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Research article

Study on diazinon toxicity reduction by electro-Fenton process: A bioassay using daphnia magna

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ABSTRACT

The realm of diazinon reduction from polluted water has witnessed a surge in the significance of advanced oxidation processes (AOPs) in recent times. However, there is a dearth of research focusing on the mitigation of its toxicity through AOPs. Thus, the primary objective of this study was to evaluate the effectiveness of the Electro-Fenton process (EFP) in the eradication and detoxification of diazinon in aqueous solutions. Synthetic wastewater samples with concentrations of 2, 2.5 and 3 mg/L were prepared. A total of 27 samples were determined using Box Behnken Design. Reaction time, pH and iron to hydrogen peroxide ratio (Fe^{2+}/H_2O_2) were examined as operational parameters under a constant current of 5.4 amps. The quantification of diazinon concentration was performed using High-Performance Liquid Chromatography (HPLC). To evaluate the detoxification of diazinon, the Daphnia magna bioassay was employed as a methodology in this study. According to the results, the EFP could reduce the diazinon to zero and the LC_{50} values are increased by applying the process. The LC_{50} values for diazinon were determined using the Daphnia magna bioassay, considering initial concentrations of 2, 2.5, and 3 mg/L at a pH of 5, a reaction time of 15 min, and an iron to hydrogen peroxide molar ratio of 2. The recorded LC50 values were 3.039, 3.076, and 3.106, respectively, indicating the lowest frequency of cumulative death in Daphnia magna. In this case, after 96 h, only 3 cases (30%) of Daphnia magna death were observed. However, for all the mentioned concentrations of diazinon, after 96 h of exposure to samples without applying the Daphnia Magna death process, it was observed between 60 and 100%. Reducing the diazinon concentration and increasing the 96-h LC_{50} showed that the EFP can reduce the toxicity of diazinon on Daphnia Magna at the same time. Therefore, EFP can be considered a superior method with low ecotoxicity.

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Table 1
Physicochemical properties of the Saad Abad Barzok River water.

Parameter	Unite	Value
pH	–	7.24
Turbidity	NTU	1.37
EC	μS/cm	971.43
Alkalinity	mg/L $CaCO_3$	300
Total hardness	mg/L $CaCO_3$	509.6
Calcium hardness	mg/L $CaCO_3$	94.8
Sulfate	mg/L	50
Chloride	mg/L	68.16

1. Introduction

A vast array of pesticides, exceeding 800 types, are manufactured globally and find widespread application in agricultural practices [1]. While pesticides bring about advantageous effects on agricultural yields, their utilization can result in a diverse range of toxic effects on non-target organisms [2]. The presence of organic and toxic compounds in the surface and groundwater caused by spraying, causes irreparable damage to the environment, especially the aquatic environment [3]. Acute effects of the pesticide on humans include headache, dizziness, muscle contraction, skin irritation, and respiratory distress, and chronic effects include cancer, neurological effects, damage to the reproductive system, and endocrine disorders [4]. Recent studies at Harvard University in Boston, USA, have shown that the risk for Parkinson's disease can be increased due to exposure to pesticides, even in small amounts, by up to 70% [5].

Meanwhile, organophosphate pesticides are toxic as they can inhibit acetylcholinesterase activity, a cholinergic enzyme primarily found at postsynaptic, when absorbed through the body's organs [6]. Phosphorus-based pesticides, specifically organophosphates, have emerged as a substitute for chlorine owing to their affordability and effectiveness against a broad spectrum of pests. Global statistics indicate that phosphorus pesticides contribute significantly to the highest mortality rates associated with pesticide exposure [7–10]. Diazinon, as one of the most extensively utilized organic phosphorus pesticides, finds widespread application in both residential and agricultural settings [11,12]. Based on the classification by the World Health Organization (WHO), diazinon has been categorized as a class two pesticide concerning its toxicity. Its adverse effects on aquatic organisms have been reported at a concentration of 350 ng/L [13,14].

In general, the removal of pollutants and pesticides from water sources is accomplished through three main approaches, which include physical, chemical, and biological methods [15–18]. The use of adsorption methods [19], nanofiltration and reverse osmosis [20,21], electrochemical [22], advanced oxidation processes [23] and a combination of the above methods have been used to remove diazinon from water sources [24]. In recent times, the application of advanced oxidation processes (AOPs) has garnered substantial attention as efficient techniques for the eradication of pesticides from water sources [25]. The mechanism underlying AOPs revolves around the generation of highly oxidizing free radicals, such as hydroxyl radicals, which possess strong oxidizing power [26]. Electro-Fenton, as an advanced oxidation method, involves the combination of two processes, namely Fenton reaction and electrocoagulation, to enhance the overall oxidation performance. For having a cheap, and efficient electrophoresis process, it is critical to reduce the contact time and eliminate the possible secondary contamination [27,28]. Disadvantages of this method are high sludge production and the need for an acidic environment to perform the reaction [29]. However, the Fenton reaction is known as a potential method for diazinon remediation [30–32] there is still a great concern for the produced effluent toxicity after the treatment as it may consist of new toxic by-products as well as the remaining diazinon in the effluent [33–35].

Meanwhile, bioassays, a procedure that uses living material to estimate chemical effects, have been known as an effective tool to survey the quality of effluent as the physical and chemical tests have some limitations in determining the status of toxins on living organisms. Consequently, the application of bioassays can be used to determine the toxicity level of the effluent. In general, the use of bioassay methods is an appropriate indicator when the contamination is widespread or when the contaminant is acutely toxic to humans. The advantages of using these bio-test methods are cheapness, requiring short time, and high efficiency [36–38]. However, the major part of the literature, only focused on the removal efficiency of AOPs and a small part of the studies evaluated the effluent quality from the toxicity standpoints [39,40].

Meanwhile, Daphnia magna has been used as a reliable indicator for ecotoxicology studies and is considered a prominent test organism for standard laboratory tests among biological species for different types of pollutants and toxic compounds [41,42] It should be noted that Daphnia magna is a group of crustaceans with an average size of 5 mm, which is very important for biological tests in infancy [38,43].

Therefore, the present study aims to evaluate the potential of an Electro-Fenton process not only with considering its degradation potential but also with its effluent quality and level of detoxification using Daphnia magna for bioassay study.

2. Methods and materials

2.1. Chemical reagents

Diazinon ($C_{12}H_{21}N_2O_3PS$; purity 95%) purchased from Sigma-Aldrich Co., Germany, and other chemicals, including ferrous sulfate

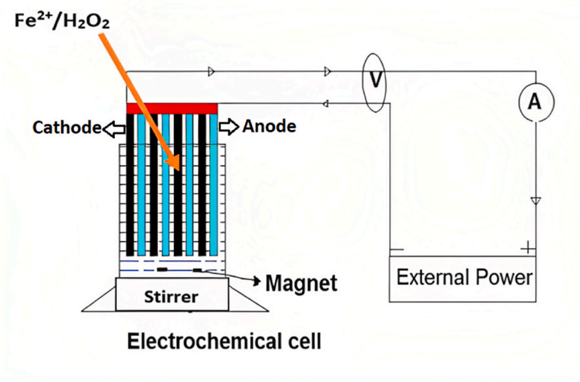

Fig. 1. The schematic of the studied electrochemical cell-based process.

Table 2
Box-Behnken design for degradation of diazinon using the EFP.

Run	Diazinon concentration (mg/L)	pH	Reaction time (min)	Fe^{2+}/H_2O_2 ratio
1	2.5	3	15	4
2	2.5	4	15	3
3	2.5	5	20	3
4	2.5	4	10	2
5	3	3	15	3
6	2	4	15	2
7	2.5	4	20	4
8	2.5	5	20	4
9	2.5	4	10	4
10	2.5	5	10	3
11	2	5	20	3
12	2	5	15	4
13	2.5	5	15	3
14	2.5	5	20	2
15	3	5	15	4
16	3	5	20	3
17	2.5	5	15	2
18	3	5	15	3
19	3	4	15	2
20	2	4	10	3
21	2.5	3	15	2
22	2.5	3	20	3
23	2	5	15	3
24	2.5	4	15	3
25	2	3	15	3
26	2.5	3	10	3
27	3	4	10	3

($FeSO_4$) as a catalyst, hydrogen peroxide (H_2O_2) as oxidant, Analytical grade sodium hydroxide (NaOH) and hydrochloric acid (HCl) procured from Merck Co., Germany, were employed for pH adjustment purposes. The preparation of the solutions under investigation was carried out using water of HPLC-grade quality.

2.2. Collection of water samples

Following prior reports documenting the presence of diazinon in water samples collected from Saad Abad Barzok river, situated near Kashan city, Iran, raw water samples were procured from the river and subsequently transported to the laboratory. The temperature of the water samples was maintained at 4 ± 1 °C. Physicochemical analyses were conducted to determine the characteristics of the water, as presented in Table 1. Notably, diazinon was not detected in the original river water samples. Consequently, the assessment of EFP performance was carried out by artificially introducing diazinon into the river water samples.

2.3. Electro-Fenton process

A 2-litre batch reactor constructed of Plexiglas was utilized in the procedure. For this particular reactor setup, eight stainless steel electrodes were utilized, each measuring 0.2 cm in diameter, 2.5 cm in width, and 15 cm in height. These electrodes served as both the anode and cathode during the EFP. At 1.5 cm intervals, the electrodes are arranged vertically and parallel to each other. Diazinon spiked samples, H_2O_2 (1.7 mM), and $FeSO_4$ (3.4, 5.1, and 6.8 mM), were manually added to the reactor, and a magnetic stirrer (300 rpm) was used to prepare the solution at a consistent concentration and distribute the chemicals uniformly. The continuous input current of 23 V and 5.4 amps was provided by an external power supply and monitored with an ammeter and voltmeter. The diazinon concentrations in the treated samples were analyzed employing high-performance liquid chromatography (HPLC). The limit of detection for diazinon was determined to be 0.05 μg/mL. The schematic representation of the reactor can be found in Fig. 1. At the desired interval, the samples were extracted from the reactor and filtrated by the 0.45 μm membrane filter and analyzed for diazinon concentration.

2.4. Statistical analysis and experimental design

To investigate the impact of key factors such as initial diazinon concentration, reaction time, pH, and the molar ratio of Fe^{2+} to H_2O_2, the Box-Behnken Design was employed using R software version 4.3.2 (RSM package). This experimental design facilitated the determination of the required number of experimental runs. The experimental framework adopted encompassed a configuration comprising four variables, each exhibiting three distinct levels, thereby generating a comprehensive set of 27 samples. The determination of the independent variable range was accomplished via a preliminary assessment approach, aligning with prior research investigations. The specific levels of the variables can be found in Table 2. It should be noted that in all 27 study runs, the effluent concentrations of diazinon were below the limit of detection (LOD).

Probit analysis was used to determine the minimum lethal concentration (LC) of 10, 25, 50, 75, and 90% and Cox regression in survival analysis was used to analyze the effect of toxicity removal on Daphnia's lifespan (SPSS software version 22).

2.5. Analytical measurement

Analysis of the samples was performed utilizing a KNAUER Azura MWD 2.1 L high-performance liquid chromatography (HPLC) system, incorporating a C_{18} column (4.6 mm × 250 mm, 5 μm) (model: Eurospher 100-5, Knauer, Azura, Germany). The mobile phase was HPLC-grade methanol and distilled water (10:90 v/v) with a flow rate of 1 mL min^{-1}. The injection volume was 20 μl and monitored at 245 nm to detect diazinon. During the analysis, the column temperature was maintained at room temperature.

2.6. Toxicity assay

The toxicity test was carried out following established protocols for measuring the acute toxicity of US-EPA (EPA-821-R-02-012). The acute LC_{50}-96h was determined by the probit analysis. Newborn Daphnia Magnas (1–3 days) were used in the present study. The toxicity of water samples treated by EFP under different conditions was compared with the untreated diazinon samples and the distilled water treated by EFP as the control sample. To measure the toxicity of each sample, 10 Daphnia Magna were added to each container. Survivors were counted up to 4 days.

3. Results and discussion

3.1. EFP performance for diazinon degradation

Table 2 presents the application of EFP in this investigation, wherein diverse combinations of pH, reaction time, and Fe^{2+}/H_2O_2 concentration were employed. The target of this approach was the elimination of diazinon, with varying concentrations, throughout 27 distinct experimental runs. The HPLC limit of detection (LOD for detecting diazinon was 0.05 μg ml^{-1}. Consequently, it can be posited that the Electro-Fenton technique demonstrates the capability to decrease the initial low concentrations of diazinon in water to levels below 0.05 μg ml^{-1}. Since diazinon was reduced to less than a detectable concentration in all experiments, it was not possible to determine the most effective parameters for removing the pesticide and to determine the optimal conditions.

Previous investigations have demonstrated the proficient elimination of pesticides from aqueous solutions through the application of EFP. Consistent with the present findings, Dominguez et al. (2018) achieved complete degradation of Lindane, an organochlorine pesticide, within a mere 15-min timeframe using the EFP, even at initial concentrations ranging from 5 to 10 mg/L [44]. Wang et al. (2018) fabricated an EFP setup employing Fe-based magnetic activated carbon as the catalyst for the degradation of the pesticide diuron. At pH = 6.7, a 10 mg/L diuron solution takes 120 min to decompose entirely [45]. In Zhao et al. (2016) study, imidacloprid degradation was achieved using an EFP approach, employing FeCuC as the cathode and boron-doped diamond as the anode. Notably, the EFP system facilitated the removal of 88% of the total organic carbon (TOC) [46]. Abessalem et al. (2010) reported an electro-Fenton process could effectively degrade a mixture of three pesticides (chlortoluron, carbofuran, and bentazone) [47]. In another study, 92% removal of diazinon by the sono-electro-Fenton process (SEFP) was reported [48].

The low initial concentration of diazinon in the samples might be one of the explanations for the high removal efficiency in our study. In previous studies, it was reported that the decreasing initial concentration of diazinon increased the effectiveness of electrochemical processes [48,49]. Under comparable experimental conditions, equivalent quantities of hydroxyl radicals are produced for each respective initial concentration of diazinon. Consequently, the hydroxyl radicals easily remove the large amount of diazinon at low concentrations. The hydroxyl ions generated, however, are insufficient to degrade the additional amount of diazinon at its greater concentrations. Furthermore, at high concentrations of diazinon, the probability of competition between generated intermediates and

Table 3
Survival rate (%) of Daphnia magna in the 96-h toxicity test.

Run	Diazinon concentration (mg/L)	pH	Reaction time (min)	Fe^{2+}/H_2O_2 ratio	Survival rate (%)
1	2.5	3	15	4	60
2	2.5	4	15	3	80
3	2.5	5	20	3	60
4	2.5	4	10	2	60
5	3	3	15	3	50
6	2	4	15	2	90
7	2.5	4	20	4	70
8	2.5	5	20	4	60
9	2.5	4	10	4	60
10	2.5	5	10	3	70
11	2	5	20	3	80
12	2	5	15	4	60
13	2.5	5	15	3	70
14	2.5	5	20	2	70
15	3	5	15	4	60
16	3	5	20	3	60
17	2.5	5	15	2	70
18	3	5	15	3	60
19	3	4	15	2	70
20	2	4	10	3	70
21	2.5	3	15	2	70
22	2.5	3	20	3	70
23	2	5	15	3	70
24	2.5	4	15	3	70
25	2	3	15	3	70
26	2.5	3	10	3	60
27	3	4	10	3	50

diazinon molecules is heightened, leading to a decrease in the overall efficiency of removal [48].

The EFP reactor in our study was operated based on the optimal pH values reported in other studies [48,50]. EFP is pH-sensitive. Suitable pH values raise the •OH redox potential while maintaining the Fe^{2+} ion [50,51]. Acidic pH levels are ideal for achieving the optimum outcomes from the EFP. The pH level in our study was between 3 and 5. According to the other researches, higher pH values diminish the EFP effectiveness [48,50,51]. The production of H_2O_2 is reduced when the pH is raised. H_2O_2 decomposes fast into water and carbon dioxide in alkaline environments. The decrease in H_2O_2 formation resulted in a decrease in OH radical production and, as a result, reduced oxidant production during the EFP [48].

The possible main reactions during the Fenton process particularly for hydroxyl radical generation and reducing Fe^{2+} to Fe^{3+} are shown in Eqs. (1)–(7). It must be noted that the redox cycle of Fe^{3+}/Fe^{2+} is critical for the continuous operation of the process [52–54] and using electro Fenton process can regenerate a useful form of iron (Fe^{2+}) to continue the oxidation phenomenon (Eq. (7)) [55].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + OH^\circ + H_2O \quad (1)$$

$$OH^\circ + \text{organic pollutant} \rightarrow \text{Products} + CO_2 + H_2O \quad (2)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2{}^\circ + H^+ \quad (3)$$

$$H_2O_2 + OH^\circ \rightarrow H2O + HO_2{}^\circ \quad (4)$$

$$Fe^{2+} + HO_2{}^\circ + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (5)$$

$$Fe^{3+} + HO_2{}^\circ \rightarrow Fe^{2+} + H^+ + O_2 \quad (6)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (7)$$

The high degradation efficiencies of the studied Fenton process are in line with many other studies that used different H_2O_2 activation methods. Li et al. (2023) reported that a wide range of pollutants such as tetracycline, methylene Blue, orange G, trichloroethylene, 4-Chloro-3-methyl phenol, mordant yellow 10, acetaminophen with high concentrations (20–200 mg/L) was degraded nearby 98–100% by H_2O_2 based processes [56]. As the studied diazinon concentrations were close to the real survey of our previous study [57]and some other studies [58], we did not change the initial concentrations and continued the toxicity experiments.

In this study, we used three levels of iron 1.7, 2.55, and 3.4 mM and an invariable amount of 0.85 mM H_2O_2. The quantity of catalyst employed plays a crucial role in determining the efficacy of EFP. Theoretically, increasing the concentration of iron increases the rate of production of hydroxyl radicals and ultimately increases the efficiency of pollutant removal. In the study of Iglesias et al. (2015), the complete mineralization of pesticides in groundwater was achieved at a higher concentration of iron in a heterogeneous EFP [59]. However, excessively increasing iron causes it to react with by-products and reduces process efficiency. In the study of Pham et al. (2021), the EFP by Fe^{2+} concentration at 0.2 mM had higher efficiency than 0.05 mM and 1 mM concentrations [50].

Table 4
Lethal concentration (LC) of diazinon before and after the EFP.

Condition or parameter	LC_{10}	LC_{25}	LC_{50}	LC_{75}	LC_{90}
Without treatment	0.183	0.895	1.645	2.478	3.191
With treatment	1.504	2.216	3.008	3.800	4.529
Difference	1.321	1.321	1.321	1.322	1.321
Ratio	8.218	2.475	1.783	1.533	1.413

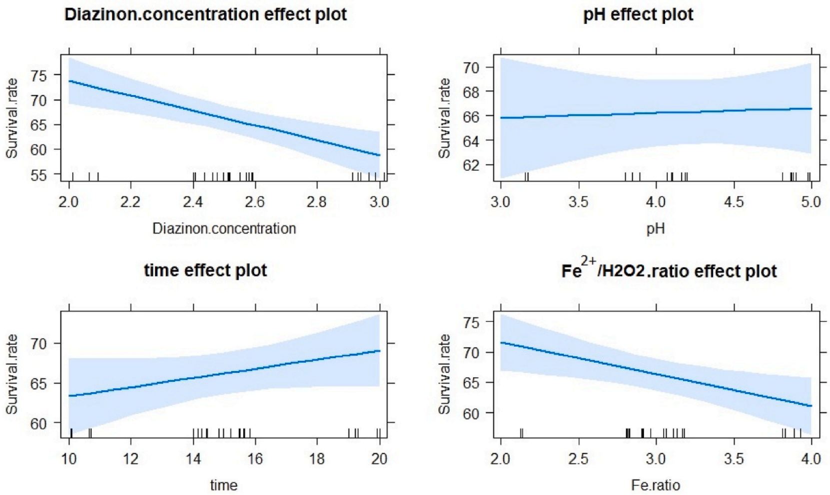

Fig. 2. The effect plots for the correlation between independent variables (diazinon concentration, pH, reaction time, and Fe^{2+}/H_2O_2 ratio with survival rate (%) of Daphnia magna.

3.2. EFP performance for toxicity reduction

Although diazinon was removed efficiently by the EFP in our study, the carbon content of the effluent and the amount of unmineralized by-products were not investigated. The formation of intermediates and by-products during the degradation of diazinon has the potential to induce toxic effects. Hence, we assessed the changes in toxicity before and after the EFP using the Daphnia magna survival test. Prior to degradation, the survival rate of Daphnia magna for un-treated diazinon was found to be 0% and was 100% for the raw water sample in the 96-h bioassay. Table 3 shows the percentage of Daphnia magna that was able to survive in the samples treated by EFP in the 96-h toxicity test.

The toxicological assessment of diazinon against Daphnia magna was conducted through a 96-h toxicity test, wherein the lethal concentration (LC) values were determined before and after subjecting the samples to the EFP. The probit model was employed for the calculation, revealing a notable reduction in the toxicity of diazinon in the treated samples, as presented in Table 4.

The effect plots and contour plots derived from Table 3 are shown in Figs. 2(a–d) and 3(a–f), respectively.

The effect plots and contour plots derived from Table 3 are shown in Figs. 2 and 3, respectively. The effect plots presented in Fig. 2 (a–d) can illustrate the correlation between the studied variables and the survival of Daphnia and the extent of the independent variable on response. According to Fig. 2(a), the initial diazinon concentration had the most significant effect on Daphnia survival and increasing the initial diazinon concentration could enhance their death rate. This may be attributed to the higher concentration of by-products produced due to the diazinon concentration. The Daphnia survival decreased from about 74% to 58% by increasing the initial diazinon concentrations. The interaction effect of initial concentrations of diazinon with the other variables (Fig. 3a–c) can also indicate a similar result as in all of these figures the survival rate of Daphnia reduced by increasing the diazinon concentration. Fig. 2 (b) illustrates that pH under the selected range (pH = 3–5) had little effect on the survival rate of Daphnia. This may be attributed to the fact that the selected range of pH was narrow and then, the impact of this important factor was not significant. In other words, although this important variable can impact the performance of Fenton-based processes, especially in acidic environments, little difference between Daphnia survival between pH 3 to 5 can demonstrate that all of the studied pHs were promising in diazinon degradation. This is in accordance with the other studies that reported the most effective range of pH close to 2–4 [60]. It should be highlighted that after the degradation experiments, the effluent pH was adjusted to a neutral level to inhibit its impact on Daphnia death.

The other important factor is reaction time. Based on Figs. 2(c), increasing the time of reaction could improve the survival rate of Daphnia magna. This may be attributed to the higher level of diazinon and its by-products degradation which resulted in lower effluent toxicity on higher reaction times (20 min) in comparison with lower times (10 min). The correlation between time and other variables (pH, diazinon concentration and Fe^{2+}/H_2O_2 ratio) are presented in Figs. 3(b, d, and f), which similarly shows the positive impact of increasing time to reduce the effluent toxicity along with the other variables.

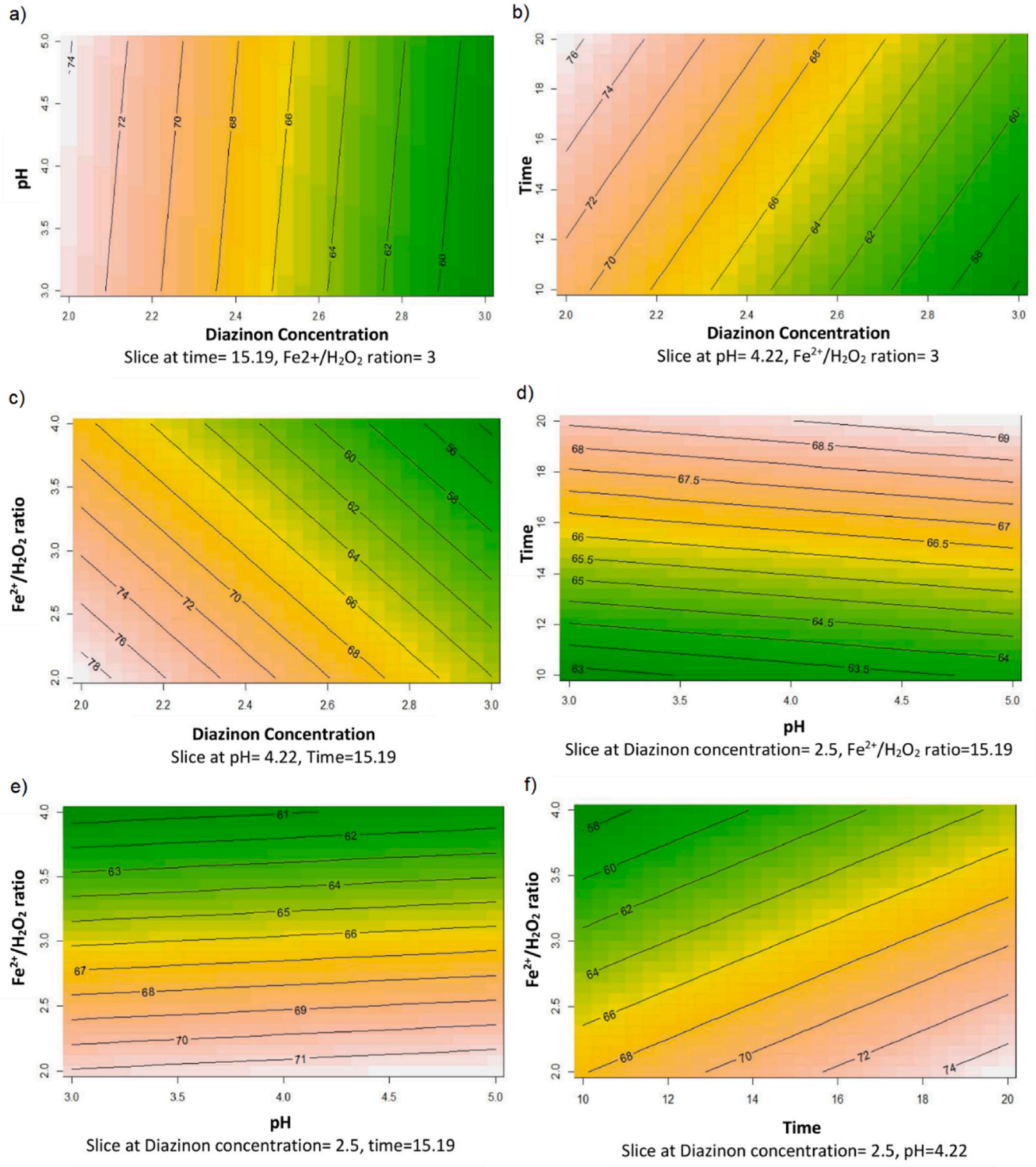

Fig. 3. The contour plots between the effect of independent variables (diazinon concentration, pH, reaction time, and Fe^{2+}/H_2O_2 ratio on the survival rate (%) of Daphnia magna.

The other remained factor is Fe^{2+}/H_2O_2 ratio (Figs. 2(d) and 3(c, e and f)). Increasing Fe^{2+}/H_2O_2 ratio had adverse effect on Daphnia survival percent. This may be attributed to the reaction that occurs between the produced hydroxyl radicals and Fe^{2+} as presented in Eq. (8) [61]. This can result in reducing the oxidation capacity of the process and subsequently, increasing the toxicity of effluent. The mentioned observation is in line with other previous studies that reported the appropriate amount of catalyst and H_2O_2 concentration are critical factors for improving the performance of the Fenton-based processes [62]. Whereas the acceptable performance of a Fenton-based process can be achieved by Fe^{2+} addition, Fe^{3+} is unavoidably produced in the process. It must be noted that Fe^{3+} has a considerable tendency for hydrolysis and precipitation [63]. Additionally, high concentrations of Fe^{2+} or Fe^{3+} may have adverse effects on Daphnia survival due to their possible toxicity.

$$Fe^{2+} + OH^{\circ} \rightarrow Fe^{3+} + OH^{-} \tag{8}$$

The present results demonstrated the lower toxicity of treated samples to Daphnia magna. However, Daphnia magna exhibited persistent toxic responses when exposed to diazinon, even after undergoing the EFP treatment. It is plausible that the treated samples harboured intermediate compounds resulting from the EFP, which could have played a role in exerting toxic effects on Daphnia magna. Similar to our results, in the studies of Gharagazloo et al. (2017) and Pham et al. (2021), daphnia magna immobilization was reported

Table 5
The coefficients of the COX regression model (with and without using process) during 96 h of survey.

-2 Log Likelihood Block 1	−2 Log Likelihood Block 0	Exp (B)	Sig.	df	Wald	SE	Regression constant	Levels of independent varaibles	Variable
2973.539	2991.914	0.588	0.0000	1	17.393	0.127	−0.531	With/Without process	Method

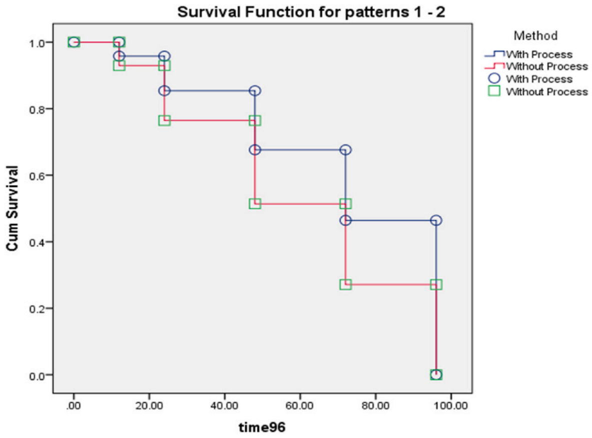

Fig. 4. The survival function for Daphnia magna (COX regression) during time with and without using the process.

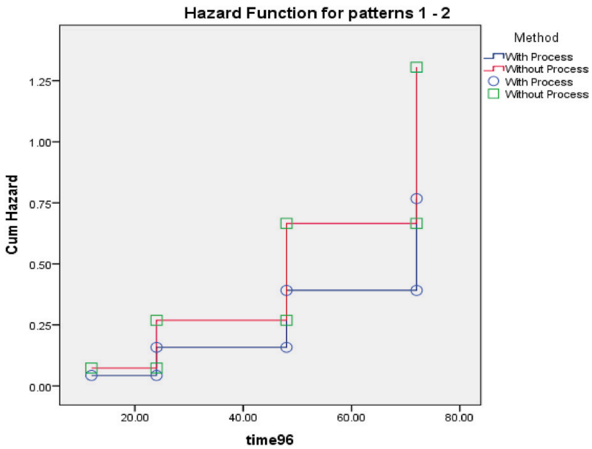

Fig. 5. The hazard function for Daphnia magna (COX regression) during time with and without using the process.

due to long-time exposure to diazinon treated by an electro-chemical process [50,64].

The coefficients of the COX regression model (with and without using process) are shown in Table 5. The survival function and hazard function for Daphnia magna with and without the process are shown in Figs. 4–7 which are in line with the results of Figs. 2 and 3. as highlighted before. The coefficients of COX's regression model for diazinon concentration (2, 2.5, and 3 mg/L) during 96 h of survey time are presented in Table 6.

Regarding the provided results in Tables 5 and 6 as well as COX regressions (Figs. 5–7), the application of the process was statistically significant in the surveillance of the Daphnia Magna (P-value$<$0.001). The death risks of Daphnia magna with and without the EFP treatment were (Exp(B) = 0.588) and (B = −0.531), respectively. These results are in accordance with Wang and Shih's (2015) study, that reported a sono-Fenton process has the potential to reduce the toxicity of diazinon with 50 mg/L concentration after 60 min of reaction time on cell viability. It was measured that the cell viability of untreated samples and deionized water (blank test) were close to 48.7% and 100%, respectively. After the diazinon treatment by the sono-Fenton process, the cell viability enhanced from 53.9% (experimental conditions: Fe^{2+} = 10 mg/L and H_2O_2 = 50 mg/L) to 85.0% (experimental conditions: Fe^{2+} = 20 mg/L and H_2O_2 = 150 mg/L), which demonstrate that the higher concentrations of Fenton's reagent could improve the target pollutant degradation and reduce its correlated toxicity [65].

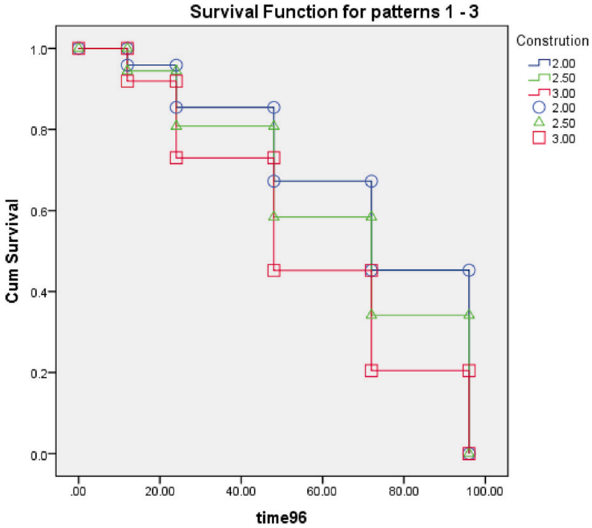

Fig. 6. The survival function for Daphnia magna (COX regression) with different diazinon concentration in the EFP.

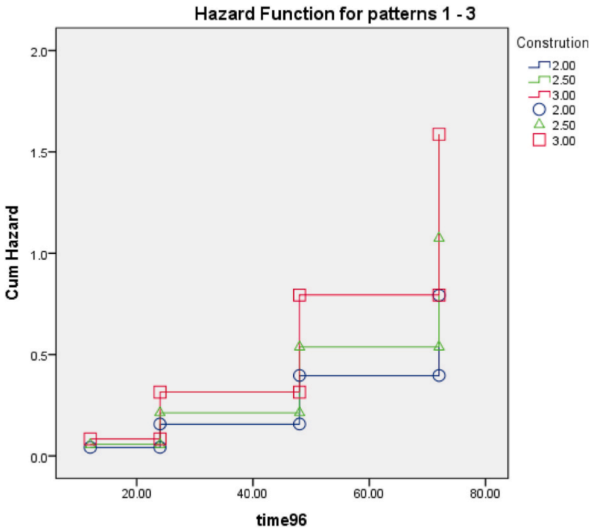

Fig. 7. The hazard function for Daphnia magna (COX regression) with different diazinon concentrations in the EFP.

Table 6
The coefficients of COX's regression model for diazinon concentration (2, 2.5, and 3 mg/L) during 96 h of survey time.

-2 Log Likelihood Block 1	−2 Log Likelihood Block 0	Exp (B)	Sig.	df	Wald	SE	Regression coefficient	Levels of independent variables	Variable
2957.65	2991.914	–	0.000	2	16.106	–	–	2	Diazinon concentration (2, 2.5, and 3 mg/L)
		0.5	0.000	1	15.029	0.179	−0.694	2.5	
		0.677	0.004	1	8.181	0.136	−0.39	3	

4. Conclusion

In the present study, the studied EFP equipped with stainless steel electrodes could effectively remediate diazinon from spiked actual river water. However, the effluent still exhibited toxicity for Daphnia magna, which indicated the presence of unknown toxic compounds in the treated samples. The performance of the process was promising as all the effluent concentrations of diazinon were below the limit of detection (0.05 μg/mL). Further studies are required to evaluate the produced active radicals and their contribution to diazinon oxidation, determine the mineralization of diazinon and propose the degradation pathway, and formation of byproducts after the EFP. Moreover, it is suggested that removing the remained iron (Fe^{2+} and Fe^{3+}) to be evaluated in future studies.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Davarkhah Rabbani: Supervision, Project administration, Funding acquisition, Conceptualization. **Rouhullah Dehghani:** Validation, Resources, Project administration. **Hossein Akbari:** Software, Formal analysis, Data curation, Conceptualization. **Hasan Rahmani:** Software, Data curation, Conceptualization. **Ehsan Ahmadi:** Resources, Conceptualization. **Amin Bagheri:** Resources, Conceptualization. **Saeid Allahi:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:Saeid Allahi reports financial support was provided by Kashan University of Medical Sciences. Saeid Allahi reports a relationship with Kashan University of Medical Sciences that includes: board membership and employment. None.

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