

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

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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
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26 Abstract

This study aiming to determine the optimal conditions to degrade an organophosphate 27 pesticide diazinon (DZN) at low levels concentrations (µg.mL⁻¹) and to identify the by-28 products generated. The degradation processes utilized were the Fenton and photo-Fenton. 29 The iron concentration $[Fe^{2+}]$, the hydrogen peroxide concentrations $[H_2O_2]$, and the solution 30 pH are the investigated parameters. The Doehlert three-parameter experimental design was 31 applied to model and optimize both degradation processes. The mathematical models 32 suggested were assessed and validated by application of analysis of variances ANOVA. In the 33 case of Fenton process, the greatest yield of degradation (79%) was obtained at 34 $[Fe^{2+}] = 35 \text{ mg.L}^{-1} (0.63 \text{ mmol.L}^{-1}), [H_2O_2] = 423 \text{ mg.L}^{-1} (12.44 \text{ mmol.L}^{-1}), \text{ and } pH = 5.0.$ 35 In photo-Fenton process, the maximum yield of degradation (96%) was obtained under the 36 conditions of $[Fe^{2+}] = 29 \text{ mg.L}^{-1} (0.52 \text{ mmol.L}^{-1}), [H_2O_2] = 258 \text{ mg.L}^{-1} (7.59 \text{ mmol.L}^{-1}) \text{ and}$ 37 pH = 4.6. QuEChERS (quick, easy, cheap, effective, rugged, and safe), as extraction 38 39 technique, and GC-MS/MS (gas chromatography coupled with triple quadrupole mass spectrometry) were used to identify the by-products degradation of DZN. The identified 40 compounds are diazoxon, triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-41 methylpyrimidine-4-ol, 2-isopropyl-6-methylpyrimidine-4-ol (IMP) and hydroxydiazinon. 42 Three possible pathways for diazinon degradation have been suggested and the hydroxylation, 43 oxidation and hydrolysis are likely probable degradation mechanisms. 44

45

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

49 **1. Introduction**

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

58 Globally, pesticides are classified into four main families, depending on their use, chemical composition, and nature of active ingredients (Kaur et al., 2019). Herbicides are a 59 class of pesticide used to control or prevent the growth of weeds (Fernanda Pereira Barbosa, 60 2019). Insecticides are used against insect eggs, larvae, and adult insects, and fungicides are 61 designed to eliminate or limit the development of parasitic plant fungi. Diazinon (DZN), an 62 63 insecticide and highly toxic organophosphate pesticide (Čolović et al., 2010), is used to control insects in residential, agricultural and livestock areas (Acero et al., 2008). Its presence 64 in surface waters is widespread due to extensive use (Real et al., 2007). For example, in the 65 USA, 6 million kg of DZN are applied annually (Real et al., 2007). Under favorable 66 environmental conditions, it can accumulate in groundwater due to its limited 67 biodegradability (Molla et al., 2019; Raeisi et al., 2016). Several pesticides are usually 68 detected in waters at the concentration range of 1–1000 µg.L⁻¹ (Jones et al., 2017). DZN has 69 been detected in surface waters at concentrations of 80 ng.L⁻¹ to 25 µg.L⁻¹ in countries such as 70 the USA, Spain, and Canada (Glinski et al., 2018; Metcalfe et al., 2019; Proia et al., 2013). 71 72 This compound is toxic to humans, inhibiting the enzyme acetylcholinesterase, which is essential for nervous system function (Shirzad-Siboni et al., 2015; Zhang et al., 2010). Fatal 73 human doses were found to be in the range of 90–444 mg.kg⁻¹ (Molla et al., 2019). Aquatic 74 system toxicity is 350 ng.L⁻¹ with a 48 h LC₅₀ of 4.4 mg.L⁻¹ in killifish (Daneshvar et al., 75 76 2007; Kazemizad et al., 2016). DZN is categorized as a WHO class II compound, considered moderately hazardous (World Health Organization, 2010). 77

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

aqueous solution by different processes (Al Momani et al., 2004a; Al Momani et al., 2004b; 81 Al Momani et al., 2009, 2007; Contreras et al., 2003). Gar Alalm et al. (2015) attempted to 82 degrade DZN by two processes and found photocatalysis degraded DZN by 40% and photo-83 Fenton by approximately 50%. Activated carbon prepared from flamboyant pods modified 84 with Fe²⁺ has also been used as a TiO₂ support, and the photocatalytic degradation using this 85 combination was approximately 80% (Hassan et al., 2017). Similarly, using tungsten-doped 86 zinc oxide nanoparticles as a catalyst, Maleki et al. (2020) observed 89% of DZN degradation. 87 Nasrollahi et al. (2020) used a biological approach involving bacterial endophytes in rice 88 89 plants to degrade DZN (50% degradation). Membrane techniques have also been investigated to eliminate DZN, and nanofibrous membranes eliminated 84% of DZN (Pordel et al., 2019). 90

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

111
$$H_2O_2 + Fe^{2+} \to Fe^{3+} + OH^- + OH \cdot$$
 Eq. 1

112
$$H_2O_2 + Fe^{3+} \to Fe^{2+} + H^+ + HO_2 \cdot$$
 Eq. 2

113
$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH \cdot \lambda < 580 \text{ nm}$$
 Eq. 3

114
$$H_2O_2 + hv \rightarrow 2 OH \cdot \lambda < 310 \text{ nm}$$
 Eq. 4

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

To date, no study has evaluated the degradation of DZN at trace levels (μ g.L⁻¹) and 124 identified DZN degradation by-products at ultra-trace levels (ng.L⁻¹), likely due to the lack of 125 126 advanced analytical methods and an efficient and rapid extraction protocol. Our study is novel in combining simple and efficient degradation processes, the application of an experimental 127 design to determine the optimal degradation conditions, and the use of efficient extraction and 128 analysis techniques to monitor DZN degradation and to determine degradation by-products at 129 ultra-trace concentrations (ng.L⁻¹) in aqueous matrices. We applied advanced oxidation 130 processes (Fenton and photo-Fenton) and a Doehlert design to optimize and model each 131 process. Hydrogen peroxide (H_2O_2), ferrous ions (Fe²⁺) concentrations and pH were 132 optimized to eliminate efficiently DZN. In the present work, extremely sensitive and reliable 133 techniques based on a QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction 134 approach and gas chromatography coupled with triple quadrupole mass spectrometry 135 136 (GC-MS/MS) were used to identify intermediate products in water. The possible pathways of the degradation of DZN were also proposed. We believe our study will inform future 137 experimental studies of organophosphate pesticide pollutant degradation in wastewater, 138 especially DZN. 139

140

141 **2.** Materials and methods

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2.1. Materials and reagents

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Diazinon was purchased from Sigma-Aldrich (99%, purity). Its chemical formula is $C_{12}H_{21}N_2O_3PS$ and the International Union of Pure and Applied Chemistry (IUPAC) name is O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate (CAS: 333-41-5). The molecular weight, the solubility in water at 20°C and the pK_a of DZN are 304.35 g.mol⁻¹, 60 mg.L⁻¹ and 2.6, respectively. Hydrogen peroxide (33%, *w/w*) and Fe²⁺ ions were produced from ferrous sulfate heptahydrate (FeSO₄, 7H₂O) as a source of Fe²⁺. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were used to adjust the solution pH in each experiment. All chemicals were of analytical reagents grade and purchased from Sigma-Aldrich, France. The ultrapure water (18.2 M Ω .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 reactor with 100 mL of ultrapure water at room temperature in the dark (25 °C). The 156 concentration of the effluent was 1 µg.mL⁻¹, prepared by dissolving DZN in ultrapure water. 157 For Fenton reagents, the added of the DZN concentration was depended on the conditions of 158 each experiment. The photo-Fenton experiments were carried out in a cubical photo-reactor 159 equipped with a cooler to maintain a constant temperature. A Pyrex crystallizer batch reactor 160 with a capacity of 250 mL was used to ensure consistent and direct exposure of the solution to 161 the lamplight supplied by Philips lamp (11 W, UVA). 162

163 **2.3. Analytical methods**

164 **2.3.1. UHPLC/DAD analysis**

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

175
$$Y_i = \frac{(c_0 - c_t)}{c_0} \times 100$$
 (Eq. 5)

in which C_0 and C_t are the DZN initial concentration and DZN concentration at a given time t in mg.L⁻¹, respectively.

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

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

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2.3.3. QuEChERS extraction method

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

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

215 **2.4. Doehlert design methodology**

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

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

229

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

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

- 234
- 235

Table 1

236 **3. Results and discussion**

3.1. Development and validation of the predictive regression models

The yields of DZN degradation estimated from the application of Doehlert design are given in Table 1 for each Fenton and photo-Fenton experiment. Two regression models are suggested, the responses considered are the degradation yield of DZN by Fenton (\hat{Y}_F) and photo-Fenton (\hat{Y}_{Ph-F}) processes.

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

The estimation of model factors shows that in the case of Fenton process, five factors 254 (including the b₀ (see Eq. 6)) are statistically significant, namely $[Fe^{2+}]$, $[H_2O_2]$, (pH *255 $[H_2O_2]$) and pH^2 , and in the case of photo-Fenton process, six factors (including the b₀) are 256 statistically significant, namely $[Fe^{2+}]$, pH, $[Fe^{2+}]^2$, $[H_2O_2]$ and pH^2 . All these factors have 257 a p-value < 0.05. The analysis of variance (ANOVA) is used systematically as the main 258 method to validate regression models in design of experiments methodology approach. To 259 validate the suggested models (including only the significant factors), a Fisher test is carried 260 261 out. The Fisher-value (F-value) of the model (estimated on basis of the ratio between model and residual mean square) and compared to Fisher-Value critical (Fcrit) were determined from 262 Fisher-Snedecor table with two degrees of freedom (df₁ and df₂) and ($\alpha = 5\%$). For Fenton 263 process model, F-value ($df_1 = 5$, $df_2 = 7$) = 10.80 and for photo-Fenton process model, F-value 264 $(df_1 = 4, df_2 = 8) = 14.46$. The F_{crit} are respectively equal to 3.97 and 3.84, then in both cases, 265 F-value > Fcrit, which means that the suggested models are validated at the fixed level of 266 significance. Based on these considerations, final models retained for both processes are given 267 by equations 7 and 8. 268

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

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

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

275

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

Modde software was used to determine the optimum points for each degradation 277 process. Results show that equation 7 describes a critical point corresponding to a maximum 278 degradation yield (96%); this is shown in Figure 1(c), plotted using the 3D graph. The factor 279 values in this case were $[Fe^{2+}] = 29 \text{ mg.L}^{-1}$ (0.52 mmol.L⁻¹); $[H_2O_2] = 258 \text{ mg.L}^{-1}$ 280 $(7.59 \text{ mmol}.\text{L}^{-1})$ and pH = 4.6. So, equation 8 does not present a critical point; in this case, the 281 extreme value theorem (Weierstrass) was applied to resolve this problem (Martínez-Legaz, 282 2014), this is confirmed by plots in 3D graph (Fig 1 (d) and (e)). The highest value 283 corresponding to the optimal value was obtained at the boundary of the study range. As seen 284 in Table 1, the greatest degradation (79%) was obtained under the conditions of run 3, 285 indicating that the optimal conditions were $[Fe^{2+}] = 35 \text{ mg.L}^{-1}$ (0.63 mmol.L⁻¹); 286 $[H_2O_2] = 423 \text{ mg.L}^{-1}$ (12.44 mmol.L⁻¹) and pH = 5.0. Furthermore, the 3D response surface 287 plot shows the highest yield corresponding to optimal values cited previously. However, on 288 the basis of experimental design results and in the case of Fenton process, pH is not a 289 significant parameter. The optimal conditions do not vary therefore greatly when the pH 290 291 changes but to take in account the conditions of iron precipitation, the pH has been fixed to 292 3.4 (the low level value).

293 294

Figure 1

These results show that the optimal concentrations of Fe^{2+} and H_2O_2 for the photo-295 Fenton process were lower than those of the Fenton process, and the yield of the degradation 296 was greater using the photo-Fenton process. These results highlight the significant effect of 297 298 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 29 mg.L⁻¹ (0.52 mmol.L⁻¹) of Fe²⁺ and 258 mg.L⁻¹ (7.59 mmol.L⁻¹) of H₂O₂ were used instead 300 of 35 mg.L⁻¹ (0.63 mmol.L⁻¹) and 423 mg.L⁻¹ (12.44 mmol.L⁻¹) of H₂O₂ to obtain 96% instead 301 of 79% for the photo-Fenton and Fenton process, respectively. These findings can be 302 explained by the fact that the ferric ions resulting from photodegradation (Eq. 1) have been 303 photochemically regenerated into ferrous ions according to equations 9 and 10. 304

$$H_2O_2 + Fe^{3+} + hv \rightarrow Fe^{2+} + H^+ + \cdot OH$$
 Eq. 9

306

$$H_2O_2 + Fe^{3+} + hv \rightarrow Fe^{2+} + H^+ + HO_2$$
 Eq. 10

307

These ions further react with H_2O_2 to produce radical hydroxyl and ferric ions, and in this manner, the cycle continues, as confirmed by other studies (Ameta et al., 2018; Audino et al., 2017; Marchetti and Bessa Azevedo, 2020).

Notably, the ratio of the reagent concentrations (H_2O_2/Fe^{2+}) under the optimal conditions for both processes are different: 20 for the Fenton process and 15 for the photo-Fenton process. These results indicate that the implementation of the process requires the 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

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

328

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

330

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

339

Figure 3

As observed in the chromatograms, the DZN retention time was 17 min, and the 340 molecular weight usually obtained was 304 uma (Fig. 3.a). Several by-products were detected 341 (Fig. 3.b), grouped in Table 2 by their retention time. By comparing Figs. 3.a and 3.b, we 342 notice the disappearance of the DZN peak, implying the total degradation of DZN after 5 min. 343 344 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 the results obtained previously. In addition, the by-products found in this work correspond to 346 the results found in previously published studies. In their study of photocatalytic DZN 347 degradation under sunlight irradiation, Molla et al. (2019) revealed eight by-products: 348 diazoxon, triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-methylpyrimidine-349 350 4-ol, 2-isopropyl-4-ethyl-6-methylpyrimidine-5-ol, 2-isopropyl-6-methylpyrimidine-4-ol and hydroxydiazinon. The six of them are the same as those in our study, which are: diazoxon, 351 352 triethyl phosphate, triethyl thiophosphate, 2-isopropyl-5-ethyl-6-methylpyrimidine-4-ol, 2isopropyl-6-methylpyrimidine-4-ol (IMP) and hydroxydiazinon. 353

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

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

Table 2

372

373 3.5. Pathways for degradation of diazinon

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

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

- 398
- 399
- 400

Figure 4

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

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

419

Table 3

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

429 **4.** Conclusion

This study investigated the degradation of DZN in water by two types of advanced oxidation processes: Fenton and photo-Fenton. The application of the Doehlert design as an experimental methodology for the optimization of the experimental parameters of the two processes allowed us to develop two mathematical regression models for each process and then determine the corresponding optimal points. Under these conditions, complete degradation of diazinon and by-products was obtained after only 5 min using the photoFenton process. Utilization of the Fenton process allowed for 85% degradation yield after 60 min. All experiments included an initial DZN concentration of 1 mg.L⁻¹, a realistic wastewater concentration. By-product identification was carried out using a new method based on the QuEChERS extraction, pre-concentration, and GC-MS/MS analysis. This methodology allowed us to determine the photodegradation by-products even at very low concentrations (ng.L⁻¹). DZN degradation using the photo-Fenton process generated six 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, Writing455 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
458 Kadmi: Supervision, Data curation, Conceptualization, Formal analysis, Methodology,
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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

464 **References**

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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.

List of tables

Run	Coded value	Actual value	Coded value X ₂	Actual value [H ₂ O ₂] (mg. L ⁻¹)	Coded value X ₃	Actual value pH -	Yield (%)	
	\mathbf{X}_{1}	[Fe ²⁺] (mg. L ⁻¹)					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 1. Experimental matrix of Doehlert and the corresponding measured responses.

Process	Conditions	Method of analysis	Elimination/ degradation yield	References	
Adsorption/ Photocatalysis	$C_0 = 40 \text{ mg.L}^{-1}$ $TiO_2 - AC = 1 \text{ g.L}^{-1}$ t = 80 min $TiO_2 = 1 \text{ g.L}^{-1}$ t = 80 min	UV/Vis spectrophotometer Unicam UV/Vis 5625, at a wavelength of 247 nm	95 55	(Hassan et al., 2017)	
Photocatalysis	$C_0 = 10 \text{ mg.L}^{-1}$ WO ₃ doped ZnO 10 mg/cm ⁻² 2% t = 180 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 khz $C_{Fe} = 20 \text{ mg.L}^{-1}$ $C_{H_2O_2} = 150 \text{ mg.L}^{-1}$ pH = 3 t = 60 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 min	Shimadzu HPLC using C-18 phenomenex reverse phase column and Diode	50.1	(Gar Alalm et al., 2015)	
Photocatalysis	Real industrial wastewater $C_0 = 11 \text{ mg.L}^{-1}$ $TiO_2 = 2 \text{ g.L}^{-1}$ pH = 3.8 t = 120 min	Array Detector (HPLC/DAD)	38.2		
Biological	$C_0 = 20 \text{ mg.L}^{-1}$ bacterial endophytes in rice plant	High-Performance Liquid Chromatography-Diode 58.5 Array Detector (HPLC/DAD)		(Nasrollahi et al., 2020)	
Membrane technique	Electrospun nanofibrous membrane $C_0 = 10 \text{ mg.L}^{-1}$ pH = 7 0.1% nanoparticules t = 60 min	Spectrophotometer DR 5000 device at 247 nm	83.7	(Pordel et al., 2019)	
Fenton	$C_0 = 1 \ \mu g.mL^{-1}$ $C_{H_2O_2} = 423.2 \ mg.L^{-1}$ $C_{Fe} = 45 \ mg.L^{-1}$ pH = 5 $t = 30 \ min$	Ultra High-Performance Liquid Chromatography equipped with a Diode Array Detector	85	This work	
Photo-Fenton	$C_0 = 1 \ \mu g.mL^{-1}$ $C_{H_2O_2} = 262 \ mg.L^{-1}$ $C_{Fe} = 29 \ mg.L^{-1}$ pH = 4.6 $t = 5 \ min$	(UHPLC/DAD) and gas chromatography coupled with triple quadrupole mass spectrometry (GC-MS/MS)	100 Total mineralization	This work	

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

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

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

