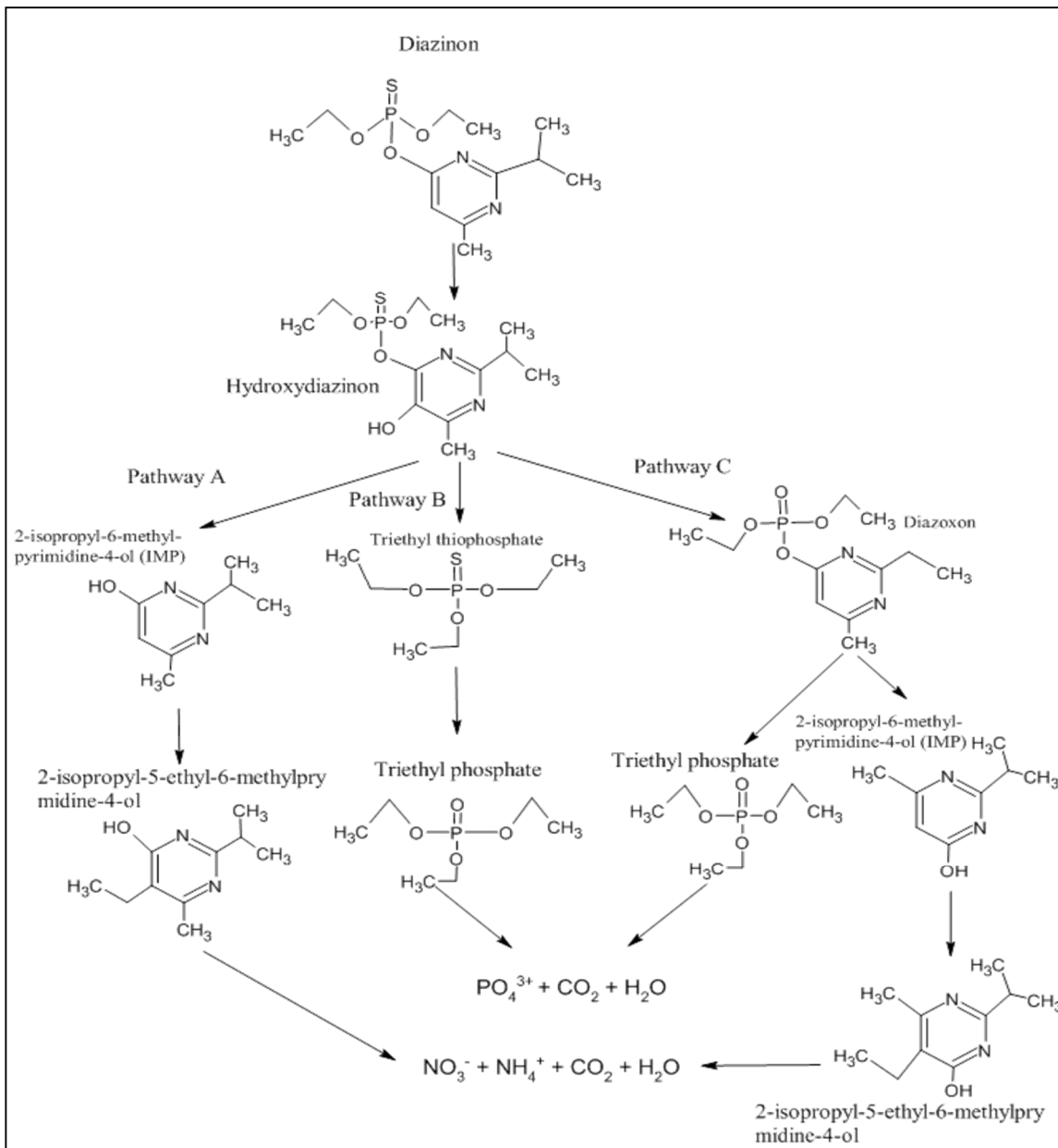


Figure 4. Proposed degradation pathways of DZN.

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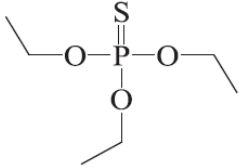
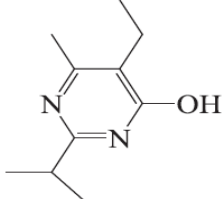
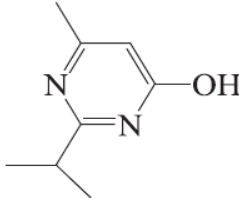
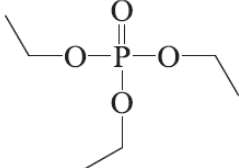
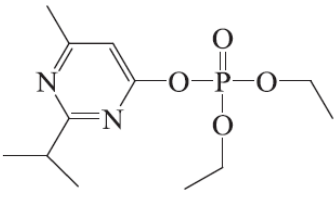
Table 1. Experimental matrix of Doehlert and the corresponding measured responses.

Run	Coded value X_1	Actual value [Fe ²⁺] (mg. L ⁻¹)	Coded value X_2	Actual value [H ₂ O ₂] (mg. L ⁻¹)	Coded value X_3	Actual value pH	Yield (%)	
							Photo-Fenton	Fenton
1	0.000	25.0	0.000	250.0	0.000	5.00	93.98	70.86
2	+1.000	45.0	0.000	250.0	0.000	5.00	82.59	71.60
3	+0.500	35.0	+0.866	423.2	0.000	5.00	72.79	78.96
4	-0.500	15.0	+0.866	423.2	0.000	5.00	61.81	68.81
5	-1.000	5.0	0.000	250.0	0.000	5.00	67.00	64.00
6	-0.500	15.0	-0.866	76.8	0.000	5.00	56.83	60.74
7	+0.500	35.0	-0.866	76.8	0.000	5.00	68.61	74.56
8	+0.500	35.0	+0.289	307.8	+0.816	6.63	78.98	62.72
9	-0.500	15.0	+0.289	307.8	+0.816	6.63	68.50	61.19
10	0.000	25.0	-0.577	134.6	+0.816	6.63	71.75	61.99
11	+0.500	35.0	-0.289	192.2	-0.816	3.37	79.64	61.47
12	-0.500	15.0	-0.289	192.2	-0.816	3.37	80.51	53.69
13	0.000	25.0	+0.577	365.4	-0.816	3.37	84.06	72.77

Table 2. Comparison studies of works aimed at the degradation and/or elimination of diazinon.

Process	Conditions	Method of analysis	Elimination/ degradation yield (%)	References
Adsorption/ Photocatalysis	$C_0 = 40 \text{ mg.L}^{-1}$	UV/Vis	95	(Hassan et al., 2017)
	$\text{TiO}_2\text{-AC} = 1 \text{ g.L}^{-1}$ $t = 80 \text{ min}$ $\text{TiO}_2 = 1 \text{ g.L}^{-1}$ $t = 80 \text{ min}$	spectrophotometer Unicam UV/Vis 5625, at a wavelength of 247 nm	55	
Photocatalysis	$C_0 = 10 \text{ mg.L}^{-1}$ WO_3 doped ZnO 10 mg/cm^{-2} 2% $t = 180 \text{ min}$ Neutral pH	Gas Chromatography/ Flame Ionization Detector (GC/FID)	99	(Maleki et al., 2020)
Sono-Fenton	$C_0 = 50 \text{ mg.L}^{-1}$ $f = 20 \text{ khz}$ $C_{Fe} = 20 \text{ mg.L}^{-1}$ $C_{H_2O_2} = 150 \text{ mg.L}^{-1}$ pH = 3 $t = 60 \text{ min}$	Gas Chromatography/ Flame Ionization Detector (GC/FID)	98.3 (degradation) 29.9 (mineralization)	(Wang and Shih, 2015)
Solar photo-Fenton	Real industrial wastewater $C_0 = 11 \text{ mg.L}^{-1}$ $C_{H_2O_2} = 1 \text{ g.L}^{-1}$ $C_{Fe} = 3 \text{ g.L}^{-1}$ $t = 180 \text{ min}$	Shimadzu HPLC using C-18 phenomenex reverse phase column and Diode Array Detector (HPLC/DAD)	50.1	(Gar Alalm et al., 2015)
Photocatalysis	Real industrial wastewater $C_0 = 11 \text{ mg.L}^{-1}$ $\text{TiO}_2 = 2 \text{ g.L}^{-1}$ pH = 3.8 $t = 120 \text{ min}$		38.2	
Biological	$C_0 = 20 \text{ mg.L}^{-1}$ bacterial endophytes in rice plant	High-Performance Liquid Chromatography-Diode Array Detector (HPLC/DAD)	58.5	(Nasrollahi et al., 2020)
Membrane technique	Electrospun nanofibrous membrane $C_0 = 10 \text{ mg.L}^{-1}$ pH = 7 0.1% nanoparticles $t = 60 \text{ min}$	Spectrophotometer DR 5000 device at 247 nm	83.7	(Pordel et al., 2019)
Fenton	$C_0 = 1 \text{ } \mu\text{g.mL}^{-1}$ $C_{H_2O_2} = 423.2 \text{ mg.L}^{-1}$ $C_{Fe} = 45 \text{ mg.L}^{-1}$ pH = 5 $t = 30 \text{ min}$	Ultra High-Performance Liquid Chromatography equipped with a Diode Array Detector (UHPLC/DAD) and gas chromatography coupled with triple quadrupole mass spectrometry (GC-MS/MS)	85	This work
Photo-Fenton	$C_0 = 1 \text{ } \mu\text{g.mL}^{-1}$ $C_{H_2O_2} = 262 \text{ mg.L}^{-1}$ $C_{Fe} = 29 \text{ mg.L}^{-1}$ pH = 4.6 $t = 5 \text{ min}$		100 Total mineralization	This work

Table 3. Identification of DZN degradation by-products with GC-MS/MS.

No.	By-products	Retention time (min)	Molecular weight (m/z)	Compounds
1	Triethyl thiophosphate	7.11	198	
2	2-isopropyl-5-ethyl-6-methylpyrimidine-4-ol	7.49	156	
3	2-isopropyl-6-methylpyrimidine-4-ol (IMP)	7.77	133	
4	Triethyl phosphate	8.56	182	
5	Diazoxon	9.44	137	
6	Hydroxydiazinon	14.23	178	