

Optimization of textile azo dye degradation by electrochemical oxidation using Box-Behnken Design

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Abstract: Degradation of textile azo dye solutions containing Methyl Orange by anodic oxidation using an electrochemical reactor was studied. The combined effect of independent parameters (current intensity, initial pH and electrolysis time) on color removal efficiency was investigated and optimized using response surface methodology. A Box-Behnken design was successfully employed for experimental design. The obtained quadratic model was statistically tested using analysis of variance (ANOVA). Results showed that the optimal operating conditions to achieve 98.51% efficiency for color removal were current intensity = 4.6 A, initial pH= 4 and electrolysis time = 65 min, at a dye concentration and temperature of 50 mg/L and 25 °C, respectively.

Keywords: Anodic oxidation; Box-Behnken design; response surface methodology; wastewater treatment; anodic oxidation; azo dye.

Introduction

The textile industry is regarded as one of the most polluting sector ¹ since it consumes large quantities of wastewaters with high azo dye contents, which are discharged into water bodies. Among these dyes, azo dyes are extensively used in textile industries ^{2,3}. These colored effluents are characterized by intense color, high chemical oxygen demand (COD) and stable chemical structure due to the existence of azo groups (-N=N-), which are responsible for dye color ⁴. The presence of such kinds of dye effluents in the aquatic environment can cause many environmental problems because they are toxic and interfere in photosynthetic processes by consuming the oxygen needed for living species ⁵.

Decontamination of dyes wastewater can be achieved through a considerable number of processes, such as adsorption ^{6,7}, coagulation ⁸, ozonation ⁹, photocatalytic ¹⁰ and electrochemical oxidation methods. Amongst these processes, electrochemical treatments have received great attention for the removal of recalcitrant organic compounds from waters. Electrooxidation (EO) is one of the most promising electrochemical technologies for the removal of toxic and persistent organic pollutants from waters ¹¹. The contaminants are destroyed by either the direct or indirect oxidation. Direct oxidation takes place directly at the anode, where the pollutants are destroyed by electron transfer reaction. In indirect oxidation, strong oxidants, such as hydroxyl radicals ([•]OH), hypochlorite/chlorine, ozone, and hydrogen

peroxide are generated on the anode surface and then chemical oxidation takes place ¹². The effectiveness of this process strongly depends on the electrode material and operational conditions.

Several research groups have reported the electrochemical oxidation of dyes in water using various electrodes materials. Rajkumar et al. ¹³ studied the treatment of C.I. Re-active Yellow 186 by EO using graphite electrodes. A maximum decolorization efficiency of 99 % and COD removal 73 % was achieved under the optimized condition (pH 3.9; NaCl concentration 0.11 M; and electrolysis time 18 min). Cotillas and coworkers ¹⁴ used boron-doped diamond (BDD) electrodes to oxidize Red MX-5B dye in aqueous solutions. The results showed a full dye and COD removal after 240 min of electrolysis. Elaissaoui et al. ¹⁵ studied the degradation of Amaranth in aqueous solution using PbO₂ anode and they reported COD and color removals of 84 and 100 %, respectively. Isarain-Chávez et al. ¹⁶ compared the oxidation behavior of five different DSA anodes (Ti/Ir-Pb, Ti/Ir-Sn, Ti/Ru-Pb, Ti/Pt-Pd, and Ti/RuO₂) for EO of methyl orange azo dye solutions. The results showed that the best performance (74 % of COD removal) was achieved using Ti/Ir-Pb anode. DSA electrodes (Ti/Pt) present high catalytic activity, especially for chlorine generation, as well as high mechanical stability. However, these anodes have a major drawback of toxic by-products formation ^{17,18}, consequently, more studies must be performed. In this context, the present study aims to evaluate the performance of the EO process with Ti/Pt electrodes.

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An experimental design based on Response Surface Methodology (RSM) was used to optimize the effects of various experimental parameters to reach the best system performance. In fact, the experimental design is a helpful tool to study a large number of factors with the minimum experimental runs¹⁹. Additionally, the possible interactions between factors can be evaluated²⁰. RSM is a mathematical and statistical method for designing experiments, building models and can be used to evaluate the relative significance of variables. The main objective of RSM is to determine optimum values of operating conditions to predict target response²¹. Box-Behnken design (BBD) is among the principal response surface methodologies used in experimental design²². It's an independent, rotatable second-order design and requires fewer runs than the other design methods. It has been applied for optimization of several processes^{23,24}. In the present work, a Box-Behnken experimental design has been chosen to optimize several experimental parameters (current intensity, initial pH and electrolysis time) that have significant effects on color removal efficiency of azo dye Methyl Orange (MO) by EO.

Experimental

Anodic oxidation experiments

The degradation of MO dye was carried out using a cylindrical tank reactor of 6 L capacity, equipped with an external water-jacket to maintain the solution temperature at 25°C using a ULTRATEMPS 2000 julabo F30 thermostat. The anode was a cylindrical platinized titanium (Ti/Pt) grid and the cathode was a rod of the same metal. These electrodes were connected to the DC power supply (EA-7015- 050). The solution was constantly stirred at 300 rpm to ensure homogeneity using a BIOBLOCK SCIENTIFIC stirrer. Each assay was performed using a solution containing 50 mg/L concentration of MO. NaCl, KCl and Na₂SO₄, at concentration 2.5 g/L, were evaluated as an electrolyte in order to know their effect on the degradation of MO. During the experiment, samples were withdrawn at different time intervals and analyzed. The solution pH was determined using a pH meter (Hach) and adjusted with sulfuric acid or sodium hydroxide. The color removal efficiency of dye solutions was monitored using a UV-Vis 1201 Shimadzu spectrophotometer at 460 nm, the maximum wavelength of MO (Figure 1), at different time intervals. The percentage of color removal efficiency (% η) was calculated as follows:

$$\% \eta = \frac{A_0 - A_t}{A_0} * 100 \quad (1)$$

Where A₀ and A_t are the absorbance at the initial time and time t at the characteristic λ_{max} = 460.

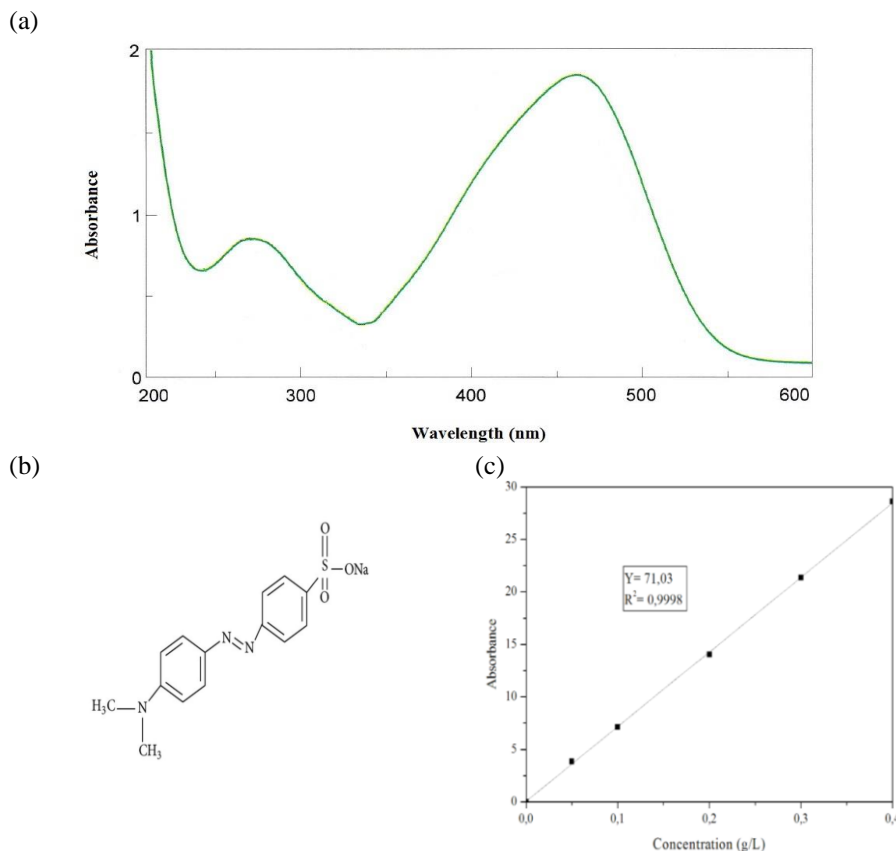


Figure 1. (a) Absorption spectra of MO (50 mg/L) before treatment, (b) azo dye structure and (c) calibration plot of solution at 460 nm.

Experimental design

Box–Behnken design and the response surface methodology were carried out in order to visualize the effects of operating parameters on the degradation of MO dye. The main selected factors were current density (X_1), initial pH (X_2) and electrolysis time (X_3). Box-Behnken design requires an experiment number according to $N = k^2 + k + cp$, where (k) is the factor number and (cp) is the replicate number of the central point ²⁵.

Table 1. Experimental ranges and levels of the independent variables.

Independent variable	Factor	Coded levels		
		-1	0	+1
Current intensity (A)	X_1	3	4	5
pH	X_2	4	7	10
Electrolysis time (min)	X_3	30	60	90

Data from the Box-Behnken design was analyzed and

fitted to a second-order polynomial model,

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$

Where Y is the response, i.e. the color removal; x_i and x_j are the independent factors, β_0 is the constant coefficient, β_i represents the coefficient that determines the influence of factor i in the response (linear term), β_{ij} refers to the effect of the interaction among variables i and j , β_{ii} is the parameter that determines the shape of the curve (quadratic effect) ^{27,28}. The experimental design, analysis of variance (ANOVA) and 3D response surface were performed using the software Minitab (version 16).

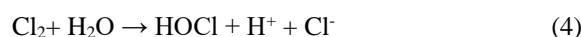
Results and Discussion

Effect of electrolyte

The effect of nature of supporting electrolyte on the dye removal efficiency was investigated. Figure 2 shows the decay of MO with electrolysis time using different supporting electrolytes (NaCl, KCl, and Na_2SO_4). It can be seen that the complete removal of

In this study, a design of 15 experiments was formulated based on 3 levels and a 3 factors experimental design, with 3 replicates at the center of the design for estimation of a pure error sum of squares ²⁶. The independent variables were coded with low level (-1), center (0) and high level (+1) as illustrated in Table 1, while color removal was the response (dependent variable). The experimental levels for each factor were selected on the basis of the preliminary results of the study.

dye is achieved in the presence of the KCl and NaCl. The graph shows that the decrease of MO concentration in the presence of KCl or NaCl is more rapid than that in the presence of Na_2SO_4 . It is well known that organic pollutants present in wastewater are primarily destroyed via indirect oxidation by strong oxidants such as hypochlorite/chlorine, generated from the anodic oxidation of chloride.



It seems that the presence of chloride plays an important role in the degradation efficiency of the EO process via the quite effective action of chlorine/hypochlorite produced during electrolysis. Therefore, the rest of experiments were performed using NaCl as supporting electrolyte.

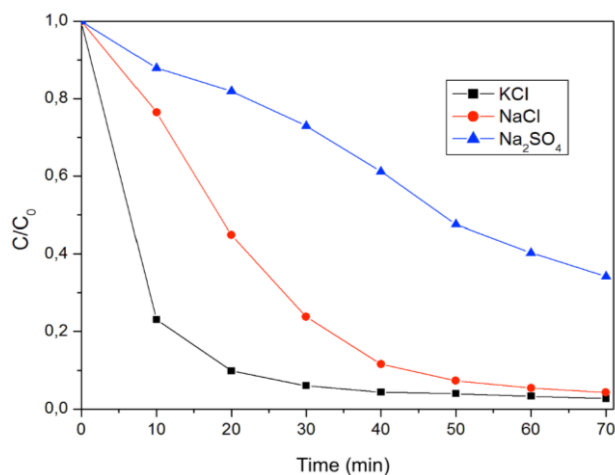


Figure 2. Influence of supporting electrolyte on MO removal ($C_0 = 50$ mg/L) at pH 7.3 using an undivided cell at 5A and different electrolytes (Na_2SO_4 ; NaCl ; KCl)

Optimization of the anodic oxidation of MO

The experimental results obtained in the trials performed with the Box-Behnken design are presented in Table 2.

Table 2. Experimental design results.

Run	Current intensity (A)	Initial pH	Electrolysis Time (min)	Coded level of variable			% MO color removal
				X ₁	X ₂	X ₃	
1	3	4	60	-1	-1	0	91.54
2	5	4	60	1	-1	0	97.97
3	3	10	60	-1	1	0	45.02
4	5	10	60	1	1	0	68.21
5	3	7	30	-1	0	-1	51.60
6	5	7	30	1	0	-1	71.78
7	3	7	90	-1	0	1	89.51
8	5	7	90	1	0	1	95.75
9	4	4	30	0	-1	-1	90.12
10	4	10	30	0	1	-1	43.03
11	4	4	90	0	-1	1	96.55
12	4	10	90	0	1	1	78.06
13	4	7	60	0	0	0	86.16
14	4	7	60	0	0	0	85.71
15	4	7	60	0	0	0	86.42

The rate of color removal varied between 43% and 97%. The second-order polynomial model (Eq. (6)) that established the correlation between the dye

removal and the independent factors (in terms of coded values) can be predicted using the coefficients given in Table 3.

$$\eta (\%) = 86.10 + 7.01 X_1 - 17.73 X_2 + 12.91 X_3 - 5.09 X_1^2 + 5.32 X_2^2 - 3.84 X_3^2 + 4.19 X_1 X_2 - 3.48 X_1 X_3 + 7.15 X_2 X_3 \quad (6)$$

The effect of initial pH on response is negative, while the effects of current intensity and electrolysis time are positive. Probability (P) values were used as a tool to evaluate the significance of each coefficient²⁹. The values of P less than 0.050 indicate that model terms have a significant influence on the dye removal efficiency (for a confidence level of 95% or more), whereas values greater than 0.100 are not significant.

Table 3 shows that the effects of initial pH and electrolysis time on color removal were highly significant with P values close to zero, followed by

the effect of current intensity (P=0.003). The factors that had relatively less effect on color removal efficiency were the interactions between electrolysis time and initial pH (P=0.012) and the quadratic terms of initial pH (P=0.039) and current intensity (P=0.045). The interaction between current intensity and electrolysis time (P = 0.117) and the quadratic terms of electrolysis time (P=0.102) were insignificant (P-value more than 0.1) and hence removed to obtain statistically significant regression model.

$$\eta (\%) = 86.10 + 7.01 X_1 - 17.73 X_2 + 12.91 X_3 - 5.09 X_1^2 + 5.322 X_2^2 + 4.19 X_1 X_2 + 7.15 B X_2 X_3 \quad (7)$$

Table 3. Estimated regression coefficients and corresponding t and P values from the data of Box-Behnken design experiment.

Term	Coefficient	Standard error	t-Value	P-Value
Constant	86.10	2.128	40.461	0.000
X ₁	7.01	1.303	5.375	0.003
X ₂	-17.73	1.303	-13.607	0.000
X ₃	12.91	1.303	9.912	0.000
X ₁ *X ₁	-5.09	1.918	-2.656	0.045
X ₂ *X ₂	-5.32	1.918	-2.772	0.039
X ₃ *X ₃	-3.84	1.918	-2.003	0.102
X ₁ *X ₂	4.19	1.843	2.276	0.072
X ₁ *X ₃	-3.48	1.843	-1.890	0.117
X ₂ *X ₃	7.15	1.843	3.880	0.012

Table 4 shows the analysis of variance (ANOVA) results from this model, where the regression model for color removal was significant with P less than 0.05. The adequacy of the model was also evaluated by developing a normal probability plot of the residuals. The residuals are normally distributed if the points on the plot follow a straight line. As observed in Figure 3, the residual behavior follows a normal distribution, which confirmed the normality

assumption. Therefore, the quadratic model built is adequate. The value of determination coefficient ($R^2=0.9860$) indicated that 98.60% of the variability observed in data can be explained by the model for color removal and this also means that only about 1.4% of the total variable was not explained by the model. The value of the adjusted determination coefficient ($R^2_{Adj}=0.9608$) is high, showing that the model was highly significant.

Table 4. Analysis of variance (ANOVA) for MO removal from Box-Behnken design.

Variation Source	Degree of freedom	Sum of square	Adjusted mean square	F-Value	P-Value
Model	9	4787.72	531.97	39.16	0.000
Residual Error	5	67.92	13.58		
Lack-of-Fit	3	67.66	22.55		
Pure Error	2	0.26	0.13		
Total	14	4855.65			

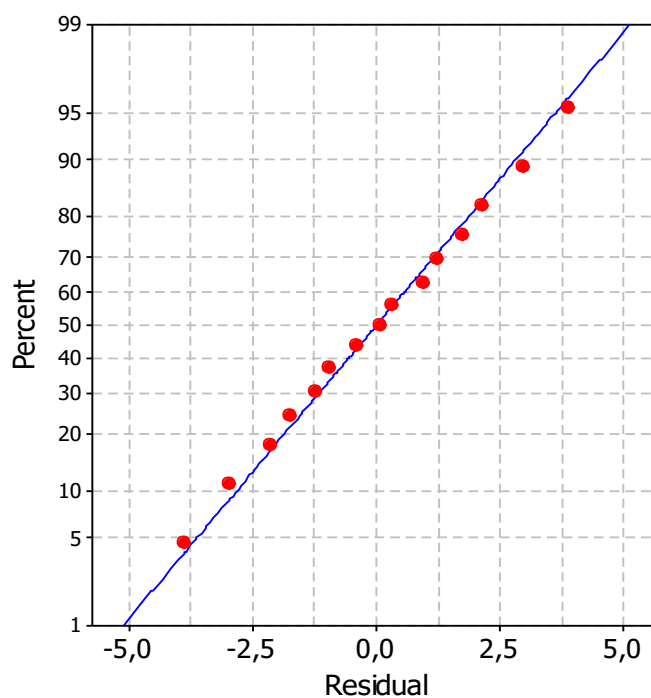


Figure 3. Normal probability plot of residuals for color removal

Pareto analysis was also used to facilitate interpretation of the results and was applied based on the following equation ^{28,29,30} :

$$P_i = \frac{b_i^2}{\sum b_i^2} \times 100 \quad (i \neq 0) \quad (8)$$

Where, b represents the related regression coefficient of the parameter. In Figure 4, the Pareto chart illustrates the percentage effect of each factor on the response. It can be seen that current intensity (7.22%) and electrolysis time (24.5%) were statically significant whereas current density (46.23%) had the

highest effect on color removal efficiency by EO process. Moreover, the interaction of pH with electrolysis time (7.51%) was also considered significant while the other terms have just a modest effect.

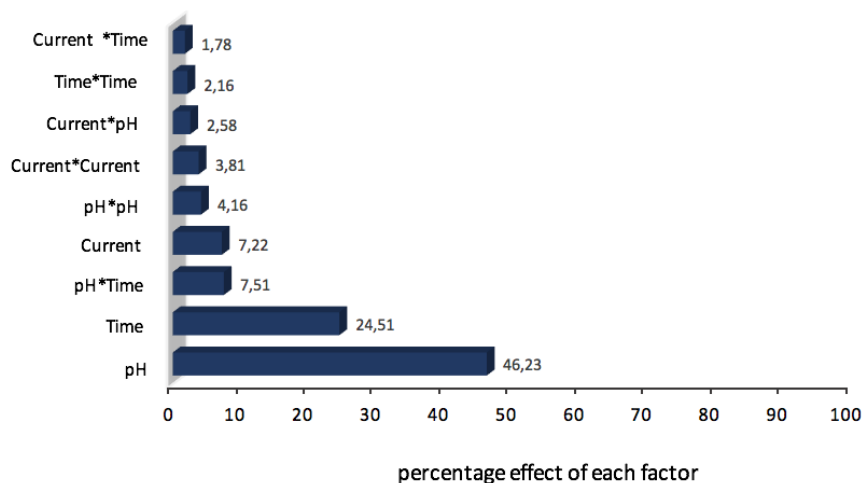


Figure 4. Pareto graphic analysis.

Response surface and contour plots for MO color removal efficiency

The response surface and contour plots were developed based on the model Eq (6), which were represented as a function of two variables, while the third was kept constant at the center level. By these plots is then possible to understand the influence of independent variables and their interactions on the response. The effect of interaction between initial solution pH and electrolysis time on color removal efficiency is shown in Figure 5, at a constant current intensity of 4A and a dye concentration of 50 mg/L. The response surface plot shows that the color removal increased considerably when prolonging electrolysis time at the highest pH of 10 and slightly at the lowest pH of 4. A similar trend was also observed for pH, but the response was sharply

increased when decreasing pH at short electrolysis time (30 min) and slightly increased at long electrolysis time (90 min). It is known that pH is an important parameter affecting the electrochemical reaction on the electrode surface³¹. The optimum pH range for dye removal was at acidic pH, which is probably due to the effect of pH on the concentrations of existing active chlorine species in the solution³². It has been reported that low pH leads to more efficient mediated oxidation of organic pollutants with these species. Chlorine is the predominant specie up to pH near 3.0, hypochlorous is produced in the pH range from 3 to 8, and hypochlorite at pH > 8.0³³. Therefore, higher rate of degradation at low pH may be due to higher oxidation potential of chlorine ($E^0 = 1.36$ V vs SHE) and hypochlorous acid ($E^0 = 1.49$ V vs SHE) rather than hypochlorite ($E^0 = 0.89$ V vs SHE).

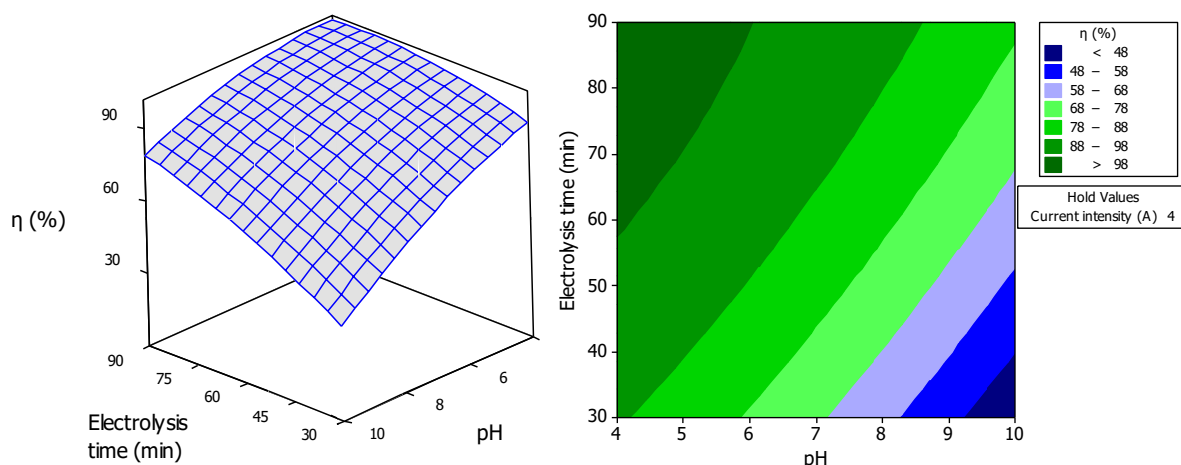


Figure 5. The response surface and contour plots of color removal efficiency as the function of electrolysis time (min) and initial solution pH.

The effect of interaction between current intensity and initial solution pH on color removal efficiency is presented in the response surface plot of Figure 6 for initial MO concentration of 50 mg/L and electrolysis

time of 60 min. As it is obvious from Figure 6, color removal efficiency increases slightly with increasing current intensity at the highest pH of 10, but it increases much more slightly at the lowest pH of 4,

from 3 to 4.25A, and then decreases from 4.25 to 5A. Moreover, a strong enhancement of the response can be observed when decreasing pH at 3A, which increase slightly at 5A. The presumed reason is that the increase of current intensity during electrooxidation enhances active chlorine generation that destroys more rapidly the conjugated chromophore system of MO, which eventually led to a greater color removal rate²³. However, the removal rate did not increase as expected with further increase

in the current density. Considering that the mediated oxidation of COD by electrogenerated active chlorine is the main process, this behavior could be related to the less production of hypochlorite, which under higher current densities, convert to a chloro oxidants of higher oxidation states (Eq. (9))³⁴. In addition, the concomitant rise in the rate of parasitic anodic oxygen evolution reaction could also contribute and negatively affect the degradation efficiency (Eq. (10))¹⁶.

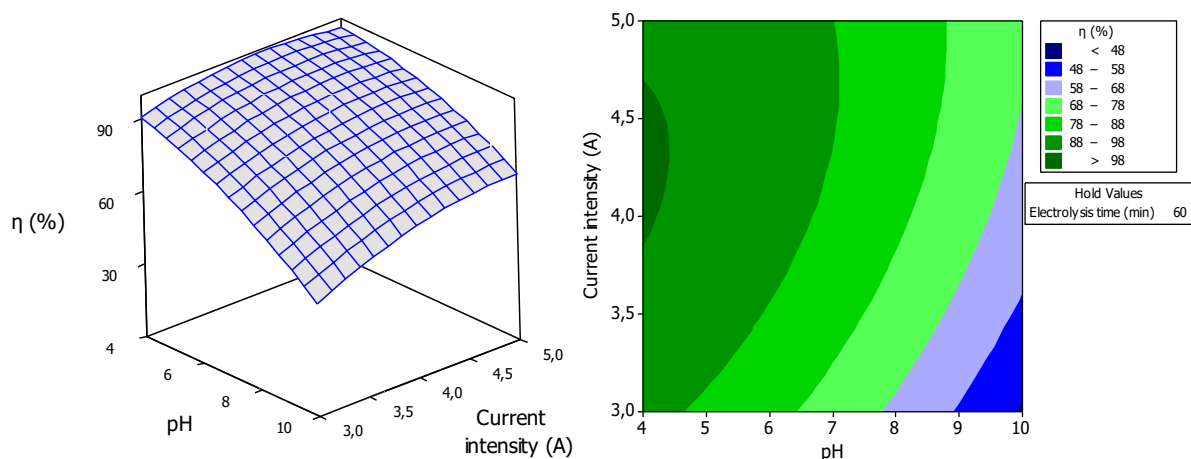
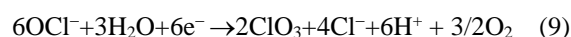


Figure 6. The response surface and contour plots of color removal efficiency as the function of initial solution pH and current intensity.

Figure 7 illustrates the response surface and contour plot for the effect of interaction between applied current intensity and electrolysis time on color removal efficiency for initial MO concentration of 50 mg/L and pH of 7. As can be seen, an increase of current intensity resulted in an increase of response considerably at the lowest electrolysis time of 30 min and slightly at the highest electrolysis time of 90 min. On the other hand, the color removal efficiency was

strongly enhanced when increasing current intensity at the lowest electrolysis time of 30 min, but rose slightly at the highest electrolysis time of 90 min from 3 to 4.6A and then slightly decreased from 4.6 to 5A. The fact that oxidation rate was not affected at increased electrolysis time can be explained by the accumulation of by-products, such as carboxylic acids, that are quite stable against further attack at Ti/Pt electrodes³⁵.

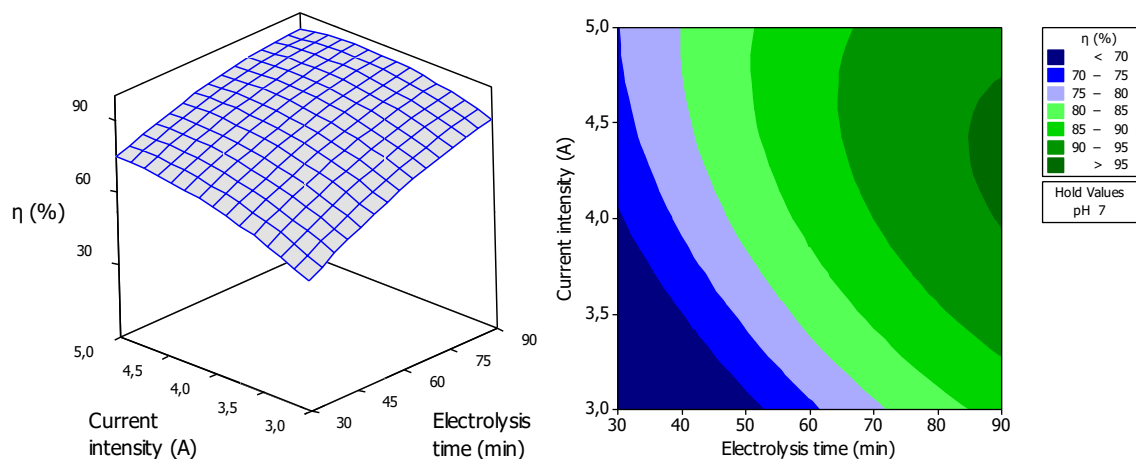


Figure 7. The response surface and contour plots of color removal efficiency as the function of electrolysis time and current intensity.

Response optimization for MO color removal

In this study, Numerical optimization was employed to determine the optimum values of the process variables for maximum MO color removal efficiency, from the model obtained using the experimental data. The optimum conditions for color removal were obtained based on RSM and desirability functions. The optimum values of the process variables for the maximum color removal efficiency were 4.6A, 4 and 65 min for current intensity, initial solution pH and electrolysis time, respectively. Under these conditions, 98.92% color removal was predicted based on desirability function of 1.00. At the optimum process parameters, the observed value of color removal efficiency was found to be 97.51% which confirms close to the predicted value. These results confirm that the strategy to optimize the color removal conditions by RSM for the treatment of MO with electrooxidation was successful.

Energy consumption

For industrial-scale applications, energy

consumption is an important parameter that can evaluate the economic feasibility of wastewater treatment using electrooxidation process. In this work, the energy consumption per 1 m³ of treated wastewater was calculated as follows:

$$E_c(\text{kWh}/\text{m}^3) = \frac{ItU_{\text{cell}}}{V_R * 3600} \quad (11)$$

Where U_{cell} is the applied voltage (V), I is the applied current (A), t is the electrolysis time (s), and V_R is the reactor volume (L). E_c values at different applied current intensities and initial pH solution are presented in Table 5. E_c is shown to be affected by the studied parameters. The energy consumption for complete MO removal increased with an increase in current intensity (from 17.18 kWh.m⁻³ at 3A to 19.69 kWh.m⁻³ at 5A), which could be attributed to the rise of cell potential and secondary reactions^{18,36}. Moreover, an increase in initial pH solution leads to higher E_c . This behavior is due to an extended electrolysis time required for total color removal at higher pH solution, which is disadvantageous for industrial-scale application.

Table 5. Energy consumption, E_c , for MO oxidation.

Parameters	Value	Color removal (%)	E (kWh.m ⁻³)
Current density (A)	3	96.58	17.18
	4	99.14	18.66
	5	98.98	19.69
pH	4	98.74	11.81
	7	98.98	19.69
	10	93.88	47.27

Conclusion

The present study has proven that the response surface methodology using Box–Behnken design is an effective technique to investigate methyl orange degradation by electrooxidation process. Three factors (current intensity, initial pH and electrolysis time) were studied. The effects of the selected parameters on the MO color removal efficiency were evaluated. The current intensity was found to be less significant than initial pH and electrolysis time. The analysis of variance (ANOVA) indicated that the proposed regression model based on Box–Behnken design was significant and could fit the experimental data well. Based on the proposed model, the optimum conditions for a maximum percentage of color removal efficiency were found to be 4.6A, pH 4 and 65min. Under these optimum values and at a dye concentration and temperature of 50 mg/L and 25 °C, respectively, a color removal rate of 98.51% can be achieved. The experimental value was in agreement with the predicted value indicating the reliability of the method used.

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