Electrochemical removal of diazinon insecticide in aqueous solution by Pb/β-PbO_2 anode. Effect of parameters and optimization using response surface methodology (RSM)

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/WER.1292

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Article type : Research Article

Practitioner Points:

1. Electrochemical degradation of diazinon insecticide using Pb/β-PbO_2 anode.
2. Effect of operating parameters on electrodegradation diazinon insecticide in electrochemical processe using Pb/β-PbO_2 anode.
3. Biodegradability study of diazinon insecticide electrodegradation using Pb/β-PbO_2 anode.
4. Optimization operating parameters using central composite design (CCD).

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Abstract

Diazinon is one of the most extensively used organophosphorus pesticides that is used against a variety of agricultural pests and disease vectors and is resistant to biodegradation; its release into the environment is a severe environmental concern due to their widespread use. The aim of this study was to investigate the electrochemical removal of diazinon insecticides from aqueous solutions and to optimize the process by response surface methodology (RSM). This is an experimental study that was performed on a laboratory scale and in a batch mood. SEM, EDX and XRD analyses were performed to accurately evaluate and characterize the coated electrode. The central composite design (CCD) was used to investigate the influence of pH, electrolysis

time, diazinon concentration and current density, as well as the effect of their interaction on the removal of diazinon during the electrochemical process. The results showed that by increasing electrolysis time and current density and decreasing diazinon pH and concentration, diazinon removal efficiency increased. According to the results, Na_2SO_4 was selected as the supporting electrolyte with the highest degradation efficiency (97.88%) compared to the other two compounds (NaCl and $NaNO_3$). The linear regression coefficient (R^2) between experiments and different response values in the model was 0.99. The results showed that the amount of AOS in the effluent of the three-dimensional electrochemical process was increased from 0.06 to 1.22 and the COD/TOC ratio decreased from 2.62 to 1.85, respectively; this indicates the biodegradability of the diazinon insecticide through the electrochemical system. The removal efficiency of COD and TOC in optimum condition was 85.78% and 79.86%, respectively. In general, the electrochemical process using Pb/β-PbO_2 electrode compared to other methods can be used as a suitable and reliable method for the treatment of effluents containing chemical toxins such as diazinon.

Keywords: Electrochemical process, diazinon insecticide, aqueous media, response surface methodology.

Introduction

Pesticide toxins used in agriculture include a variety of organochlorine, organophosphorus, carbamates, and pyritoids. Organochlorine pesticides are less used because of creating the pesticide resistance, but organophosphorus pesticides and carbamates pesticides have the highest consumption against the plant pests. Organophosphorus compounds are the largest and most diverse pesticide group available, which includes about 40% of the world's registered pesticides (Jonidi-Jafari *et al.*, 2017; Samarghandi *et al.*, 2017; Samarghandi *et al.*, 2019). Diazinon is one of the most widely used organophosphorus pesticides for agricultural pest control (Jonidi-Jafari *et al.*, 2017). Diazinon is a moderately dangerous insecticide according to the WHO classification (Slotkin *et al.*, 2019). This toxin, unlike chlorine toxins, does not accumulate in the human body and breaks down faster(Samarghandi *et al.*, 2017). Therefore, one of the environmental concerns is the introduction of diazinon toxin into surface water and groundwater aquifers. This toxin inhibits acetylcholinesterase activity and possibly damages the sex cells and the reproductive tract (Pordel *et al.*, 2019). It has also been reported that diazinon has a

destructive effect on the immune system (Immunotoxic), cells (Cytotoxic), and women (Genotoxic)(Zhang *et al.*, 2010). Thus, it is important to remove these compounds from the environment, especially potable water. The maximum permissible limit announced by the US Environmental Protection Agency (EPA) for most organophosphorus pesticides in drinking water is less than 30 µg/L(Amani *et al.*, 2017). For removal of diazinon, different methods, e.g., degradation with ultrasonic wave (Wang and Shih, 2016; Zhang *et al.*, 2010), biodegradation (Azizi *et al.*, 2019; Cycoń *et al.*, 2009), ozonation (Ayoubi-Feiz *et al.*, 2019; Wu *et al.*, 2009), adsorption (Dehghani *et al.*, 2019), electrochemical method (Lazarević-Pašti *et al.*, 2013) and photocatalytic degradation (Maleki *et al.*, 2019; Mirmasoomi *et al.*, 2017) have been used.

Each of the above methods has limitations, including the need for integration of several methods for the complete treatment of pesticides containing wastewater, the need for chemicals and the lack of complete treatment (Azizi *et al.*, 2019). Researchers are always looking for suitable and environmentally friendly ways to completely remove the pollutants without creating secondary pollutants.

Among the new methods, the electrochemical methods have received much attention for removal of pesticide. The electrochemical method, known as green chemistry (Ansari and Nematollahi, 2018; Lazarević-Pašti *et al.*, 2013), is particularly popular. In the electrochemical oxidation processes, the electron is the major reagent for oxidation of the pollutant, instead of the toxic reagents; therefore they are considered as environmentally friendly emergent techniques for water treatment (Susree *et al.*, 2013; Zarei *et al.*, 2018). The degradation process occurs by the direct reaction of organics at anode surface through charge transfer but, at high current, the action of oxidizing the agents produced at the anode mainly manages the favorable performance of the process (Asaithambi *et al.*, 2012; Susree *et al.*, 2013). During the electrochemical oxidation, the organics are destroyed by physisorbed M(^{o}OH) radicals which are formed by the water oxidation (Afsharnia *et al.*, 2018; Asaithambi *et al.*, 2012; Susree *et al.*, 2013). The advantages of electrochemical processes (ECPs) include environmental compatibility, versatility, ease of automation, and high energy efficiency, simple control of the reaction rate by adjusting the electrical current and Process safety regarding the operation in mild conditions (Ghanbari and Moradi, 2016; Kapałka *et al.*, 2010). Despite extensive studies on the application of various electrochemical processes in wastewater treatment, the application of these studies has been limited due to the use of expensive electrodes such as platinum, titanium, and diamond alloys,

etc. The use of PbO_2 anodes due to their high electrical conductivity and oxidation power and low cost seems to be interesting for practical applications (Dargahi *et al.*, 2019). Dargahi et al. conducted a study for the electrocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide by lead dioxide electrodes and reported that PbO_2 electrodes had good efficiency in the degradation of the studied herbicide (Dargahi *et al.*, 2019). In another study, Ansari et al. implemented a study entitled "comprehensive study on the electrocatalytic degradation, electrochemical behavior and degradation mechanism of malachite green using electrodeposited nanostructured β-PbO2 electrodes" and identified that different PbO2 electrodes have good dye degradation efficiency (Ansari and Nematollahi, 2018).

Therefore, in the present study, the electrochemical process using Pb/β-PbO2 anode was inspected for the degradation of diazinon in aqueous solution. The experiments of the present study were designed and analyzed using the central composite design (CCD) along with response surface methodology (RSM), which can represent accurate statistical tools for the design and optimization of the studied process. Investigation of the effect of parameters including current density (*j*), electrolysis time, initial diazinon concentration and pH of solution on the electrodegradation of diazinon was also performed. Besides, the Average Oxidation State (AOS), COD/TOC ratio for removal of diazinon were evaluated.

Material and methods:

Materials

The chemicals used in this were included Diazinon, (the chemical formula of $C_{12}H_{21}N_2O_3PS$ and the purity of 98%), Lead nitrate ($Pb(NO_3)_2$, >99% purity) and nitric acid (HNO_3, 95% purity) and Sodium Sulfate (Na_2SO_4, 99% purity) which were purchased from Sigma Aldrich (St. Louis, MO, USA and NaOH and HCl which purchased from Merck CO (Darmstadt, Germany). The characteristics of diazinon were summarized in table S1. The adjustment of the pH of the solution was done by 1N HCl and NaOH.

Analysis procedures

The electrical current was supplied by the direct current (DC) power supply (DAZHENG PS-305D, China) with the electric current of 0-5A and voltage of 0-40 V.

A UV-Vis spectrophotometer (DR 5000, HACH, USA) was employed to determine the residues of diazinon in the solution, after electrolysis.

Moreover, the assessment of the mineralization of the diazinon in the solution was carried out through the estimation of Chemical Oxygen Demand (COD) by COD ampoules (HACH Chemical) using a spectrophotometer (DR 5000, HACH, USA). The total organic carbon (TOC) values of the diazinon insecticide were determined by the TOC analyzer (Elementar, Germany).

Electrochemical system design

This study was an experimental study in which the electrochemical degradation of diazinon insecticide in a Plexiglass reactor with a useful volume of 100 cc was investigated. The schematic of the reactor is shown in Fig. S1. In this reactor, lead dioxide electrode coated on the lead substrate (Pb/β-PbO2) with dimensions of 65 mm × 30 mm × 5 mm as anode and stainless steel 316 with dimensions of 65 × 30 × 1 mm as the cathode was used. The set of electrodes consisted of a cathode and two anodes with a distance of 10 mm. The electrodes were vertically and parallelly inserted inside the reactor. In order to provide the desired potential, three different compounds of sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and sodium nitrate ($NaNO_3$) were used as supporting electrolyte.

During the operation of the process, monitoring of the degradation of diazinon, formation of the intermediates, and removal of COD was also carried out.

After collecting the samples at predetermined time intervals, the sample was filtrated by the 0.45 µm membrane filter, and the concentration of diazinon was measured using a UV- Vis spectrophotometer at λ_{max}=247 nm. The accuracy of the values obtained by UV- Vis spectrophotometer was tested by employing an HPLC device.

The estimation of the COD and TOC evolution was performed at the beginning of the process and the end of the degradation. Moreover, the determination of the effect of the electrochemical degradation process in biodegradability of the solution contaminated by diazinon pesticide was carried out using the average oxidation state (AOS) and carbon oxidation state (COS). The calculation of AOS and COS are done by equations 1 and 2 (Jaafarzadeh *et al.*, 2018b):

$$\mathrm{AOS} = 4 - 1.5\frac{\mathrm{COD}}{\mathrm{TOC}} \qquad (1)$$

$$COS = 4 - 1.5\frac{COD}{TOC_i} \qquad (2)$$

Where TOC is reported in moles of C per liter, and COD is expressed in mg/L of O_2 per liter.

Preparation of Pb/β-PbO_2 anode

The preparation of lead substrate (dimensions of 65 mm × 30 mm × 5 mm) was performed to ensure good adhesion of PbO_2 prior to coating. In order to increase the adhesion of PbO_2, the surface of lead electrodes was mechanically polished using different grades of sandpaper. Then, to eliminate fine particles or any other particles on the metal surface and to completely clean the electrode surface, the lead substrate was immersed in the hot H_2SO_4 solution at 65°C for 30 min. The formation of PbO_2 was done out by electrochemical oxidation of lead in H_2SO_4 solution (1M) at 25°C through applying anodic current density of 25 mA/cm^2 at 90 min (Dargahi et al, 2018; Dargahi *et al.*, 2019).

Mixing and homogenization of the samples were done by a magnetic stirrer at 450 rpm. All batch experiments were repeated two times at room temperature.

Specification of the coated electrode

The surface morphology of PbO_2, which is covered on the lead substrate, was investigated by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy. X-ray diffraction (XRD) was also used to determine the characteristics of the surface composition of the coated electrodes. All experiments were performed at room temperature

Experimental design using CCD

Response surface methodology (RSM) is a set of statistical techniques employed for the optimization of the processes in which the response is affected by a number of variables. This method generates a polynomial using the samples and data obtained and explains the relationships between these data. Recently, for analyzing and generating polynomials in this method, different statistical models such as central composite design (CCD) and BOX Benkhan are used. In the present study, the statistical design of experiments and the analysis of data in the

electrochemical system were performed using Central Composite Design (CCD) by Design Expert statistical software (version 10). Designing experiments with the CCD approach is recognized as the strongest and most effective subgroup of the RSM response procedure. This approach has also been reported as a very effective method in modeling and optimizing wastewater treatment processes (Almasi *et al.*, 2016; Dargahi *et al.*, 2017; Sarafrazi *et al.*, 2019; Sharma *et al.*, 2019). According to Table 1, the domain and levels of variables (current density, electrolysis time, diazinon concentration and pH of solution) were investigated for diazinon removal at five levels with codes −α, −1, 0, +1, and + α. Based on CCD, 30 runs were designed. The laboratory conditions used in this study are shown in Table 1. Data obtained from the responses of the RSM model were calculated using analysis of variance (ANOVA). Each of the response variables for the desired response (diazinon elimination) was presented as a function of the independent variables in the form of the polynomial regression model of Equation 3 ():

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{i=i+1}^{k} \beta_{ij} X_i X_j \qquad (3)$$

Where Y is the response variable of each factor level (diazinon removal efficiency), β_0 is the intercept, β is the regression coefficient calculated from the values obtained from *Y*. The X_iX_j and X_i^2 segments, respectively, are interactive and quadratic interaction terms (Sharma *et al.*, 2019; Shokoohi *et al.*, 2017).

The fitting quality of the multi-nominal equation was evaluated using the obtained coefficients R^2 and Adjusted-R^2 values to measure the fit of the model. $P < 0.05$ was considered as suitable significant.

To give greater insight into the CCD results, Pareto analysis was used to calculate the percentage effect of each independent variable (P_i) on the removal of diazinon (Eq. 4)(Asadzadeh *et al.*, 2018):

$$P_i = \left(\frac{b_i^2}{\sum b_i^2}\right) \times 100 \qquad i \neq 0 \qquad (4)$$

Results and Discussion

Characterization of Pb/β-PbO_2 electrode

The scanning electron microscopy (SEM) technique was used to evaluate the microstructures of the anodic layer of PbO_2-coated by electrochemical coating on the lead substrate, and their

images were presented at different magnifications (2 and 20 μm). Figure S2 shows that β-PbO_2 is formed with a regular structure at the surface of lead electrodes and has very suitable stability.

Elemental analysis of the Pb/β-PbO_2 electrode was performed using energy dispersive X-ray (EDX) spectroscopy, and the results were presented in Figure S3. As the results show, the weight percent of oxygen (O) and Lead (Pb) as the main elements in the β-PbO_2 coating were 18.9% and 82.1% for lead electrode, respectively.

X-ray diffraction pattern (XRD) was used to determine the phases and crystallinity of PbO_2 and the purity of the substrate coated. Figure S4 shows the XRD of the Pb/β-PbO_2 electrode. The XRD results show the tetragonal structure of β-PbO_2. According to the results, the main peaks observed at 2θ for the coated electrode were 25.4°, 32.0°, 36.2°, 49.1°, and 65.5°. The crystallographic plates obtained for these peaks were also (110), (101), (200), (211) and (220), respectively.

Determination of the type of supporting electrolyte

The supporting electrolyte is one of the most important parameters which influences the electrochemical degradation process. Because the presence of supporting electrolyte is one of the factors affecting the current applied to the electrochemical system. For this reason, its type and concentration must be selected in such a way, which can impose reasonable voltage on the process. In this study, three different compounds including sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and sodium nitrate ($NaNO_3$), were employed as supporting electrolytes for electrochemical degradation of diazinon. The results showed that Na_2SO_4 had the highest degradation efficiency of diazinon (97.88%) compared to the two other electrolyte compounds (NaCl and $NaNO_3$) (Fig. 1). The Na_2SO_4 as supporting electrolyte has a two-way effect. First, it increases the electrical conductivity and consequently the current density in the solution. The second role is the formation of oxidizing species such as hydroxyl radicals through the electrolysis of water or by the semi-chain reactions (Domínguez *et al.*, 2010; Samarghandi *et al.*, 2019). Actually, the supporting electrolyte, by a direct effect on both the current density and the type of electrode material, plays a critical role in the decomposition of pollutants in electrochemical processes. In a study conducted by Jafarzadeh et al. (2018) to degrade 2,4-D herbicides from aqueous solutions by EO/Oxone process, the results showed that, among the three supporting electrolytes investigated (Na_2SO_4, NaCl and $NaNO_3$), the Na_2SO_4 was the best supporting electrolyte (Jaafarzadeh *et al.*, 2018a).

Statistical analysis of the process

Central Composite Design (CCD) was employed to find the relationship between process responses and variables. Equation 1 shows the models with the coded factors; according to the calculations, the diazinon values obtained from the experiments were proportional to the quadratic model. Therefore, the model was studied and analyzed, as the model selected in the present study.

In equations (5), the positive effect of a factor is indicative of this fact that the factor level increase has a direct effect on removal efficiency and leads to its increase, but the negative effect of the factor indicates that there is no increase in efficiency by enhancing the factor level increases. The coefficients of the factors in the above equation (5) reveal the importance of each parameter so that the pH had the highest importance in the removal of diazinon. Figure 2 shows the Pareto graphic analysis. Considering the results of Fig. 2, it is proposed that, among the variables, pH (A) variable was the most important factor in diazinon degradation with 30.4%. The percentage effects of concentration (D), electrolysis time (B) and current density (C) in the removal of diazinon were found to be 29.49%, 13.36%, and 9.33%, respectively. In other literature, the pH of the solution has been introduced as an effective factor in the degradation of organic and inorganic compounds formed in the oxidation process (Ansari and Nematollahi, 2020; Samarghandi *et al.*, 2019).

$$\text{Diazinon degradation (\%)} = +81.31 - 8.01\,A + 3.52\,B + 2.46\,C - 7.77\,D + 0.81\,AB + 0.41\,AC - 0.80\,AD - 0.36\,BC - 0.18\,BD + 0.75\,CD - 0.40\,A^2 - 0.02\,B^2 - 0.31\,C^2 - 0.52\,D^2 \quad (5)$$

Table 2 also represents the results of ANOVA for the desired response (diazinon degradation). ANOVA analysis was used to control the significance and fit of the model. The results of ANOVA analysis with F-values and P-values of each model expression for the electrode investigated are presented in Table 2. In the statistical analysis of ANOVA, the significant level of P-value has shown to determine the significance of the model in each response. P values (0.0001) of diazinon insecticide degradation indicate that the sentences in the models discussed are significant ($P < 0.05$). The linear regression coefficient (R^2) between experiments and different response values in the model was 0.99. However, the value of R^2 must be consistent (close to) R^2 adj. When these two values are very different, insignificant expressions may be involved in the model. In the present study, the value of R^2 adj (0.9858) is very close to R^2.

Accuracy measurement is an indication for the determination of the error rate in the experiments, and a ratio greater than 4 is desirable. The accuracy and precision values (46.96) in the experiments performed in this study were significantly greater than 4. Also, the standard deviation values (1.31) were low.

In the case of the normality of the data, as shown in Fig. 3a, it is clear that most data have no much deviation from the straight line, and this is indicative of a normal distribution of data. In the graph, the constancy of variance between samples (Figure 3b Residuals variations) does not follow a specific trend, which indicates the constancy of variances.

In the represented externally studentized residuals versus the run (Fig. 3c), any observable trend demonstrates the independence of the residuals to the runs.

Thus, it can be concluded that the Quadratic model presented in Table 2 is meaningful and sufficient. The effect of each of the studied factors (pH, current density, electrolysis time and initial concentration) on diazinon insecticide removal is shown in Figure 2 (d). According to Fig. 2 (d), the pH and concentration parameters have an indirect relationship with the removal efficiency and the current density and electrolysis time parameters have a direct relationship with the removal efficiency.

Optimization of Process and Validation of Model

Graphical optimization is a multilayer map to show the areas in which the response values that are considered as the criterion are obtained. The optimal region is identified on the basis of a variable (diazinon insecticide degradation), which is considered as the criterion for the Pb/β-PbO_2 electrode. Figure S5 shows graphical optimization at electrolysis time and pH. This figure represents the different values of the response (dark area) in the variable space. The yellow areas represent the regions that provide the desired response values at 120 min electrolysis. In order to verify the accuracy of the model, a point was selected between the optimal region (conditions indicated by the flag in Fig. S5), and the electrochemical process was operated based on it to compare the actual values with the predicted values (Table 3). The accuracy of the optimal conditions was checked by DES using standard deviation for each response, and the actual values were obtained to be very close to the predicted model values. Using the software, 92.87% degradation of diazinon was optimized through calculating the optimized model factors of pH 6.5, diazinon concentration 60.0 mg/L, electrolysis time 82.0 min and current density 9.6 mA/cm^2 for used Pb/β-PbO_2 anode.

In this study, in order to determine the biodegradability of diazinon in electrochemical process effluent effluent, AOS, COS and COD/TOC ratio parameters were investigated under optimum laboratory conditions (TOC_0 = 41.26 mg/L, COD_0 = 108.33 mg/L, initial diazinon concentration= 60 mg/L, pH=6.5, electrolysis time = 82 min and current density = 9.6 mA/cm2). The results showed that the amount of AOS and COS in the effluent of the electrochemical process was increased from 0.06 to 1.22 and 0.06 to 3.44, respectively. the COD/TOC ratio was decreased from 2.62 to 1.85, respectively; this reveals the biodegradability of the diazinon insecticide by the electrochemical system. The removal efficiency of COD and TOC in optimum condition was 85.78% and 79.86%, respectively.

The effect of parameters in degradation of diazinon

In order to determine the efficiency of the electrochemical process with the Pb/β-PbO_2 electrode, the efficiency of diazinon removal from aqueous solutions was considered as a response for the CCD method.

Three-dimensional (3D) and contour plots were employed for assessment of the effect of interactions on the efficiency of the electrodegradation process. These mentioned plots are utilized as a graphical demonstration of regression equations for estimation of the optimality of variables and better recognition of the interactions between variables within the scope of the study. The results of the interaction between the 4 independent variables and the response are represented in Fig. 4. For the interaction of BA, at different electrolysis time, the removal efficiency of diazinon was developed by a decrease in pH values from 10.0 to 4.0. The plots also accentuated the great removal of diazinon in acidic conditions (pH= 4) and high electrolysis time (120 min) (Fig 4a). Considering the previous studies, the electrochemical process efficiency is obtained in the acidic pH values (Dargahi *et al.*, 2019). When the solution has a low pH, the best situation for increasing the production of $^{\circ}OH$ radicals exists. In addition, in the acidic condition, these radicals have greater potential for degradation of the pollutants, which is led to increasing the oxidation efficiency. This is consistent with the results of the Dargahi et al. (2018) study; In their study, the removal efficiency of the pollutant had an indirect relationship with pH, so that by decreasing the pH and increasing the electrolysis time, the removal efficiency of the pollutant increased (Daraghi et al, 2018). For interactions between current density and pH (AC), the removal efficiency of diazinon revealed an increasing trend by increasing current density (Fig. 4b). So that, the highest diazinon removal efficiency was obtained at the highest current density.

The reason for the increase in efficiency can be attributed to the greater production of hydroxyl radicals (Ansari and Nematollahi, 2020).

For the interaction between pH and diazinon concentration (AD), the removal efficiency of diazinon at different concentrations of diazinon was increased by decreasing diazinon concentration from 150 to 30 mg/L (Fig. 4c). The decrease in the diazinon degradation efficiency with increasing concentration may be due to the fact that there are same conditions for all samples, and as a result, the amount of hydroxyl radicals produced is equal at each initial concentration of diazinon, and therefore at low concentrations of diazinon, the hydroxyl radicals are easily capable to remove a high percentage of the contaminants present in the reaction chamber; however when the concentration of the contaminant increases, the hydroxyl ions produced are not sufficient for further degradation of the contaminant.

The results related to the interaction between current density and electrolysis time (BC) revealed that, by increasing the current density and electrolysis time, the efficiency was enhanced (Fig. 4d). For the interaction between diazinon concentration and electrolysis time (BD), an increase in efficiency was observed by decreasing diazinon concentration and increasing electrolysis time (Fig. 4e). For the interaction between diazinon concentration and current density (DC), decreasing diazinon concentration and increasing current density leads to enhancing the efficiency (Fig. 4f).

Diazinon insecticide degradation mechanism by Pb/β-PbO_2 electrode

During the oxidative degradation of pollutants by PbO_2 electrodes, they are mostly mineralized on the surface of the electrode by the electro-generated physisorbed $HO^{\bullet}$. The initial reaction in both active and non-active of MOx anodes is the generation of adsorbed hydroxyl radical MOx(HO•) via the oxidation of water molecules (Eq. 6) (Brillas and Martínez-Huitle, 2015; Dai *et al.*, 2016; Martinez-Huitle *et al.*, 2015).

$$MOx + H2O \rightarrow MOx(HO\bullet) + H+ + e- \quad (6)$$

In the next step, the electrochemically generated MOx(HO•) that is one of the strongest oxidant mineralized organic matter (Eq. 7) (Brillas and Martínez-Huitle, 2015; Dai *et al.*, 2016; Martinez-Huitle *et al.*, 2015). The produced MOx(HO•) can also generate O_2 gas (Eq. 8). This reaction competes with the reaction represented in Eq. 7.

$$R + MOx(HO\bullet) \rightarrow mCO_2 + nH2O + xH+ + ye- \quad (7)$$

$$2\ MOx(HO\bullet) \rightarrow 2\ MOx + O_2 + 2H+ + 2e- \quad (8)$$

The value of oxygen evolution over-potential sturdily influences the extent of oxygen evolution reaction, so that, the oxygen evolution reaction is dominant for the electrodes with low oxygen evolution over-potential. In spite of this, the oxygen evolution is difficult, reaction (7) occurs faster than reaction (8) and efficiency of the mineralization reaction is improved when the oxygen evolution over-potential is higher (Brillas and Martínez-Huitle, 2015; Dai *et al.*, 2016; Martinez-Huitle *et al.*, 2015).

The detection and identification of the intermediates and products in the electrochemical degradation of diazinon using Pb/β-PbO2 anode was carried out through conducting a series of experiments at optimal conditions by Liquid chromatography-mass spectrometry (LC-MS) (Shimadzu LCMS 2010 A). based on this, the main products obtained from degradation of degradation were [diazinon], [2-Hydroxydiazinon], [Hydroxydiazinon], [O,O-diethyl O-(4-ethylpyrimidin-2-yl) phosphorothioate], [Diethyl thiophosphoric acid], [2-Isopropyl-6-methyl-4-pyrimidinol], [Pyrimidin-2-yl hydrogen phosphonite] and [Ethane-1,2-diol].

Comparison of degradation of diazinon using other methods

In this section, the results obtained in present study were compared with the results of the other studies conducted for removal of diazinon (Table 4); based on our review, numerous methods such as photocatalytic degradation Process, nano photocatalytic process process, adsorption process, sonophotocatalytic process and biological Process have been studied for the removal of diazinon insecticide (Azizi *et al.*, 2019; Darbandi *et al.*, 2016; Farzadkia and Esrafily, 2014; Nikzad *et al.*, 2019). In Table 4, various factors including initial pH, reaction time, initial catalyst, initial diazinon concentration, diazinon and COD removal efficiency have been considered for comparison between the our results and the previous studies; the results of this comparison were indicative of obtaining comparatively better results in this study compared to the results of the mentioned studies. Moreover, the acidic pH, the lowest concentration of diazinon and the highest reaction time were introduced as the best conditions to achieve the highest removal efficiency by all of the methods mentioned.

Conclusion

This study appraised the capability of the electrochemical process using Pb/β-PbO2 anode in the removal of diazinon insecticide. In order to analyze the resulting data, response surface

methodology (RSM) was used to demonstrate the effect of operating variables and interaction effect on the response. The effect of main parameters such as solution pH, electrolysis time, diazinon concentration and current density on removal efficiency of diazinon were investigated. The results were indicative of the high dependency of the removal efficiency on the main parameters and the highest removal efficiency of diazinon was acquired by reducing pH and initial concentration of diazinon and increasing the current density and electrolysis time.

The removal efficiencies of COD and TOC in optimum condition were 85.78% and 79.86%, respectively. In general, it can be concluded that the electrochemical process with Pb/β-PbO_2 electrode has high efficiency for efficient and rapid removal of diazinon and can be used to remove toxic pollutants in various chemical industries.

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Table 1. Experimental ranges and levels of the independent variables, and results of Central composite design (CCD) of experiment along with actual and predicted values of Diazinon

Experimental factors and their levels

Independent Variables	**Symbol**	**Unit**	**-α**	**-1**	**0**	**+1**	**+α**
pH	A	-	4	5.5	7	8.5	10
Electrolysis time Initial	B	mg/L	40	60	80	100	120
Current density	C	min	2	4	6	8	10
diazinon concentration	D	mA/cm^2	30	60	90	120	150

Results of CCD

Run	**A:pH**	**B: time (min)**	**C: *j* (mA/cm^2)**	**D: C_0 (mg/L)**	**Diazinon degradation (%)**	
					Actual	**Predicted**
1	8.5	60	4	120	56.65	55.33
2	7	80	2	90	73.87	75.16
3	5.5	60	8	60	93.54	93.80
4	7	80	10	90	85.45	84.99
5	8.5	100	8	60	86.77	86.88
6	8.5	60	8	60	78.57	78.56
7	8.5	100	8	120	70.85	70.87
8	7	80	6	90	82.65	81.31
9	8.5	60	8	120	63.65	63.28
10	8.5	100	4	60	85.67	83.39
11	7	120	6	90	87.45	88.26
12	8.5	60	4	60	72.66	73.63
13	7	80	6	150	63.36	63.69
14	7	80	6	90	79.77	81.31
15	5.5	100	4	60	95.71	96.97
16	10	80	6	90	62.95	63.67
17	8.5	100	4	120	63.73	64.36
18	7	80	6	90	81.26	81.31
19	7	80	6	30	94.25	94.76
20	7	80	6	90	80.7	81.31
21	7	80	6	90	81.34	81.31
22	7	80	6	90	82.16	81.31

23	5.5	60	4	120	74.63	75.41
24	5.5	60	4	60	92.21	90.47
25	5.5	60	8	120	81.19	81.75
26	5.5	100	8	60	99.25	98.85
27	5.5	100	8	120	86.16	86.08
28	5.5	100	4	120	82.88	81.18
29	7	40	6	90	74.14	74.17
30	4	80	6	90	95.61	95.72

Table 2. Statistical models obtained from the analysis of variance for response surface reduced quadratic model for optimization of diazinon degradation.

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	3479.71	14	248.55	144.70	< 0.0001	significant
A-pH	1541.44	1	1541.44	897.42	< 0.0001	significant
B-Time	297.79	1	297.79	173.37	< 0.0001	significant
C-j	145.04	1	145.04	84.44	< 0.0001	significant
D-Concentration	1448.02	1	1448.02	843.02	< 0.0001	significant
AB	10.66	1	10.66	6.21	0.0249	significant
AC	2.58	1	2.58	1.50	0.2396	not significant
AD	10.47	1	10.47	6.09	0.0261	significant
BC	2.07	1	2.07	1.21	0.2892	not significant
BD	0.5329	1	0.5329	0.3103	0.5857	not significant
CD	9.12	1	9.12	5.31	0.0359	significant
A^2	4.49	1	4.49	2.61	0.1268	not significant
B^2	0.0183	1	0.0183	0.0107	0.9191	not significant
C^2	2.63	1	2.63	1.53	0.2351	not significant

D^2	7.51	1	7.51	4.37	0.0539	not significant
Residual	25.76	15	1.72			
Lack of Fit	20.50	10	2.05	1.95	0.2394	not significant
Pure Error	5.27	5	1.05			
Cor Total	3505.47	29				

Std. Dev: 1.31; Mean: 80.493; C.V. %: 4.3; R^2: 0.9927; Adjusted R^2: 0.9858; Predicted R^2: 0.99642; Adeq Precision: 46.96; PRESS: 125.66; model Suggested: Quadratic.

Diazinon degradation (%) =+81.31 -8.01 A +3.52 B +2.46 C -7.77 D +0.81 AB +0.41 AC -0.80 AD -0.36 BC -0.18 BD +0.75 CD -0.40 A^2 -0.02 B^2 -0.31 C^2 -0.52 D^2

Table 3. Verification of experimental results at optimum conditions.

Optimum condition	**Diazinon degradation (%)**
Experimental results	82.56 %
Model response	CI low: 79.95, CI high: 83.22
Error	1.52
Standard deviation	± 1.31

Table 4. Comparison of degradation of diazinon using other methods

Type of process	**Parameters**	**Degradation (%)**	**COD (%)**	**Ref.**
Photocatalytic degradation Process	Conc. diazinon (40 mg/L), Conc. TiO2 NPs (0.2-0.6 g/L), Reaction time (20-120 min) and pH (4-10)	99	65	Farzadkia et al (2014)
Nano Photocatalytic	Conc. diazinon (15-100 mg/L), Conc. NPs (0.2-2 g/L),	95	*	Darbandi et

process	Reaction time (2-30 min) and pH (3-9)			al (2016)
Adsorption process	Conc. diazinon (5-30 mg/L), adsorbent dose (0.4 g/L), , Time (0-180 min) and pH (7)	78	*	Nikzad et al (2015)
Photocatalytic process	Conc. diazinon (5-50 mg/L), Conc. catalyst (0.25-2 g/L), Reaction time (0-120 min) and pH (3-11)	85	*	Jonidi-Jafari et al (2014)
Sonophotocatalytic process	Conc. diazinon (20-100 mg/L), Conc. nTiO2+Fe (0-0.2-0.6 g/L), Reaction time (20-100 min) and pH (5.5=9.5)	85	*	Tabasideh et al (2017)
Biological Process	Con. diazinon (mg/L) = 10-50, Time (hr) = 12-36, filling fraction (%) = 25-75, Con. Catalyst (g/L) = 0.2-0.6, pH = 5.5-9.5.	97.6	*	Azizi et al (2019)
Electrochemical process	Conc. diazinon (30-150 mg/L), Current density (2 -10 mA/cm^2), Electrolysis time (40-120 min) and pH (4-10)	98	86	Present study

* Not considered.

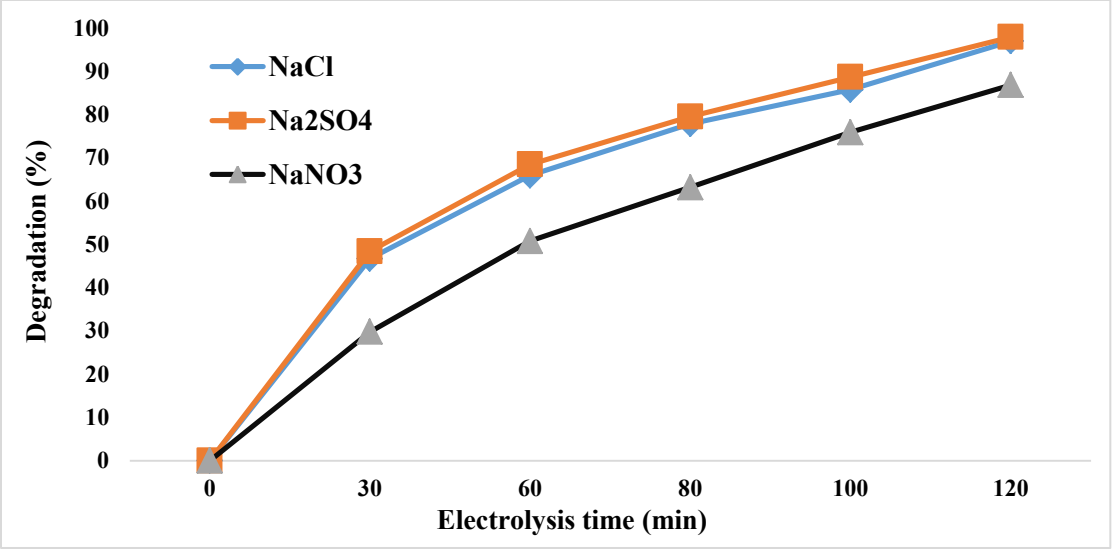


Fig. 1. The effect of supporting electrolyte on Diazinon removal in elecrodegradation process (pH= 4.0, initial diazinon concentration= 30 mg/L, supporting electrolyte= 0.5 g/L, j= 8 mA/cm^2)

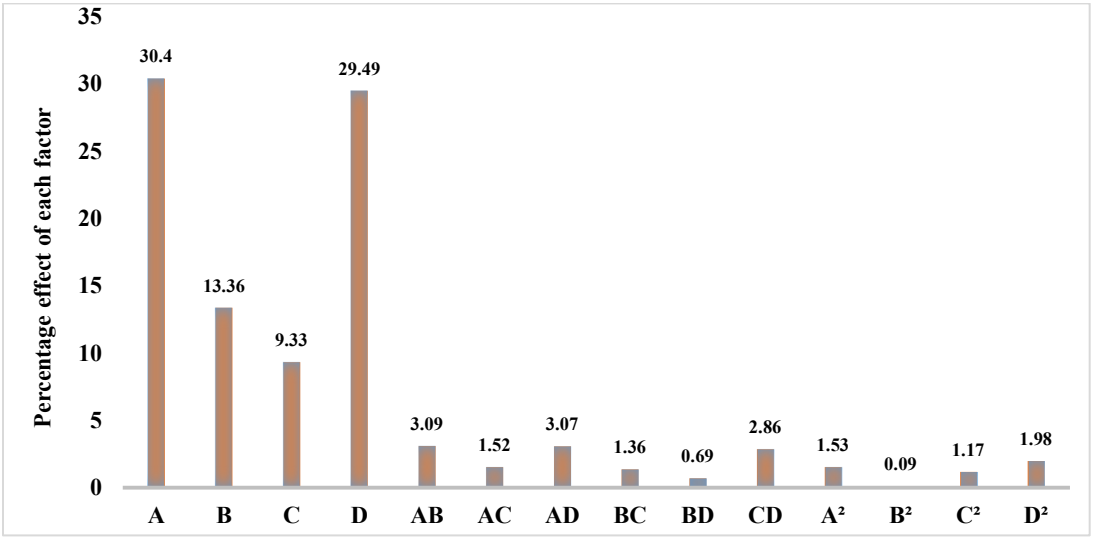


Fig. 2. Pareto chart of the main effects obtained from the screening experiments for removal of diazinon.

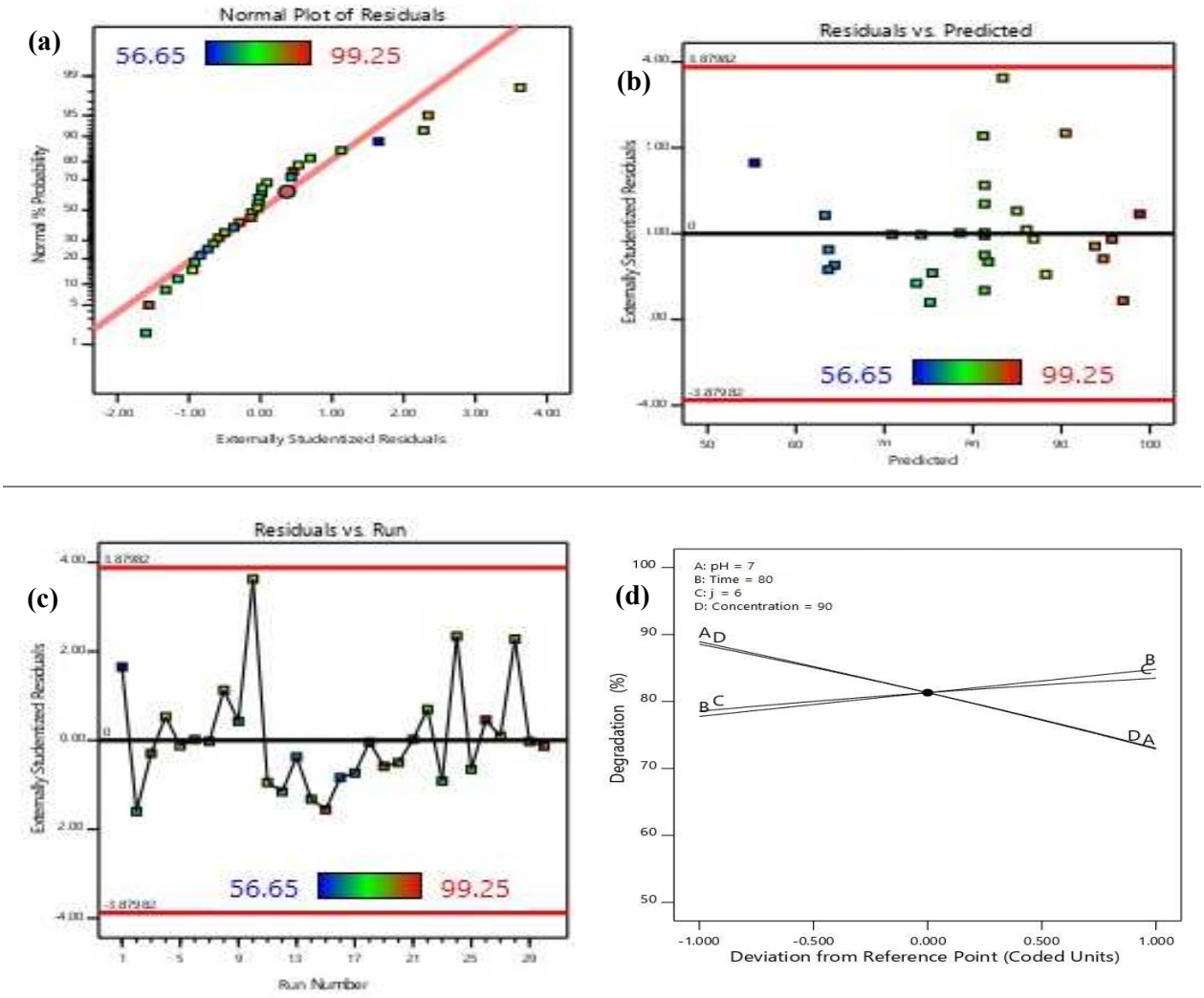
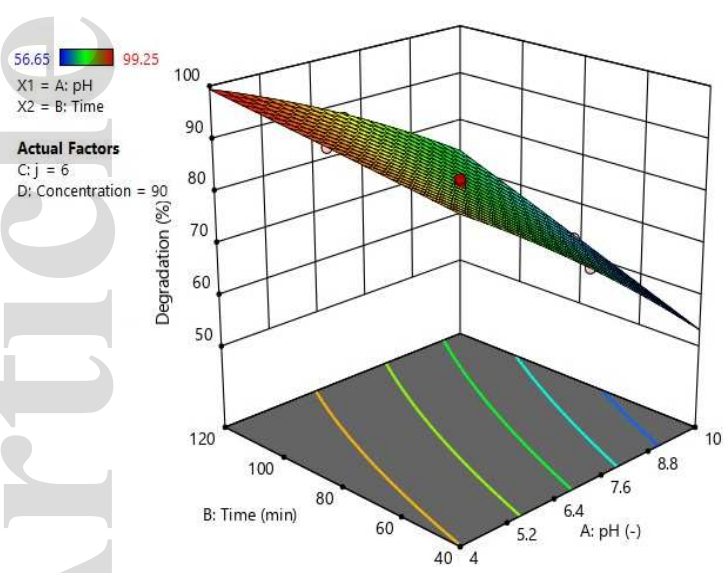
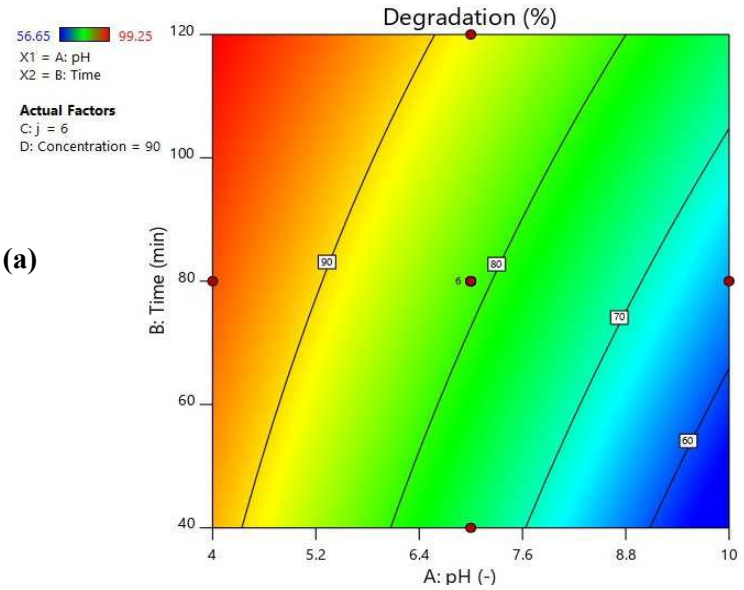
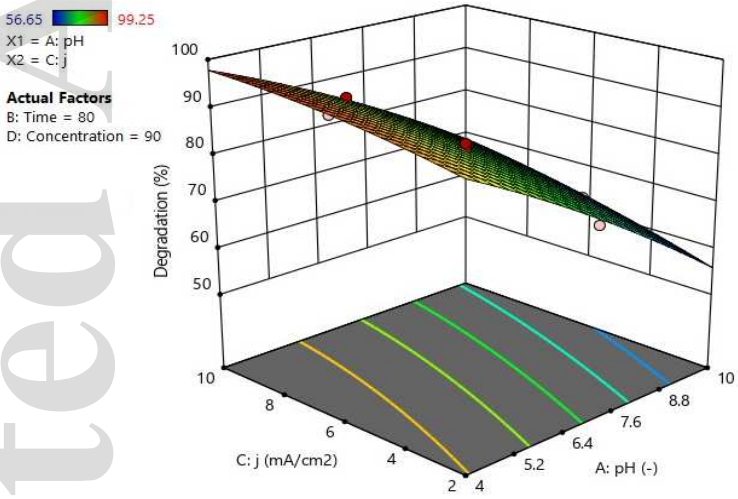


Fig. 3. (a) Normal probability distribution of residuals, (b) Residuals versus predicted, (c) Externally studentized residuals versus run and (d) Perturbation plot for diazinom degradation.



(a)





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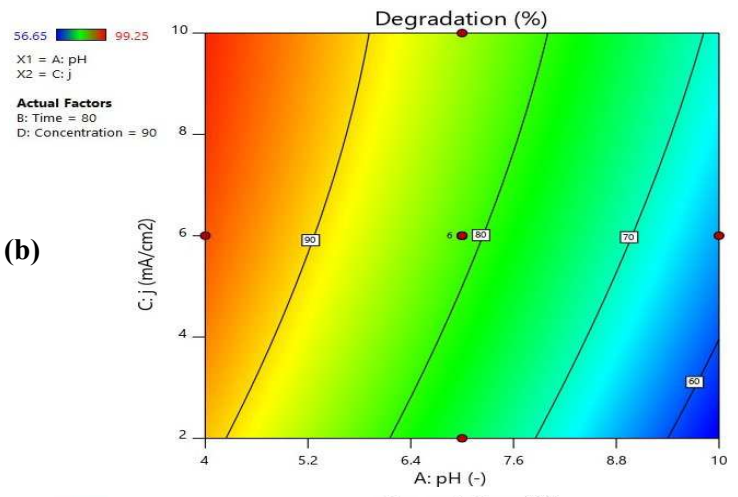

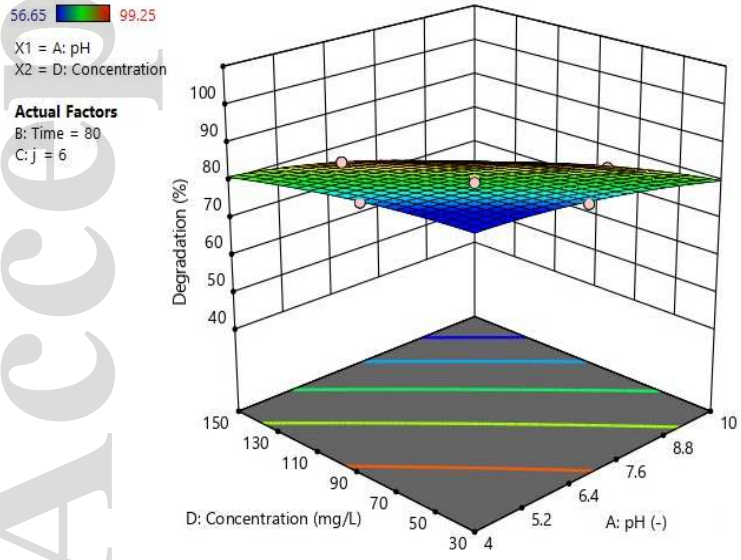

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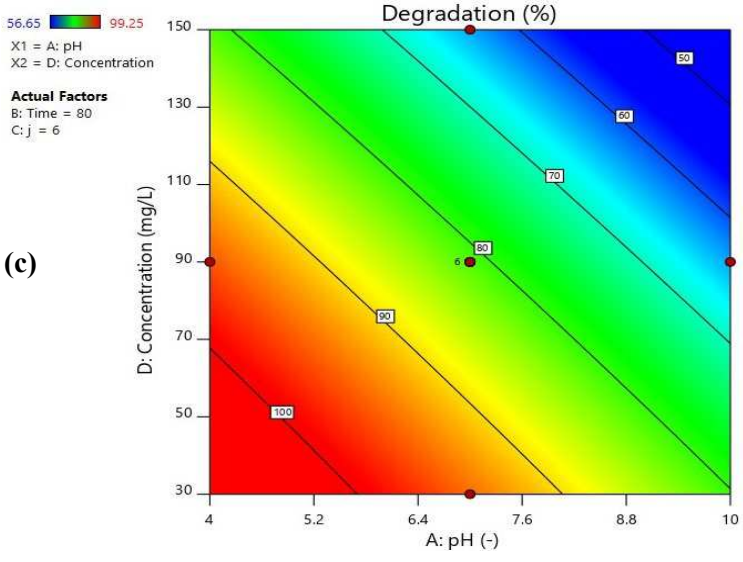

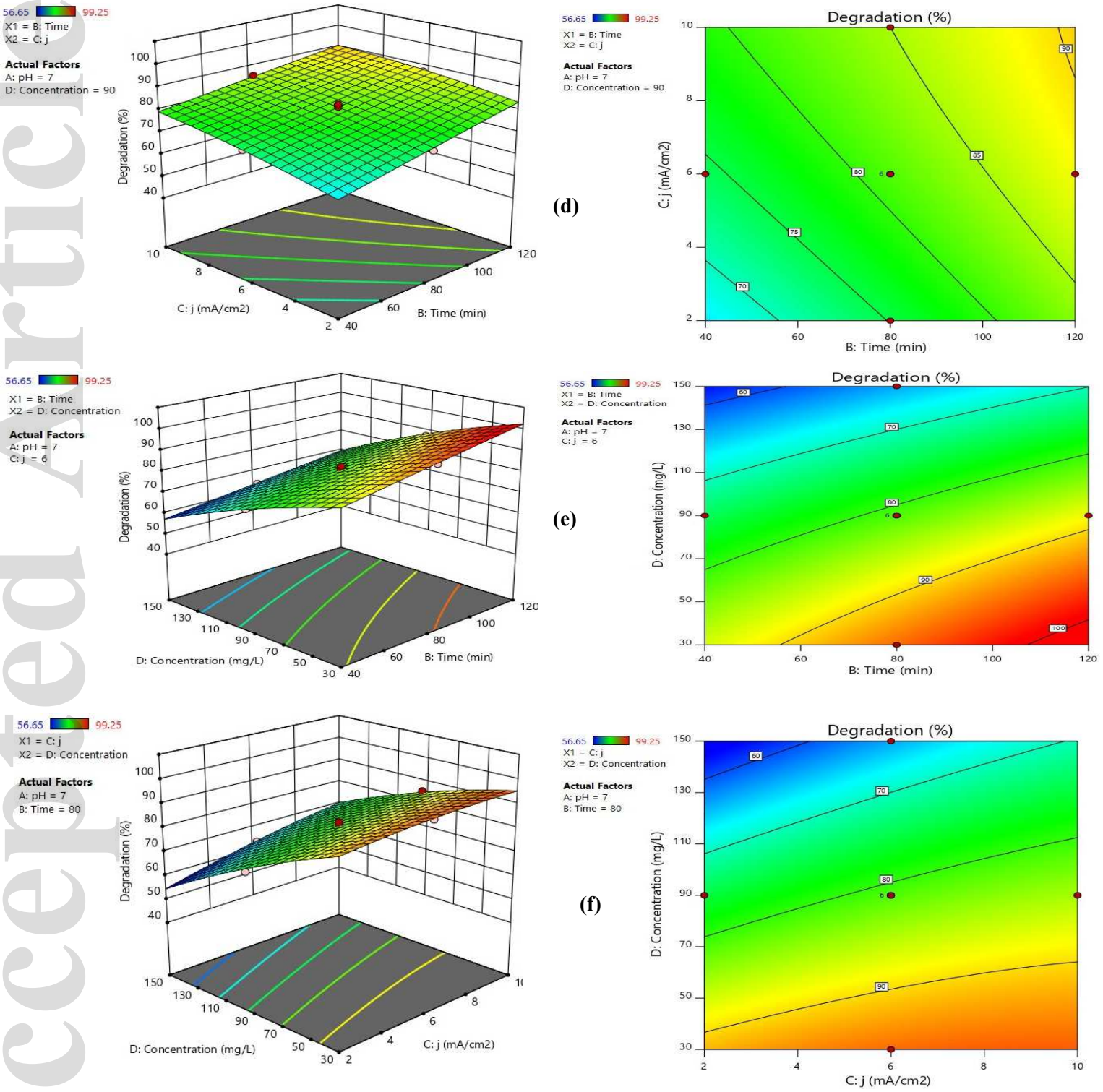

Fig. 4. Three-dimensional (3D) and contour plots for diazinon degradation using electrochemical degradation process: effects of (a) pH and electrolysis time, (b)) pH and current density, (c) pH and initial diazinon concentration, (d) current density and electrolysis time, (e) electrolysis time and initial diazinon concentration and (f) current density and initial diazinon concentration.