



Study on the degradation of dicofol via electrochemical oxidation process: simulation and validation

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ABSTRACT

In this work, the preparation and characterization of an iridium coated titanium anode (Ti/IrO₂) and a ruthenium coated titanium anode (Ti/RuO₂) for dicofol (DZ) degradation is examined using the electrochemical oxidation process (EO). X-ray diffraction (XRD) and scanning electron microscope (SEM) are used to characterize the metal oxide-coated anodes. The operating parameters in EO, including current density, electrolyte (NaCl) dose, pH, and electrolysis time for the degradation of dicofol, are studied in detail. Box-Behnken response surface design (BBD) incorporated in response surface methodology (RSM) is used to optimize and model the dicofol degradation process. The dicofol degradation and electrical energy consumption are taken as responses. Numerical optimization is used to determine the optimal conditions (current density of 0.1 A/m², electrolyte dose of 3.5 mM, pH of 7, and electrolysis time of 8 min). Ninety-three percent of dicofol is degraded with an electrical energy consumption value of 0.75 KWh/m³ using Ti/IrO₂ anode under optimal conditions.

1. Introduction

Pesticides have been widely used in many fields such as livestock farming, aquaculture, and agriculture [1]. In the last few decades, pesticides have been considered environmental micropollutants due to their ubiquitous presence in water resources at concentrations ranging from ng to µg/L [2]. Since they are molecules designed to be biologically active at very low concentrations, their presence is a source of concern for both humans and the ecosystem [3]. Many kinds of pesticides,

including dicofol, have negatively impacted water bodies. Dicofol is an organochlorine pesticide that contains hydroxyl ions in its structure. It is widely used in the remediation of bugs like red, which affect vegetables and fruits [4,5]. Dicofol (DZ) is not readily degradable, and hence, there is a need to develop an inexpensive and competent technique to remove the DZ from wastewater. Presently, techniques like UV irradiation and advanced oxidation processes (AOP), including ozonation, chlorination, electrochemical process, are most commonly used to remove various

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pesticides from wastewater [6]. Among these AOP's, the electrochemical oxidation (EO) process is considered an economical process [7]. The EO process offers high removal efficiencies, it's easy to operate, and requires no additional auxiliary oxidation agents (e.g., H_2O_2) [8]. Various types of wastewater containing phenol, pentachlorophenol, tannery, textile wastewater, pharmaceutical industrial effluent, deproteinated whey wastewater, dairy manure, and microorganic pollutants were examined using the EO process. However, the salient feature in EO is to find an appropriate role of the anode for the effective degradation of various pesticides and organic matter [9]. Also, EO mainly depends on the hydroxyl radicals (OH), which play a prominent role in the degradation of toxic matters, including pesticides. Thus, there is a research gap between the degradation of pesticides and the type of anode used during the EO process [10]. Therefore, identifying the role of the anode during the EO process for pesticide degradation is a crucial issue. Nowadays, industrial use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological solutions, thus reducing operational and investment costs. Such DSA-type materials have been used for the oxidation of model aqueous solutions containing non-biodegradable organics, typically found in pharma effluents. Recent DSA research emphasis focuses on titanium-based anodes coated with various oxide materials such as IrO_2 , Ru_2 , and SnO_2 . These electrodes have been used widely and successfully as an anode for chlor-alkali production and electro-oxidation of wastewater due to their excellent electrocatalytic activity [11]. However, best of our knowledge, the application of the EO process to degrade the DZ using a different anode [Iridium coated titanium anode (Ti/ IrO_2) and a ruthenium coated titanium anode (Ti/ RuO_2)] has not yet been investigated or published in the open literature. Moreover, the process variables such as current density, pH, electrolyte (NaCl), and time play a crucial role in the EO process. Therefore, the optimization of these process parameters will enhance the efficacy of EO and reduce chemical waste. Usually, the optimization of process parameters is carried out by conducting different experiments at a wide range and identifying the conditions that give

maximum degradation efficiency. However, this process is tedious, consumes a lot of chemicals, and needs more human working hours. Therefore, a statistically valid design of experiments (DOE) is designed to mitigate these issues and statistically optimize the process. This approach reduces the human resource and the number of experiments, providing an in-depth understanding of the interaction between the parameters. In this regard, popular response surface methodology (RSM) is used as a statistical tool for modeling and investigating multivariable systems where several variables influence the primary response. Additionally, RSM provides more information from a few numbers of experiments. In recent years some scholars have effectively used the RSM to investigate the interactive effects of independent variables in many fields include wastewater treatment. An iridium coated titanium anode (Ti/ IrO_2) and a ruthenium coated titanium anode (Ti/ RuO_2) have been synthesized. These synthesized anodes are used to degrade the dicofol using an electrochemical oxidation process in the present research. Characterization of the anodes is examined by SEM and XRD studies. The interactive and individual effects of process parameters, including current density, pH, treatment time, and electrolyte, are studied using RSM coupled with BBD. Finally, the performance of the EO process is determined using DZ degradation and the electrical energy consumption of each anode.

2. Materials and methods

2.2. Reagents and chemicals

Dicofol was purchased from local suppliers, and its chemical structure is shown in Figure 1. The properties of dicofol are as follows: $C_{14}H_9Cl_5O$; 2, 2, 2-Trichloro-1;1-bis (4-chlorophenyl) ethanol; and pure dicofol that is a white crystalline solid. All the chemicals were of analytical grade solutions prepared with sterile distilled water. The metal salts of ruthenium chloride (III) hydrate ($RuCl_3 \times H_2O$, 99.99%) and iridium chloride hydrate ($IrCl_3 \times H_2O$, 99.0%) were purchased from Sigma chemicals, India, and used without further purification. Polyvinyl alcohol (PVA) (99%) or anhydrous citric acid (CA) (99.5%) dissolved in ethylene glycol (EG) (99.8%) were used as the

solvents and purchased from Sigma chemicals, India.

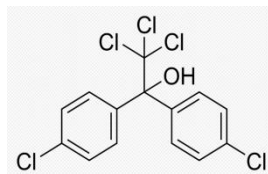


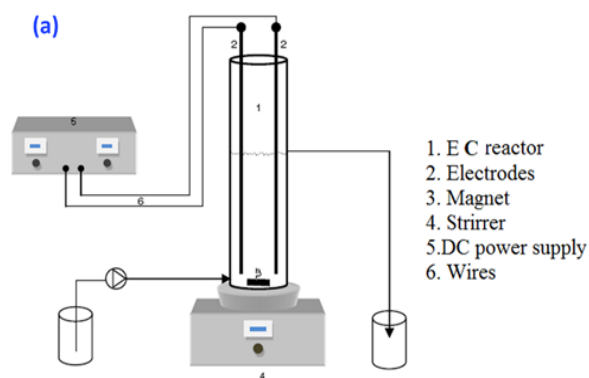
Fig.1. Chemical structure of dicofol.

2.2. Anode fabrication and characterization

Titanium plates having a dimension of 1 cm × 1 cm × 0.5 mm were used as metallic support. Ruthenium chloride and iridium chloride with a molar ratio of Ru/Ir = 0.5/0.5 were dissolved in 1 mL of ultrapure water; then, 3 mL of the PVA 10 wt% stock solution was gradually added. It was kept under stirring until a homogeneous solution was obtained. By employing a solution of CA in EG as a solvent in a ratio of 3:10 (CA: EG), the solution was stirred and heated to 90 °C for complete dissolution and used as a precursor solution. Finally, the obtained precursor solutions were brushed over the titanium plates, heated to 130 °C for 30 min, and calcinated at 400 °C for 5 min. This procedure was repeated for both methods until a mass loading of 1.2 mg/cm² was achieved. Scanning electron microscopy (SEM), Jeol JSM 500F, Japan, and X-ray diffraction spectroscopy (XRD), PANalytical, The Netherlands, were used to examine the size and crystalline phase of synthesized electrodes [10].

2.3. Electrochemical degradation of dicofol

A schematic diagram of the electrochemical (EO) oxidation reactor is shown in Figure 2a. The electrochemical batch mode experiments were carried out with a sufficient magnetic stirring of 275 rpm in an undivided electrochemical cell at room temperature. This cell contained two electrodes with an inter-electrode distance of 2 cm using a Ti/IrO₂ electrode or Ti/RuO₂ electrode as the anode [11]. All the degradation studies were carried out for a volume of 240 mL of 0.05 mM DZ sample. The DC power supply equipment maintained the desired current density. After pH adjustment, the degradation started immediately after the power supply was on. After the EO process for both anodes, the samples were withdrawn for DZ concentration analysis [12].



(b)

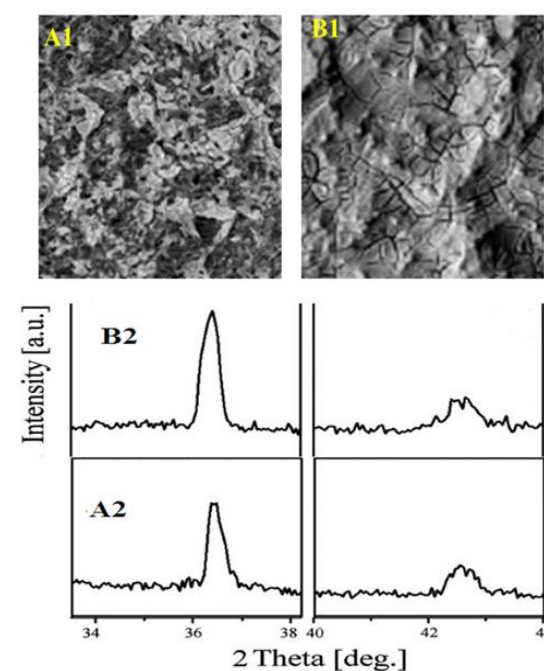


Fig.2 (a) Schematic diagram of electrochemical oxidation process experimental setup. (b) SEM and XRD results. A1-SEM result of Ti/IrO₂, B1-SEM result of Ti/RuO₂, A2- XRD result of Ti/IrO₂, B2-XRD result of Ti/RuO₂

2.4. Analytical methods

The concentration of dicofol was quantified by a spectrometer (Agilent 1260, USA). After electrochemical experiments, the sample of 50 ml was collected in a conical flask, 1ml of pyridine and 2 ml of 5 M NaOH were also added. This mixture was heated in a water bath for 3 minutes and immediately cooled in ice-cold water. In this cooled mixture, initially, 1ml of glacial acetic acid, 2 ml of 4-amino acetanilide, and 1 ml of 10 M HCL was

added and shaken thoroughly. This mixture was left for ten minutes, and 5 ml of amyl alcohol was also added. The sample of the mixture was extracted and observed using a spectrophotometer at 525nm for dicofol concentration. The degradation efficiency (RE) was obtained as follows [13]:

$$RE = \left(\frac{c_0 - c_e}{c_0} \right) \times 100 \quad (1)$$

where c_0 and c_e are the initial and final concentrations of dicofol, respectively. The pH is measured/adjusted using a pH meter (FE20, Mettler Toledo). The electrical energy consumption is calculated using the following equation [14]:

$$E = \left(\frac{VIt}{V_s} \right) \quad (2)$$

where E is the electrical energy (KWh/m³), V_s is the volume of solution (L), I is the current in ampere (A), V is the cell voltage in volt (V), and t is the time of EO (h).

2.5. RSM-BBD design

In the present study, independent variables, namely current density (A), pH (B), treatment time (C), and electrolyte dose (D), were coded at three levels (low, middle, and high, being coded as -1, 0 and +1) as follows (Table 1) [15]:

$$x_i = \frac{X_i - X_{cp}}{\nabla X_i} \quad (3)$$

where x_i is the dimensionless value of an independent variable; X_i is the real value of an independent variable; X_{cp} is the real value of an independent variable at the centre point, and ∇X_i is the step change of the real value to a variation of a unit of the variable i . Here, Y_1 (DZ degradation in Ti/IrO₂ anode), Y_2 (EEC for Ti-IrO₂ anode), Y_3 (DZ degradation in Ti-RuO₂ anode), and Y_4 (EEC for Ti-RuO₂ anode) were taken as dependent variables. Twenty-nine experiments were designed according to BBD, and multi regression analysis using analysis of variance (ANOVA) was carried out to identify the best-regression model.

3. Results and discussions

3.1. SEM and XRD results

SEM observations are carried out to understand variations in the morphology and structure of the two electrodes, including Ti/IrO₂ and Ti/RuO₂

(Figure 2). Several crystallite agglomerates are seen on the surface of electrodes (Ti/IrO₂ and Ti/RuO₂). Some of the residues scatter in the flat area, while others are distributed along the ridges. The aggregation of crystallites is also found to be minimal in both anodes from the XRD experiments. And this may be attributed to the formation of a stable anatase phase, resulting in the formation of small particles with a high surface area, which is most suitable for the EO process [16]. There are several pores on the surface of the electrodes, contributing to the increased catalytic property and more reactive surfaces. These results are well matched with electro-oxidation of fish meal industry wastewater in a stirred batch reactor using a Ti/RuO₂ anode.

Table 1. Process variables and their ranges.

Variable (unit)	Factors			
	X	-1	0	1
Current density (A)	A	0.1	0.2	0.3
pH	B	5.5	7	8.5
Electrolysis time (min)	C	1	5.5	10
Electrolyte dose (mM)	D	1.7	3.4	5.1

3.2. Effect of current density

The DZ degradation concerning the current density on two different anodes are investigated (Figure 3). It is found that the DZ degradation on Ti/IrO₂ is more competent than that on Ti/RuO₂. As demonstrated in Figure 3a and b, the DZ degradation increases with the treatment time, and the performance on Ti/IrO₂ is much greater concerning Ti/RuO₂ at the same current density. For instance, at the current density of 0.3 A/m², the DZ is almost completely degraded on the Ti/IrO₂ anode after 9 min of treatment, while the removal ratio is less than 25% for the Ti-RuO₂ electrode. Furthermore, a high current density promoted the degradation ratio, which is more noteworthy on Ti/IrO₂ than Ti/RuO₂. Accordingly, more energy consumption (EEC) is required on the Ti-RuO₂ electrode when the applied current density increases [17]. As shown in Figure 3c-d, for the Ti-RuO₂ electrode, the EEC value increased from 0.2 to 1.8 KWh/m³ at a current density of 0.1 A/m²; however, this is much less in Ti/IrO₂ anode. Comparably, the degradation on the Ti/RuO₂

electrode seemed to be more sensitive to the applied EEC, which led to a sharp EEC rise even for a small increase in the DZ degradation. On the Ti/IrO₂ electrode, it is also observed that EEC is almost linearly increased when the degradation is 90%. Similar results were reported for the effect of the ruthenium oxide/titanium mesh anode microstructure on electro-oxidation of the pharmaceutical effluent.

3.3. Effect of pH

The pH is an essential factor for DZ degradation in the EO process. Figure 4 indicates the effect of pH on the DZ degradation on the (a) Ti/IrO₂ and (b)

Ti/RuO₂ electrodes. The degradation of performance dependence with pH is the same and favoured at near-neutral conditions for both electrodes. For example, for a DZ degradation of 60% at a pH of 7, the required EEC is about 3 KWh/m³; however, it increases to about 5 KWh/m³ at a pH of 8.5. This result confirms that the effect of pH on the degradation of Ti/IrO₂ is not significant, which is in agreement with similar works published on orange II oxidation on Ti/IrO₂ electrodes [18]. And this indicates that the degradation on Ti/IrO₂ was executed better in the broad ranges of pH than Ti/RuO₂ electrodes in terms of DZ degradation and EEC.

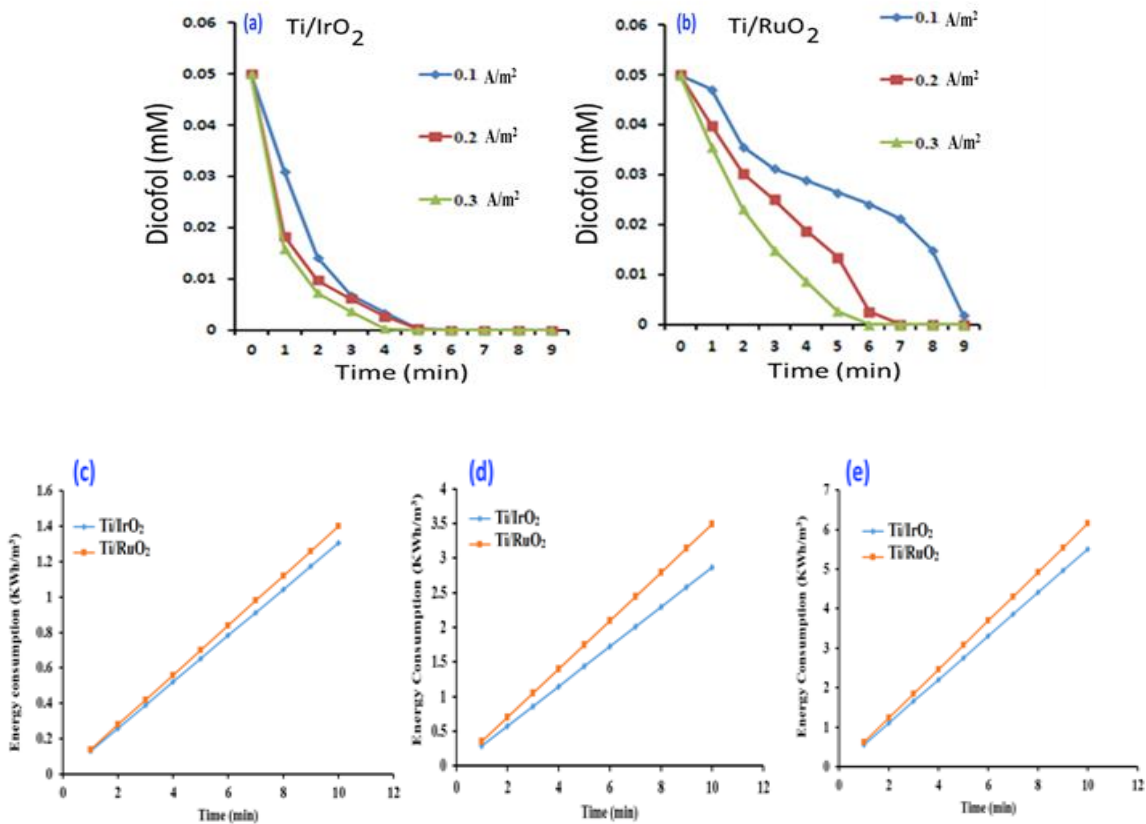


Fig. 3. Effect of current density on Dicofol degradation on two different anodes (a-b) treated time and (c-e) electrical energy consumption.

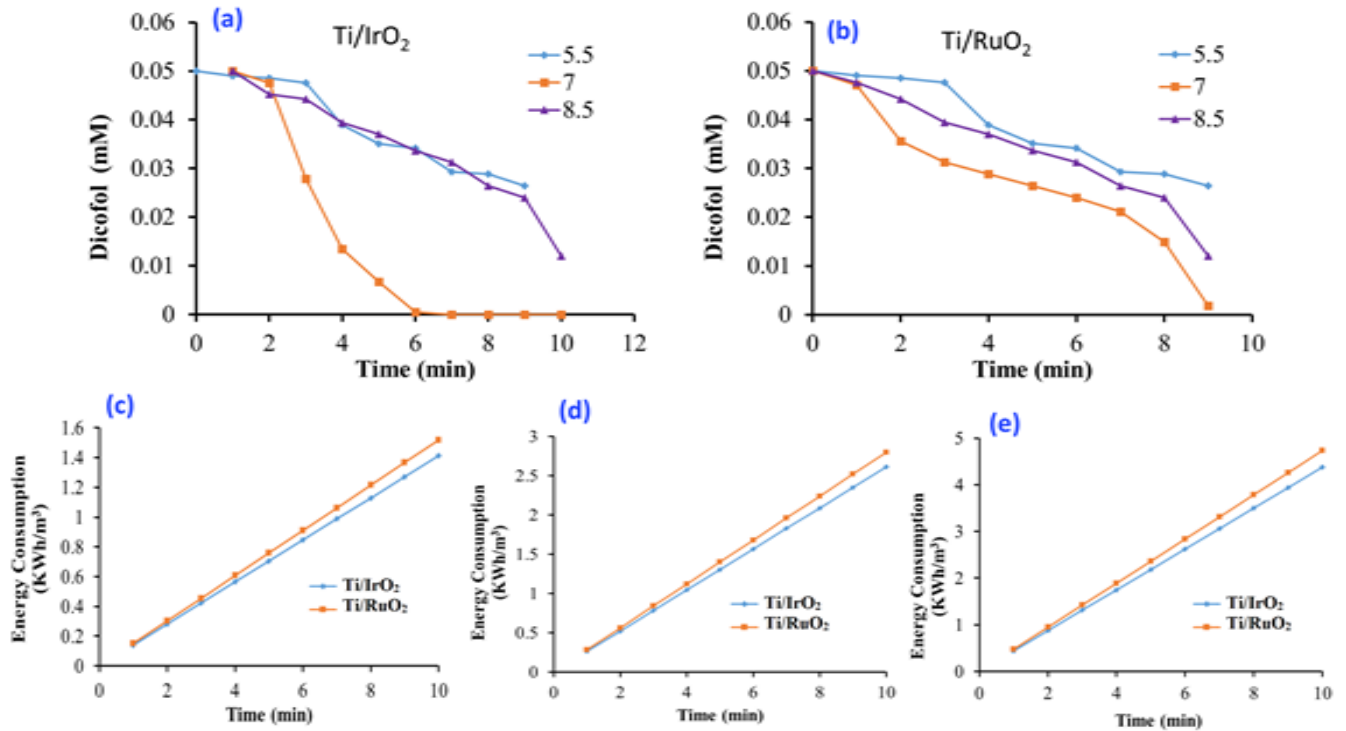


Fig. 4. Effect of pH on Dicofof degradation on two different anodes (a-b) treated time and (c-e) electrical energy consumption.

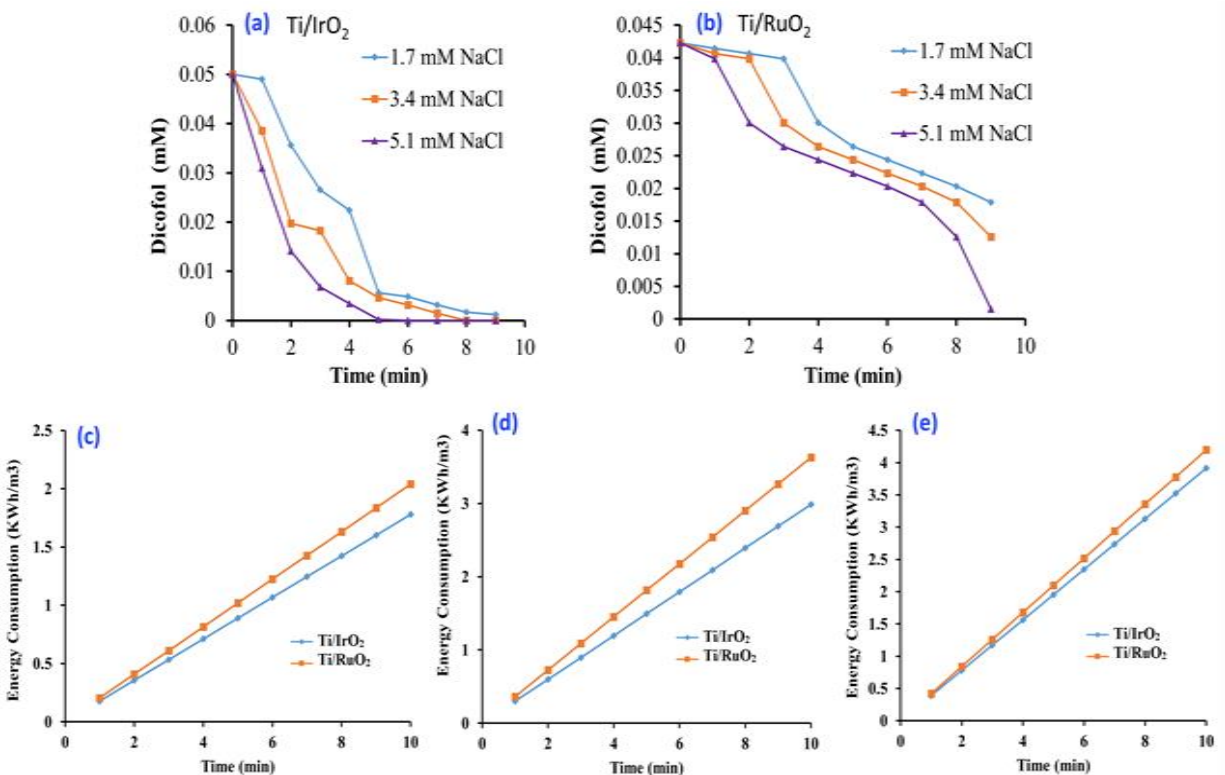


Fig. 5. Effect of electrolyte dosage on Dicofof degradation on two different anodes (a-b) treated time and (c-e) electrical energy consumption.

3.4. Effect of electrolysis time

One of the essential parameters in the EO process is electrolysis time, which affects the economy of the process and its efficiency. To examine the effect of electrolysis time on DZ degradation efficiency, experiments were carried out for different electrolysis times from 0 to 10 min, and the results are shown in Figure 4 (a-d). Figure 4 shows the effect of electrolysis time on the DZ degradation on the (a) Ti/IrO₂ and (b) Ti/RuO₂ electrodes. The results show that the DZ degradation increases with increasing electrolysis time up to 7 min for both electrodes. This observation can be defined as the contribution of oxidation by the strong oxidizing agents generated in the EO process in degrading the DZ during electrolysis [19]. However, regarding EEC, the Ti/IrO₂ anode shows a smaller EEC compared to Ti/RuO₂ at the same conditions. These results imply that the EEC is directly proportional to electrolysis time for both electrodes. Electrochemical oxidation of resorcinol for wastewater treatment using a Ti/TiO₂-RuO₂-IrO₂ electrode confirms the trends associated with this study.

3.5. Effect of electrolyte dose

During the electrochemical oxidation process, electrolyte dose is an essential parameter in DZ degradation. It is associated with the conductivity and the formation of various active chlorines during the EO process. A higher voltage is required for the EO process to reach the desired current density for the low electrical conductivity of a solution. This issue can be overcome by using a supporting electrolyte [20]. Also, it is reported that the DZ degradation is a lot higher on NaCl than Na₂SO₄ for the methylene blue wastewater treatment. Therefore, this study investigated the degradation of DZ with various NaCl doses. As shown in Figure 5, the presence of NaCl upholds the degradation of DZ on both electrodes. It can be observed that the DZ degradation is directly proportional to the supporting electrolyte concentration. The results show that increasing the supporting electrolyte concentration increases the mass transfer and decreases energy consumed. Also, Ti/IrO₂ shows higher DZ degradation than Ti/RuO₂ anode in all NaCl doses.

3.6. Development of model

The RSM-BBD experiments for the process parameters like current density (A), pH (B), electrolysis time (C), and electrolyte dose (D) are given in Table 2. Various responses like Y₁ (DZ degradation in Ti/IrO₂ anode), Y₂ (EEC for Ti/IrO₂ anode), Y₃ (DZ degradation in Ti/RuO₂ anode), and Y₄ (EEC for Ti/RuO₂ anode) are considered as dependent variables. Using the ANOVA approach, the BBD experimental data used a sequential model sum of squares (Table 3) and model summary statistics (Table 4).

Table 2. BBD and their experimental results.

Run	A	B	C	D	Y ₁	Y ₂	Y ₃	Y ₄
1	0.3	8.5	5.5	3.4	85	2.50	82	2.50
2	0.1	8.5	5.5	3.4	43	0.85	39	0.85
3	0.2	8.5	5.5	1.7	38	1.72	35	2.15
4	0.1	7	10	3.4	86	1.30	81	1.40
5	0.2	7	5.5	3.4	97	1.58	93	1.92
6	0.2	8.5	5.5	5.1	66	1.76	65	2.09
7	0.2	7	5.5	3.4	84	1.58	80	1.92
8	0.2	7	1	5.1	35	0.29	31	0.35
9	0.2	5.5	10	3.4	94	3.06	87	4.08
10	0.1	5.5	5.5	3.4	79	0.81	74	1.03
11	0.2	8.5	1	3.4	20	0.31	18	0.33
12	0.2	5.5	5.5	5.1	77	1.71	73	2.14
13	0.2	8.5	10	3.4	70	3.20	66	3.79
14	0.2	7	5.5	3.4	90	1.58	84	1.92
15	0.3	5.5	5.5	3.4	88	3.13	83	3.33
16	0.2	7	10	5.1	89	2.87	85	3.49
17	0.3	7	5.5	5.1	87	2.58	82	3.72
18	0.3	7	1	3.4	55	0.55	49	0.64
19	0.3	7	10	3.4	98	5.51	94	6.40
20	0.2	5.5	1	3.4	20	0.30	16	0.30
21	0.2	7	1	1.7	65	0.29	64	0.35
22	0.2	7	5.5	3.4	85	1.58	81	1.92
23	0.1	7	1	3.4	66	0.13	65	0.14
24	0.2	5.5	5.5	1.7	55	1.62	51	2.02
25	0.3	7	5.5	1.7	74	2.58	70	3.29
26	0.2	7	10	1.7	79	2.87	73	3.49
27	0.1	7	5.5	1.7	85	0.72	81	0.77
28	0.1	7	5.5	5.1	85	0.72	81	0.77
29	0.2	7	5.5	3.4	89	1.58	85	1.92

Table 3. Sequential model sum of squares.

Source	Sum of squares	DF	Mean square	F Value	Prob > F	Remarks
<u>Sequential model sum of squares for Y₁</u>						
Mean	149666.77	1	149666.77			
Linear	6397.72	4	1599.43	5.21	0.0036	
2FI	1002.48	6	167.08	0.47	0.8201	
Quadratic	4476.60	4	1119.15	8.28	0.0012	Suggested
Cubic	1733.78	8	216.72	8.15	0.0099	Aliased
Residual	159.60	6	26.60			
Total	163436.95	29	5635.76			
<u>Sequential model sum of squares for Y₂</u>						
Mean	83.72	1	83.72			
Linear	36.64	4	9.16	50.52	< 0.0001	Suggested
2FI	3.70	6	0.62	17.17	0.0042	
Quadratic	0.28	4	0.07	2.62	0.0801	
Cubic	0.32	8	0.04	4.75	0.0368	Aliased
Residual	0.05	6	0.01			
Total	124.71	29	4.30			
<u>Sequential model sum of squares for Y₃</u>						
Mean	132832.62	1	132832.62			
Linear	5707.83	4	1426.96	4.56	0.0070	
2FI	1179.78	6	196.63	0.56	0.7575	
Quadratic	4355.12	4	1088.78	7.69	0.0017	Suggested
Cubic	1813.60	8	226.70	8.07	0.0101	Aliased
Residual	168.50	6	28.08			
Total	146057.45	29	5036.46			
<u>Sequential model sum of squares for Y₄</u>						
Mean	120.02	1	120.02			
Linear	53.83	4	13.46	51.56	0.0074	
2FI	5.25	6	0.88	15.57	< 0.0001	Suggested
Quadratic	0.09	4	0.02	0.33	0.8528	
Cubic	0.70	8	0.09	2.34	0.1577	Aliased
Residual	0.22	6	0.04			
Total	180.11	29	6.21			

Table 4. Model summary statistics.

Source	Std.Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	Remarks
<u>Model summary statistics for Y₁</u>						
Linear	17.5267	0.4646	0.3754	0.2177	10771.99	
2FI	18.8119	0.5374	0.2804	0.2779	17597.41	
Quadratic	11.6293	0.9625	0.9250	0.9404	10459.69	Suggested
Cubic	5.1575	0.9884	0.9459	0.4305	7842.12	Aliased
<u>Model summary statistics for Y₂</u>						
Linear	0.4258	0.8938	0.8761	0.8345	6.78	
2FI	0.1896	0.9842	0.9754	0.9516	1.98	Suggested
Quadratic	0.1626	0.5910	0.6819	0.7480	2.13	
Cubic	0.0917	0.9988	0.9942	0.8226	7.27	Aliased
<u>Model summary statistics for Y₃</u>						
Linear	17.6977	0.4316	0.3369	0.1652	11039.98	
2FI	18.7635	0.5208	0.2546	0.3367	17677.33	
Quadratic	11.8987	0.9501	0.9002	0.9206	10968.62	Suggested
Cubic	5.2994	0.9873	0.9405	0.3156	9051.70	Aliased
<u>Model summary statistics for Y₄</u>						
Linear	0.5109	0.8958	0.8784	0.8372	9.78	
2FI	0.2371	0.9832	0.9738	0.9467	3.21	Suggested
Quadratic	0.2570	0.5846	0.5692	0.6114	5.33	
Cubic	0.1933	0.9963	0.9826	0.4626	32.29	Aliased

The results indicate the second-order polynomial model is the best fit for DZ degradation. For EEC, the 2FI model is found to be the best fit. The developed polynomial equations in terms of coded factors are given below.

$$Y_1 = 89 + 3.59A - 7.52B + 21.23C + 3.57D + 8.30AB + 5.78AC + 3.23AD - 0.99BC + 1.50BD + 9.99CD + 3.54A^2 - 20.94B^2 - 15.67C^2 - 8.41D^2 \quad (4)$$

$$Y_2 = 1.70 + 1.03A - 0.024B + 1.41C + 0.011D - 0.17AB + 0.95AC + 0.034BC - 0.013BD \quad (5)$$

$$Y_3 = 0.43 + 70.01A + 4.80E-03B - 6.10E-03C - 0.02D - 0.02AB - 0.04AC + 0.02AD - 0.06BC - 8.30E-03BD - 4.64E-03CD - 0.08A^2 - 0.05B^2 - 0.03C^2 - 0.03D^2 \quad (6)$$

$$Y_4 = 2.03 + 1.24A - 0.099B + 1.71C + 0.040D - 0.16AB + 1.13AC + 0.11AD - 0.078BC - 0.046BD \quad (7)$$

ANOVA is used for the statistical analysis of the quadratic regression model. And it showed that the R² value of >0.85 confirmed that the model could explain 85% of the variations. A low value of CV and the p-value indicated the good reliability of the experiment's values. A high F-value indicates the ability of the model to elucidate the EO process statistically. Also, the predicted versus the actual plot (Figure 6) denotes the adequacy of the model to represent the DZ degradation [21]. The relationship between process parameters and DZ degradation is illustrated by the three-dimensional response surface contour plots shown in Figures. 7–8. These results are in close agreement with the two-dimensional plots. The Ti/RuO₂-IrO₂-SnO₂ anode for electrochemical degradation of the pollutants in pharmaceutical wastewater results are well agreed with the above-mentioned RSM results.

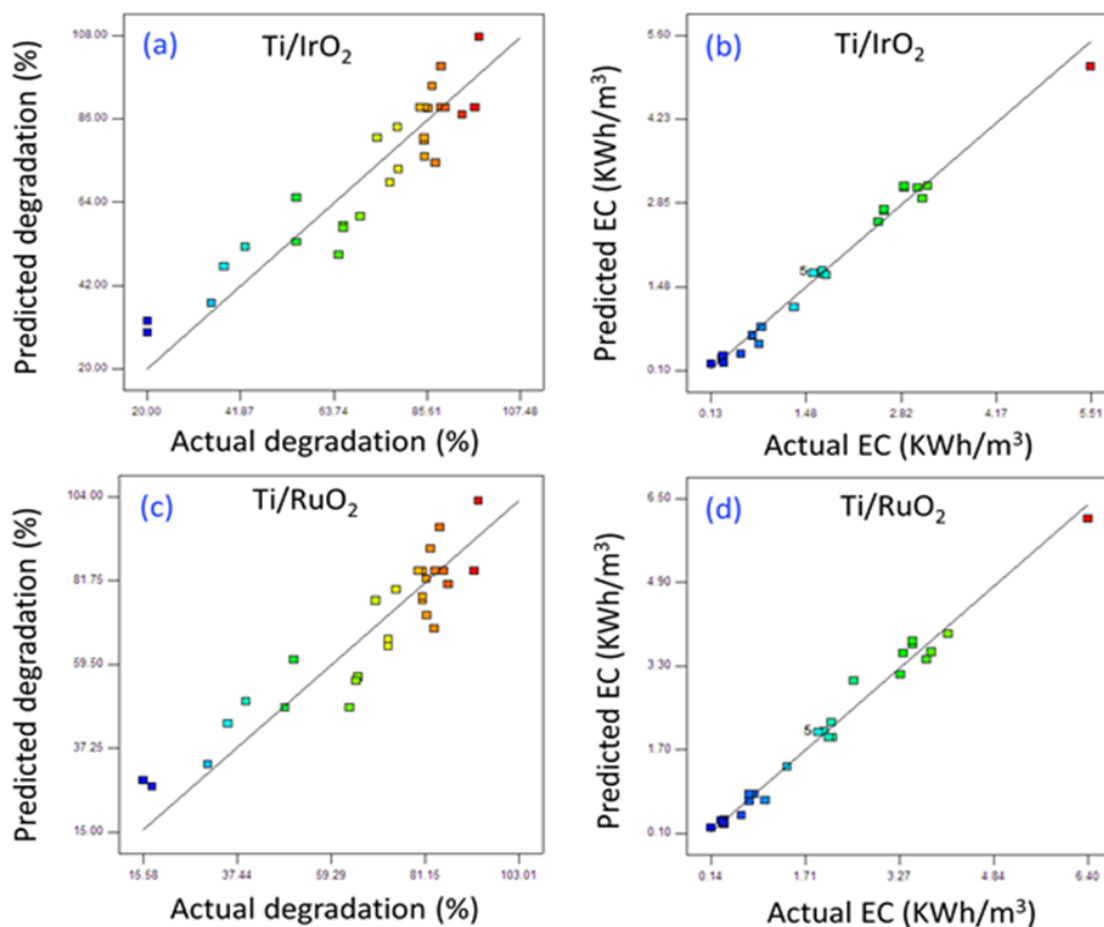


Fig.6. Actual versus predicted plot for responses (Degradation and EC (energy consumption) for Ti/IrO₂ and Ti/RuO₂).

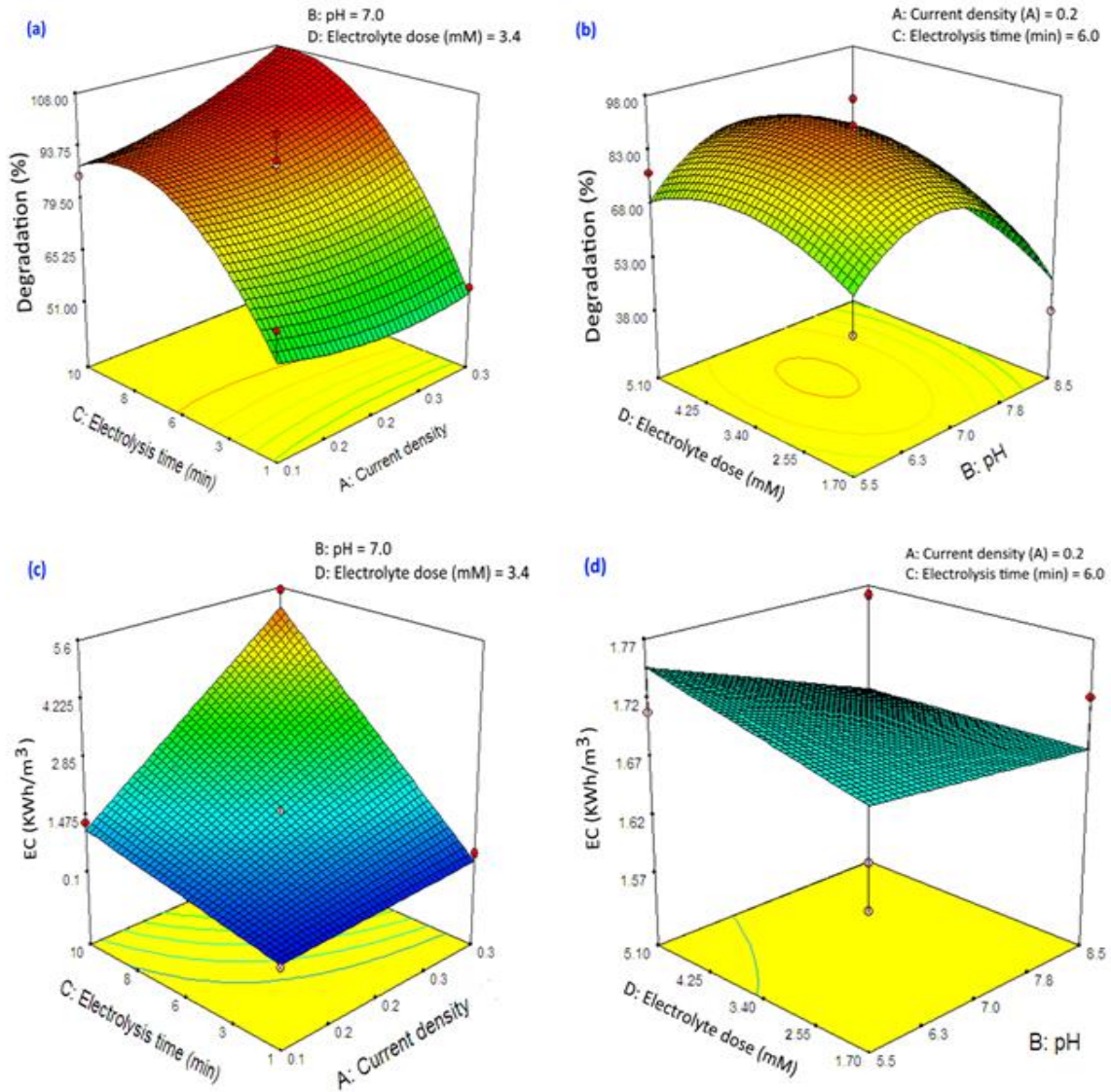


Fig.7. 3D response surface plots for Ti/IrO₂ electrode with responses degradation and EC (energy consumption).

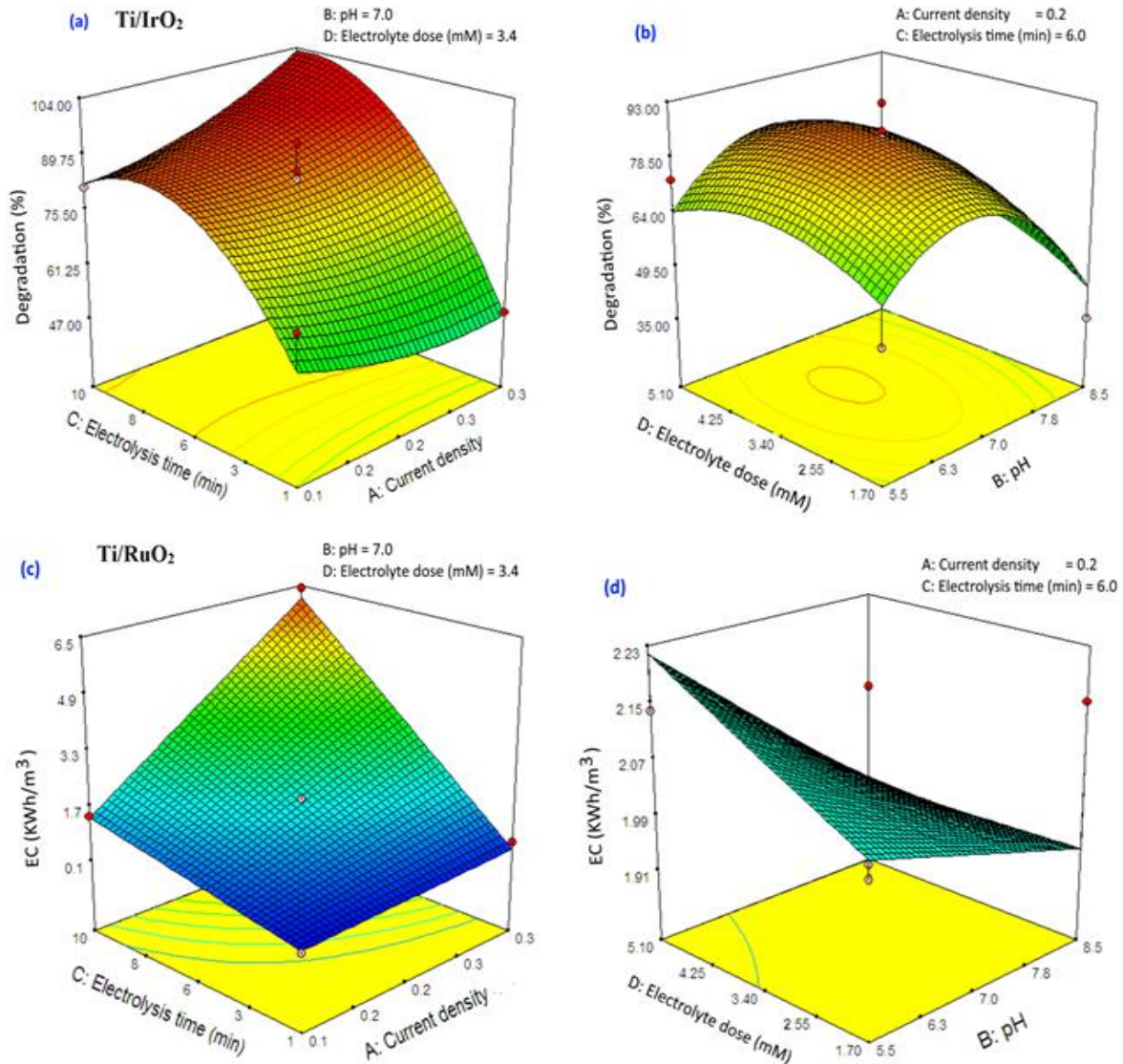


Fig.8. 3D response surface plots for Ti/RuO₂ electrode with responses degradation and EC (energy consumption).

3.7. Optimization of EO parameters

Optimizing the EO process to degrade the DZ is a crucial phenomenon associated with the degradation efficiency and economy of the process. Through the outcomes of the numerical optimization technique, the optimum conditions in the maximum DZ degradation are selected. The report indicates that the optimized conditions for current density, electrolyte dose, pH and electrolysis time are 0.1 A/m², 3.5 mM, 7 and 8 min, respectively. Under these conditions, 93 % of dicofol is degraded with an electrical energy consumption value of 0.75KWh/m³ (Ti/IrO₂ anode). For similar conditions, 83% of dicofol is degraded with an electrical energy consumption value of 0.98 KWh/m³ in the Ti/RuO₂ anode. Experiments are

performed to find the suitability of the predicted values, and the results are in close agreement with the experimental data.

4. Conclusions

Box-Behnken experimental design (BBD) is employed for the EO process to degrade the dicofol. SEM and XRD are used to characterize both anodes, including Ti/IrO₂ and Ti/RuO₂. A second-order polynomial model is designed with an R² value (> 0.80) for DZ degradation and EEC. The optimum conditions are a current density of 0.1 A/m², electrolyte dose of 3.5 mM, pH of 7, and electrolysis time of 8 min. Ninety-three percent of dicofol is degraded with an electrical energy consumption value of 0.75 KWh/m³ (Ti/IrO₂ anode) under optimal

conditions. And this result indicates that the EO process is a suitable method for the degradation of DZ.

References

- [1] Paździor, K., Bilińska, L., Ledakowicz, S. (2019). A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. *Chemical engineering journal*, 376, 120597.
- [2] Ghanbari, F., Moradi, M. (2015). A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: Electrical energy consumption and biodegradability improvement. *Journal of environmental chemical engineering*, 3(1), 499-506.
- [3] Zazou, H., Afanga, H., Akhouairi, S., Ouchtak, H., Addi, A.A., Akbour, R.A., Assabbane, A., Douch, J., Elmchaouri, A., Duplay, J., Jada, A., Hamdani, M. (2019). Treatment of textile industry wastewater by electrocoagulation coupled with electrochemical advanced oxidation process. *Journal of water process engineering*, 28, 214-221.
- [4] Mollah, M., Morkovsky, P., Gomes, J., Kesmez, M., Parga, J., Cocke, D. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of hazardous materials*, 114(1-3), 199-210.
- [5] Hendaoui, K., Ayari, F., Rayana, I.B., Amar, R.B., Darragi, F., Trabelsi-Ayadi, M. (2018). Real indigo dyeing effluent decontamination using continuous electrocoagulation cell: Study and optimization using response surface methodology. *Process safety and environmental protection*, 116, 578-589.
- [6] Duan, J., Pang, S.-y., Wang, Z., Zhou, Y., Gao, Y., Li, J., Guo, Q., Jiang, J. (2021). Hydroxylamine driven advanced oxidation processes for water treatment: A review. *Chemosphere*, 262, 128390.
- [7] Faouzi, A.M., Nasr, B., Abdellatif, G. (2007). Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond. *Dyes and pigments*, 73(1), 86-89.
- [8] Panizza, M. and Cerisola, G. (2005). Application of diamond electrodes to electrochemical processes. *Electrochimica acta*, 51(2), 191-199.
- [9] Aravind, P., Subramanyan, V., Ferro, S., Gopalakrishnan, R. (2016). Eco-friendly and facile integrated biological-cum-photo assisted electrooxidation process for degradation of textile wastewater. *Water research*, 93, 230-241.
- [10] Brillas, E., Martínez-Huitle, C.A. (2015). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied catalysis B: Environmental*, 166-167, 603-643.
- [11] Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., Scialdone, O. (2015). Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: A critical review. *Chemical reviews*, 115(24), 13362-13407.
- [12] Rekhate, C.V., Srivastava, J.K. (2021). Effectiveness of O₃/Fe²⁺/H₂O₂ process for detoxification of heavy metals in municipal wastewater by using RSM. *Chemical engineering and processing process intensification*, 165, 108442.
- [13] Flores, N., Brillas, E., Centellas, F., Rodríguez, R.M., Cabot, P.L., Garrido, J.A., Sirés, I. (2018). Treatment of olive oil mill wastewater by single electrocoagulation with different electrodes and sequential electrocoagulation/electrochemical fenton-based processes. *Journal of hazardous materials*, 347, 58-66.
- [14] Singh, B., Kumar, P. (2020). Pre-treatment of petroleum refinery wastewater by coagulation and flocculation using mixed coagulant: Optimization of process parameters using response surface methodology (RSM). *Journal of water process engineering*, 36, 101317.
- [15] Martínez-Huitle, C.A., Panizza, M. (2018). Electrochemical oxidation of organic pollutants for wastewater treatment. *Current opinion in electrochemistry*, 11, 62-71.
- [16] Meganathan, R., Varadarajan, R. (2021). Electro-oxidation of fish meal industry wastewater in a stirred batch reactor using a Ti/RuO₂ anode. *Water practice and technology*, 16(4), 1488-1497.

- [17] Raju, G.B., Karuppiah, M.T., Latha, S.S., Parvathy, S., Prabhakar, S. (2008). Treatment of wastewater from synthetic textile industry by electrocoagulation–electrooxidation. *Chemical engineering journal*, 144(1), 51-58.
- [18] Chatzisyneon, E., Xekoukoulotakis, N.P., Coz, A., Kalogerakis, N., Mantzavinos, D. (2006). Electrochemical treatment of textile dyes and dyehouse effluents. *Journal of hazardous materials*, 137(2), 998-1007.
- [19] Rajkumar, D., Palanivelu, K., Mohan, N. (2001). Electrochemical oxidation of resorcinol for wastewater treatment using Ti/TiO₂-RuO₂-IrO₂ electrode. *Journal of environmental science and health, Part A*, 36(10), 1997-2010.
- [20] Vahidhabanu, S., John Stephen, A. (2015). Effect of ruthenium oxide/titanium mesh anode microstructure on electrooxidation of pharmaceutical effluent. *International journal of waste resources*, 05(04) 1-5.
- [21] Palma-Goyes, R.E., Guzmán-Duque, F.L., Peñuela, G., González, I., Nava, J.L., Torres-Palma, R.A. (2010). Electrochemical degradation of crystal violet with BDD electrodes: Effect of electrochemical parameters and identification of organic by-products. *Chemosphere*, 81(1), 26-32.