

Treatment of reactive dyebath wastewater by electrocoagulation process: Optimization and cost-estimation

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Abstract—Reactive dyestuff is commonly used in the textile industry. Reactive dyebath wastewater (RDW) was treated with a batch, monopolar, parallel lab scale electrocoagulation process (EC) having 0.042 m² effective electrode area. The effects of process parameters, such as initial pH, current density and electrolysis period on COD and color removal efficiency, were investigated by using response surface methodology (RSM). At the optimal conditions, 85.8% color and 76.9% COD removal were obtained with 1.84 €/m³ operating cost for Al electrode, while 92.0% decolorization and 80.9% COD removal were obtained with 1.56 €/m³ operating cost for an iron electrode. The iron electrode was found superior to aluminum as a sacrificial anode material in terms of COD and color removal with low cost. The cost of electrical energy, electrode, and chemical consumptions for electrocoagulation were considered to find an optimum and feasible solution. As a result, the operating cost consists of approximately 2% for energy, 28% for electrode and 70% for chemical consumption for both electrodes. Based upon the data, it is clearly seen that operating cost covers mostly for HCl to adjust pH due to the high pH and alkalinity of RDW, which was neglected in many studies. The first-order reaction kinetics with a higher slope for the color were well fitted, resulting in faster color removal than that of COD for both electrodes.

Keywords: Electrocoagulation, Kinetic, Optimization, Operating Cost, Reactive Dye

INTRODUCTION

The textile industry is characterized by intensive water consumption and wastewater generation [1]. Textile wastewater composition and discharge into the receiving water body has become a global problem both environmentally and aesthetically [2]. Colored effluents have shown toxic effects for aquatic organisms and decrease the light permeability of the aquatic environment and negatively affect natural photosynthetic activity [3-5]. Reactive dyes are widely used for cotton fabric in the textile industry. Reactive dyeing process has some negative aspects, such as low fixation efficiency (20-40%) and intensive water usage in the washing process [6,7]. Performing the dyeing process expediently with the desired removal efficiency is possible by adding some dye auxiliary chemicals, which makes difficult the treatment [8].

There are many studies on decolorization and COD from textile wastewater using treatment methods such as biological processes [9-11], chemical coagulation [12,13], electrocoagulation [14-16], membrane filtration [17,18], adsorption [19,20] and advanced oxidation processes [21-23]. Conventional methods cannot be used with confidence because they are limited due to complex wastewater character and strict discharge limit by the reason of regulation in legislation. Technically applicable, economical sustainable meth-

ods and their optimizing the operating conditions have gained huge importance for solving environmental problems arising from textile wastewater in recent years. As a result, the electrocoagulation process, which is as an alternative treatment method, has become widespread. Many researchers reported that the electrocoagulation process was applied successfully for industrial wastewater such as textile [24], paper [25], olive oil [26], dairy [27], tannery [28], slaughterhouse [29], and metal plating [30,31].

Metal ions formed by dissolution of the anode electrode (aluminum or iron) react with OH⁻ ions formed at the cathode electrode thus metal hydroxides which are insoluble and have a very high adsorption capacity. In this process, pollutants can be removed by a combination of coagulation, adsorption, flotation, and precipitation [32]. Iron and aluminum electrodes are constituted prevalently due to being cheap, easily accessible and having proven applicability [33]. Electrocoagulation process can be designed either horizontally or vertically according to the way where the electrode plates are placed, as single-pole parallel, single-pole series and bipolar as to the connection type [34-38]. pH, current density and efficiency, electrode connection type, electrode material, inner-electrode distance, temperature, and electrolysis time become important factors on process efficiency to reveal the pollutant removal mechanism at electrocoagulation process [29,39-41].

Metal hydroxide types, which occur in the electrocoagulation process and play an important role in pollutant removal, and floc load case (positive in acidic conditions, negative in alkali conditions) change according to medium pH [42]. In the electrocoagu-

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Table 1. Chemical composition of the simulated RDW and its characteristics

Ingredients			RDW characteristics			
Reactive Red 195 (RR 195)	mg/L	50	Color	436 nm	cm ⁻¹	0.807 (±0.04)
Reactive Yellow 145 (RY 145)		42		525 nm		1.268 (±0.07)
Reactive Blue 221 (RB 221)		77		620 nm		0.932 (±0.05)
Sequestering Agent	g/L	0.60	COD		mg/L	416 (±12)
Anti-creasing Agent		0.25	Chloride			16 772 (±124)
Sodium Chloride		30.00	Alkalinity		mg/L CaCO ₃	14 915 (±163)
Sodium Carbonate		15.00	pH		-	11.39 (±0.07)

lation process, the medium pH is a continuous variable during treatment. Thus, the initial pH value must be controlled and should be adjusted if necessary [43].

Solved metal ion amounts (metal flocs) are controlled by applied current and electrolysis time via Faraday law. If the potential is sufficiently high in the galvanic cell, secondary reactions may occur at the anode surface [44]. If the electrolysis time is high more than necessary, additional treatment cost and increased in produced sludge will be observed in electrocoagulation cell [45].

Most of the studies focus on the traditional approach to optimize the treatment process by using electrocoagulation [29,46,47]. This approach does not consider the cross effects of independent variables and it is time-consuming, which leads to poor optimization [48]. The optimization of operating conditions is of great importance in terms of sustainability and producing economical solutions. RSM is an applicable statistical method to optimize color removal from textile wastewater. A combination of mathematical and statistical techniques was developed to produce an adequate relation between dependent and independent variables with a limited experimental run [49-52]. Analysis of variance (ANOVA) is used to determine the significance of the independent process variables and the adequacy of the models.

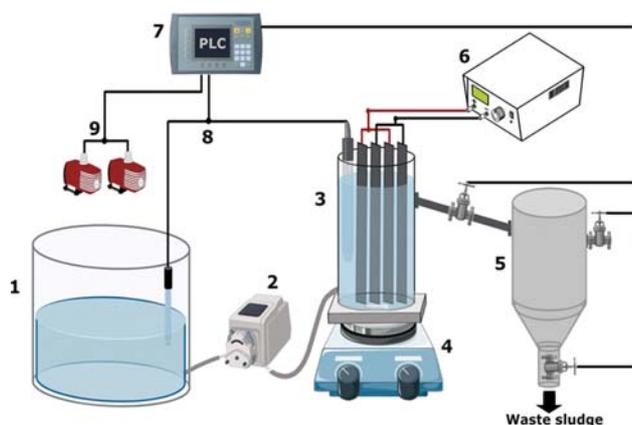
There are many previous studies on dye removal of textile wastewaters by EC; however, limited research is available about the effect of dyeing auxiliaries on EC performance. In addition, the determination of the total operating cost considering the cost of acid consumption for pH adjustment is very important, when textile wastewater is produced by reactive dyeing due to its alkaline characteristic. The objective of this study was to find optimum conditions to remove color and COD from RDW with cost-effective approach using RSM.

MATERIALS AND METHODS

1. Reactive Dye bath Wastewater (RDW)

The reactive dyes and auxiliary chemicals used in this study were supplied from a local factory that manufactures integrated textiles. The simulated reactive dye bath wastewater (RDW) was prepared daily based on the cotton fiber dyeing procedure of the textile plant, including three reactive dyes and auxiliary chemicals such as NaCl, Na₂CO₃, sequestering and anti-creasing agents.

20% of the dyestuffs and 100% of dye auxiliaries is considered to remain in the exhausted RDW [53]. Therefore, a mixture of dyestuffs and dye auxiliaries was dissolved in deionized water and

**Fig. 1. Schematic view of experimental setup.**

- | | |
|---------------------|----------------------------|
| 1. Feeding tank | 6. DC power supply |
| 2. Peristaltic pump | 7. PLC |
| 3. EC | 8. Multi-parameter sensors |
| 4. Magnetic stirrer | 9. Acid/base dosing pumps |
| 5. Sedimentation | |

boiled for 3 h. Later on, the mixture was cooled to room temperature for overnight. Chemical components and quantities used for preparation simulated RDW and wastewater characteristics are summarized in Table 1.

2. Experimental Setup and Procedure

Experimental studies were carried out on a 30 cm high, 10 cm diameter cylindrical EC reactor made of polyethylene with an effective volume of 2.5 L at room temperature. Four parallel monopolar electrodes (aluminum or iron) with an active surface area of 0.042 cm² were placed vertically at a distance of 5 mm in the reactor. The current and voltage control is provided by a digital DC power supply (0-30 V, 0-10 A, EA Elektro-Automatic) (Fig. 1) [54].

EC was operated in a fed-batch mode. Appropriate electrodes (aluminum or iron) were placed in the EC unit and then 2.5 L of RDW, of which initial pH was adjusted to the desired value by using HCl and NaOH, was fed to the EC unit via the peristaltic pump. Aqueous phase in the EC reactor was stirred at 200 rpm.

After each run, samples were taken from the supernatant to monitor color and COD removal efficiencies. Samples settled down for 30 min and passed through glass fiber filters (pore size 0.45 μm). To determine mass lost for electrode consumption, electrodes were washed and cleaned based on the procedure of published previous studies [14,24].

Table 2. The process variables, their coded levels and actual values

Variables	Code	Coded levels				
		-1.68 (- α)	-1	0	1	1.68 (+ α)
		Actual values				
pH	X_1	3.3 (Al)	4.0 (Al)	5.0 (Al)	6.0 (Al)	6.7 (Al)
		4.0 (Fe)	5.0 (Fe)	6.5 (Fe)	8.0 (Fe)	9.0 (Fe)
Current Density (A/m ²)	X_2	29.7	45	67.5	90	105.3
Electrolysis Time (min)	X_3	4.8	15	30	45	55.2

3. Experimental Design

Design Expert 8.0.6 software was applied for the experimental design and data analysis. In the present study, the three most important operating variables such as initial pH, current density (CD, A/m²) and electrolysis time (t, min) were optimized. Eight-star points ($\alpha=\pm 1$), six axial points ($\alpha=\pm 1.68$) and three replicates at the center point ($\alpha=0$) were chosen as experimental points for the optimization of EC used for the color and COD removal efficiencies (Table 2). The ranges of experimental variables were determined based on preliminary experimental studies and the values given in the literature [55-57].

Central composite design (CCD) was used to demonstrate the relationship between the controllable input variables and responses. Chosen responses were obtained from the lowest-order polynomial models based on result of the runs. For evaluation of experimental data, the response variable was fitted by a second-order quadratic polynomial model given in Eq. (1).

$$Y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n a_{ii} x_i^2 + \sum_{i < j}^n \sum_j a_{ij} x_i x_j + \varepsilon \quad (1)$$

where a_0 , a_i , a_{ii} , a_{ij} represent the constant, linear, quadratic and interaction coefficient; x_i and x_j represent the independent coded variables and ε is the random error.

4. Analytical Procedure

Analytical grade chemicals were used in this study except dye auxiliary and dyestuffs. pH was measured by a pH meter (WTW 340i) based on ISO 10523. Decolorization was determined based on absorbance measurements. The color was measured according to standards of European Norm EN ISO 7887 using a UV/Vis spectrophotometer (Hach Lange DR 5000 model UV-Vis) having a path length of 10 mm quartz cuvettes at three wavelengths representing yellow (436 nm), red (525 nm) and blue (620 nm) color. The COD analysis was based on the German Standard (DIN 38 409, H 41-2) due to the high chloride content of the treated samples. This method is mandatory to remove chloride interference by using HCl absorber. Measurements of alkalinity and chloride ion concentrations were also performed by the standard methods according to (SM 2320 B) and (SM 4500-Cl⁻ B), respectively.

5. Kinetic Assessment

The samples were taken from the EC at specified time intervals to follow changes in color and COD removal efficiencies for kinetic studies at optimum conditions. The substrate (COD and color) removal rate can be expressed as a first-order kinetic model according to Eq. (2) [7].

$$\frac{dC_t}{dt} = -kC_t \quad (2)$$

where C_t remaining COD (mgL⁻¹) or color (absorbance, cm⁻¹) at any electrolysis time t (min) and k is kinetic constant (min⁻¹). According to the Eq. (2), a plot of $\ln(C_0/C)$ against t will give a straight line with a slope of k .

6. Operating Cost

The total operating cost of treated RDW can be calculated by considering three parameters (energy, electrode material, and chemical consumption) as a major cost component by using Eq. (3) [2].

$$\text{Operating Cost} = \alpha \cdot C_{\text{Energy}} + \beta \cdot C_{\text{Electrode}} + \gamma \cdot C_{\text{Chemical}} \quad (3)$$

where C_{Energy} , $C_{\text{Electrode}}$ and C_{Chemical} is energy, electrode and the chemical consumption, respectively. α is cost of the electrical energy (0.072 €/kWh) [58], β is cost of the electrode materials (1.65 €/kg for Al and 0.85 €/kg for Fe) [59], and γ is the cost of the chemical (0.05 €/L for HCl) according to the Turkish market [60].

Energy consumption (C_{Energy}) was determined using Eq. (4) [61],

$$C_{\text{Energy}} = \frac{U \cdot I \cdot t}{V} \quad (4)$$

where C_{Energy} , I , U , t , and V is the energy consumption (kWh/m³), the current (A), the potential (V), the electrolysis time (h) and the volume of treated wastewater (m³), respectively.

$C_{\text{Electrode}}$ is determined by measuring the weight loss of the electrodes because theoretical dissolution is not an actual situation. Actual weight loss changes were based on process dynamics and reactions on the anode surface. The current efficiency was determined based on a previous study [43] (Table 3). C_{Chemical} is calculated based on the cost of acid (HCl) consumption during the pH adjustment.

RESULTS AND DISCUSSION

1. Model Fitting and Validation

To determine the combined effect of process variables such as initial pH, current density and time on COD and color removal efficiencies, experiments were conducted for different combinations of these independent variables by using CCD design to reduce the number of experiments. A total of 17 experiments for each pair of aluminum and iron electrodes were performed as Table 3. The experiments were performed in a random order to avoid systematic error.

The experimental findings obtained from CCD were evaluated by ANOVA in the confidence level of 95% to check the fitting of the experimental values to the predicted ones. The order of the polynomial model should be kept as low as possible. A second-

Table 3. The coded design of experiments and actual responses for EC using Al and Fe electrodes

Run	Variables			Response for Al electrodes							Response for iron electrodes						
	X ₁	X ₂	X ₃	CR λ ₅₂₅ (%)	COD (%)	CE (%)	C _{Energy} (€/m ³)	C _{Electrode} (€/m ³)	C _{Chemical} (€/m ³)	Total cost (€/m ³)	CR λ ₅₂₅ (%)	COD (%)	CE (%)	C _{Energy} (€/m ³)	C _{Electrode} (€/m ³)	C _{Chemical} (€/m ³)	Total cost (€/m ³)
1	-1	-1	-1	65.69	58.6	169	0.01	0.22	1.34	1.57	74.6	74.3	104	0.01	0.18	1.10	1.29
2	1	-1	-1	39.67	60.1	142	0.01	0.19	1.18	1.38	61.7	62.5	104	0.01	0.18	0.88	1.07
3	-1	1	-1	69.95	61.7	162	0.03	0.42	1.34	1.79	81.2	78.4	107	0.03	0.37	1.30	1.70
4	1	1	-1	51.18	63.2	140	0.03	0.37	1.18	1.58	73.5	68.3	105	0.03	0.36	0.88	1.27
5	-1	-1	1	70.27	64.8	161	0.04	0.63	1.34	2.01	83.5	81.5	107	0.03	0.55	1.30	1.88
6	1	-1	1	47.32	67.5	140	0.04	0.55	1.18	1.77	76.3	67.3	98	0.03	0.50	0.88	1.41
7	-1	1	1	83.04	68.6	159	0.09	1.26	1.34	2.69	86.4	82.2	105	0.08	1.08	1.30	2.46
8	1	1	1	68.45	71.8	144	0.09	1.10	1.18	2.37	80.7	69.5	101	0.08	1.03	0.88	2.00
9	-1.68	0	0	71.21	53.4	182	0.04	0.70	1.36	2.10	67.8	70.9	103	0.04	0.53	1.36	1.93
10	1.68	0	0	35.65	62.5	136	0.04	0.53	1.06	1.63	58.4	57.7	107	0.04	0.53	0.66	1.23
11	0	-1.68	0	74.76	69.2	152	0.01	0.26	1.30	1.57	82.8	78.4	114	0.01	0.26	1.10	1.37
12	0	1.68	0	83.36	77.7	156	0.08	0.96	1.18	2.22	92.6	84.9	102	0.07	0.81	1.10	1.98
13	0	0	-1.68	57.18	61.3	155	0.01	0.10	1.30	1.41	71.2	66.3	106	0.01	0.09	1.10	1.19
14	0	0	1.68	84.62	78.4	147	0.08	1.08	1.30	2.45	95.1	82.4	98	0.07	0.92	1.10	2.09
15	0	0	0	84.35	76.2	146	0.04	0.57	1.30	1.91	92.4	82.0	108	0.04	0.55	1.10	1.69
16	0	0	0	88.25	78.2	151	0.04	0.58	1.30	1.92	95.4	80.5	107	0.04	0.55	1.10	1.68
17	0	0	0	88.41	78.1	153	0.04	0.61	1.30	1.95	93.6	80.5	103	0.04	0.53	1.10	1.67

CR λ₅₂₅: Color removal at 525 nm; CE: Current efficiency; C_{Energy}: Electrical consumption; C_{Electrode}: Electrode consumption; C_{Chemical}: Chemical consumption

order polynomial equation was fitted to CCD model. The fitted regression models obtained in terms of coded factors are used to investigate the effects of process variables on the EC. The non-significant terms are excluded by backward elimination procedure and only statistically significant terms were used in the models. The proposed models are presented in Eqs. (5) and (6) for the Al electrode and Eqs. (7) and (8) for Fe electrode:

$$Y_{1,CR_{525nm}} = +87.31 - 10.41x_1 + 4.70x_2 + 6.50x_3 - 12.91x_1^2 - 3.85x_2^2 - 6.73x_3^2 \quad (5)$$

$$Y_{2,COD} = +77.62 + 1.77x_1 + 2.09x_2 + 4.24x_3 - 7.34x_1^2 - 1.86x_2^2 - 3.13x_3^2 \quad (6)$$

$$Y_{3,CR_{525nm}} = +93.79 - 3.61x_1 + 3.09x_2 + 5.57x_3 - 10.81x_1^2 - 2.11x_2^2 - 3.72x_3^2 \quad (7)$$

$$Y_{4,COD} = +81.30 - 5.20x_1 + 1.74x_2 + 3.23x_3 - 5.97x_1^2 - 2.42x_3^2 \quad (8)$$

Positive and negative signs in equations refer to a synergistic or antagonistic effect of each term on a response. The proposed models for Fe and Al electrodes fitted very well to the experimental data so that it could be used to navigate the design space according to the descriptive statistical analysis given in Table 4. The proposed model results indicate that all models are significant, lack of fits are non-significant (p-value is less than 0.05).

Table 4. ANOVA results for response parameters for Al and Fe electrodes

Response	Elc	R ²	R ² _{adj}	Pred-R ²	SD	CV	PRESS	F-value	Prob>F	AP
CR λ ₅₂₅ (%)	Al	0.95	0.92	0.82	4.79	7.01	838.71	31.51	<0.0001	17.56
COD (%)		0.97	0.95	0.86	1.81	2.68	143.11	49.08	<0.0001	20.38
C _{Energy} (€/m ³)		0.99	0.99	0.99	0.0008	1.80	0.0000	4873.6	<0.0001	205.77
C _{Electrode} (€/m ³)		0.99	0.99	0.99	0.0212	3.55	0.0136	815.09	<0.0001	91.27
C _{Chemical} (€/m ³)		0.96	0.94	0.82	0.0207	1.64	0.0210	65.37	<0.0001	25.13
Total cost (€/m ³)		0.99	0.99	0.99	0.0339	1.78	0.0292	483.52	<0.0001	70.10
CR λ ₅₂₅ (%)		Fe	0.97	0.95	0.90	2.54	3.15	207.96	53.7	<0.0001
COD (%)	0.95		0.93	0.82	2.18	2.92	193.73	42.5	<0.0001	22.06
C _{Energy} (€/m ³)	0.99		0.99	0.99	0.0006	1.49	0.000	7166.0	<0.0001	250.26
C _{Electrode} (€/m ³)	0.99		0.99	0.99	0.0216	4.07	0.0120	971.6	<0.0001	90.10
C _{Chemical} (€/m ³)	0.92		0.91	0.89	0.055	5.12	0.0639	171.1	<0.0001	34.71
Total cost (€/m ³)	0.98		0.97	0.95	0.06	3.78	0.1070	149.87	<0.0001	41.35

SD: Standard deviation, CV: Coefficient of variance, PRESS: Predicted residual error sum of squares, AP: Adequate precision, P: Probability of error

The large value of F indicates that most of the variation in the response (COD and color removal efficiencies) could be explained by the proposed model. The $\text{Prob}>F$ is less than 0.05 indicates that the model is considered to be strongly statistically significant [62]. Between 0.05 and 0.10 it is marginally significant. Although the larger F values, when the number of design variables is large, it is more appropriate to look at the value of R^2_{adjusted} because R^2 always increases as the number of terms in the model is increased, while R^2_{adjusted} actually decreases if non-significant model terms are added. Even in the worst case, the value of correlation coefficient indicates ($R^2=0.92$ for a chemical cost ($\text{€}/\text{m}^3$) in use of Fe electrode) that only less than 8% of the total variation could not be explained by our model. Olmez [63] put forward that R^2 must be at greater than 0.80 to a good fit. In this study, the values of R^2_{adjusted} for Al and Fe electrodes are 0.95 for COD, 0.93 for CR λ_{525} and 0.95 for COD, 0.93 for CR λ_{525} , respectively. An R^2_{adjusted} close to the R^2 values (the difference was less than 0.2 for all models) ensures a satisfactory adjustment of the proposed models to the experimental data [64].

Based on the data given in Table 2, most of the CV values were less than 5% and also the pure error was very small for all responses, which showed very good precision and reliability for the experiments [61]. The desired value of adequate precision (AP) must be 4 or more [50].

The adequacy of models was confirmed by constructing diagnostic plots (Fig. 2) using predicted data versus actual data obtained from the experimental run. An adequate agreement between the actual value and the predicted data was obtained from the fitted regression models.

2. Effect of Operating Parameters and Optimization

The response surface plots for the variations of COD and color

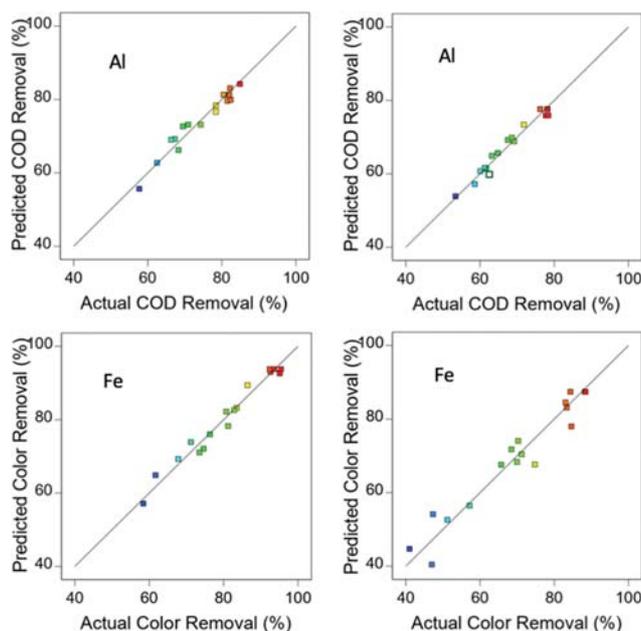


Fig. 2. Diagnostic plots for the model adequacy.

removal efficiencies according to the important parameters such as initial pH, current density, and electrolysis time fitted to the data obtained from the CCD experiments are presented in Fig. 3 (for Al electrode) and Fig. 3 (for Fe electrode). In each plot, two variables were demonstrated in one 3D surface plots, while the other process variable was kept at an optimum level ($\alpha=0$).

Color and COD can be removed from the RDW by either complexation or electrostatic attraction followed by coagulation in EC.

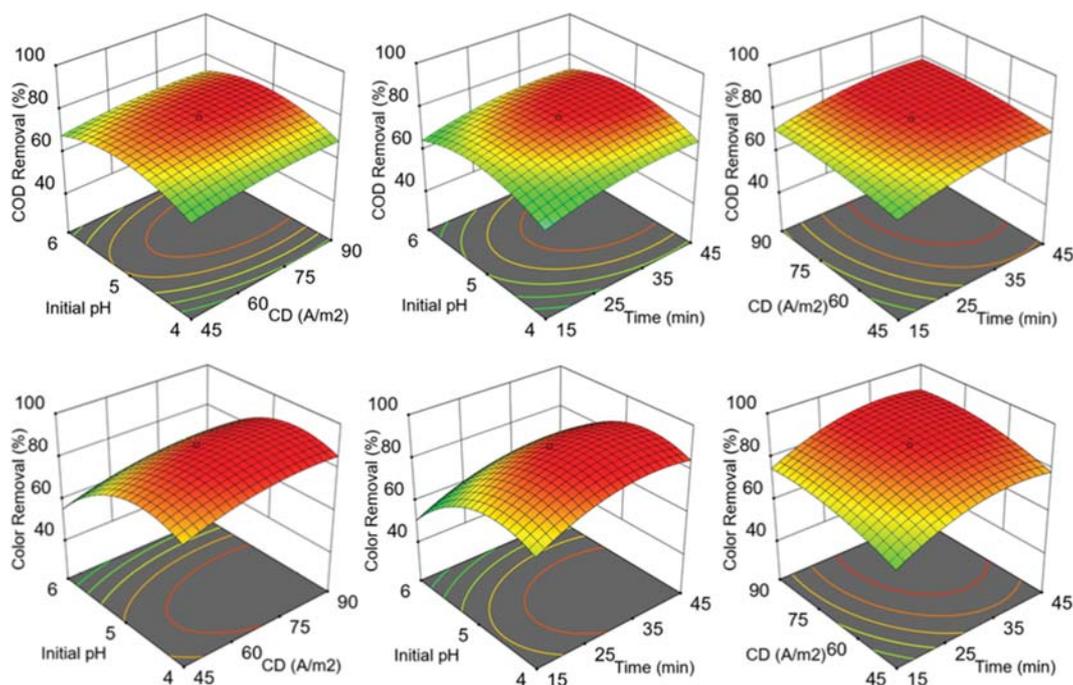


Fig. 3. Effects of pH, current density, and electrolysis time on COD and color removal by using Al electrode.

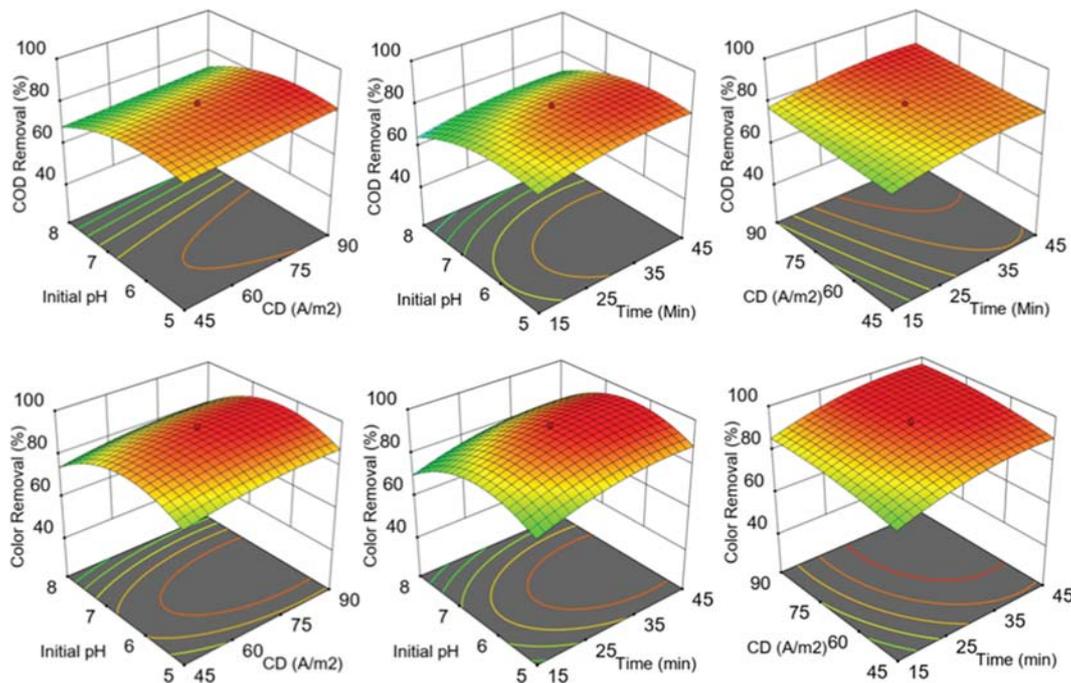


Fig. 4. Effects of pH, current density, and electrolysis time on color and COD removal by using Fe electrode.

It is clearly seen from Fig. 3 and Fig. 4 that the effects of initial pH, current density and electrolysis time were significant on COD and color removal for both electrode type. The formation of monomeric and polymeric species having different absorbing capacity was controlled by pH of aqueous phase. The efficiencies of color and COD removal were found to increase with increasing pH up to 5.0 and 6.5 for Al and Fe electrode, respectively. Thereafter, there was a drastic decrease in the color and COD removal efficiencies for both electrodes. Bayramoglu et al. [65] reported that optimum pH depends on electrode type in the treatment of textile wastewater, and they suggested the optimum pH was 5 and 7 for aluminum and iron electrode, respectively. The amount of floc production is a function of current density and electrolysis time. As a general, an increase in current density and electrolysis time resulted in enhanced COD and color removal in all runs. For example, when the current density was applied 45 A/m² to the Fe electrodes for 15 minutes, the color and COD removal were 79% and 74%, respectively. Both the current density and electrolysis time were increased to 80 A/m² and 40 minutes, and the removal efficiencies were increased by approximately 20% for color and COD. In one of the previous studies, maximum Reactive Red 43 (RR43) removal efficiency for iron electrode was given 99% for highest current density (35 A/m²) and electrolysis time (24 min) [66].

Based on our results, iron electrode can be preferred to aluminum due to better color and COD removal. For example, when the aluminum electrode was used, the highest color and COD removal efficiencies were 88.41% and 78.4%, respectively. However, if the iron electrode was used, the highest color and COD removal efficiencies were 95.4% and 84.9%, respectively.

Optimization is used to determine the optimum values of process variables to reach maximum color and COD removal in terms of cost-effective approach for both electrodes. Operating cost estimation and minimization is an important aspect of wastewater treatment [67]. Electrical energy, electrode, and chemical consumption during the electrocoagulation have to be considered to find an optimum and feasible solution. Maximized COD and color removal, minimized operating cost were selected to find an optimum solution by assigning the same weight and the same importance to each of the responses. Based on the desirability functions obtained by model fitting optimum conditions were determined as given in Table 5.

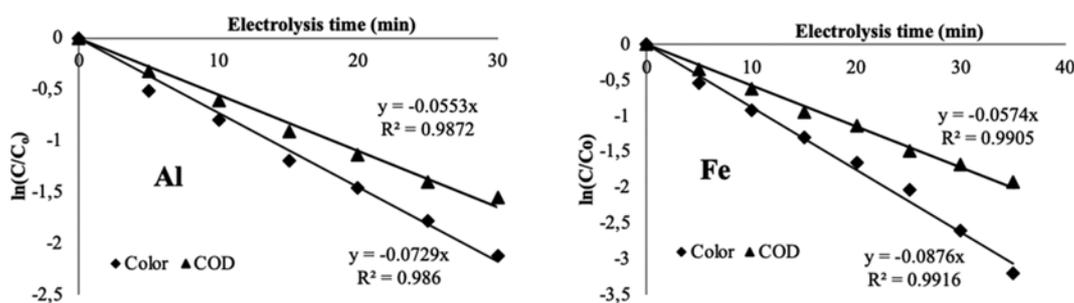
At the optimum, energy consumption (0.502 kWh/m³ equal to 0.036 €/m³ for Al and 0.403 kWh/m³ equal to 0.029 €/m³ for Fe), electrode consumption (0.328 kg/m³ equal to 0.542 €/m³ for Al and 0.530 kg/m³ equal to 0.451 €/m³ for Fe) and chemical consumption (21.82 L/m³ equal to 1.091 €/m³ for Al and 26.06 L/m³ equal

Table 5. Optimization results

	Operational conditions			Responses		
	X ₁	X ₂	X ₃	Color removal (%)	COD removal (%)	Operating cost (€/m ³)
Al	5.01	64.00	28.5	85.8	76.9	1.84
Fe	6.35	55.3	30.5	92.0	80.9	1.56

Table 6. Model validation and confirmation test results

Run	Independent variables			Color removal (%)			COD removal (%)		
	X ₁	X ₂	X ₃	Exp.	Model	Error (%)	Exp.	Model	Error (%)
Al Electrode									
1	4.7	75	25	88.17	87.49	-0.77	74.28	75.16	+1.18
2	4.0	50	15	67.27	65.59	-2.49	57.21	58.40	+2.08
3	5.2	90	20	76.22	78.23	+2.63	77.40	73.71	-4.76
4	6.0	40	30	49.58	52.50	+5.88	65.63	66.73	+1.67
5	4.4	60	40	91.25	88.25	-3.29	72.11	74.45	+3.25
Fe Electrode									
1	6.1	70	20	87.70	88.93	+1.40	82.45	78.89	-4.32
2	7.5	55	30	85.17	84.20	-1.13	71.39	73.86	+3.46
3	5.0	60	25	86.36	83.06	-3.82	76.20	78.22	+2.65
4	8.0	90	40	77.99	82.41	+5.66	68.51	72.35	+5.61
5	5.0	40	30	76.74	79.66	+3.81	81.01	79.01	-2.47

**Fig. 5. The first order kinetics for color and COD removal for Al and Fe electrodes.**

to $\text{€}/\text{m}^3$ for Fe) were determined. The use of aluminum electrodes in EC studies requires more energy and electrode consumption, resulting in high treatment cost. And also, Al electrode gives better color and COD removal relatively lower pH when compared with an iron electrode. As a result, it surprising that operating cost consists of approximately 2% for energy, 28% for electrode and 70% for chemical consumption for both electrodes. Based upon the data, it is clear that operating cost covers mostly for HCl utilization to adjust pH due to the high pH and alkalinity of RDW which was neglected in many studies.

As a result, the iron electrode is found superior to aluminum as a sacrificial anode material in terms of COD and color removal efficiencies with low cost. Our findings are compatible with previous studies [39,55]. Theoretical results predicted by RSM after multi-objective numerical optimization were used to confirm the adequacy and validity of quadratic models. For the validation test, operational conditions were randomly selected from lower to upper limit values of independent variables (Table 6).

The results show that COD and color removal efficiencies obtained by experimental studies in optimized conditions were found to be very close to that predicted by the model. This is confirming that the RSM could be adequately used to optimize the process variables.

3. Kinetic Studies

Kinetic studies were performed under optimum operating con-

ditions. The color and COD removal efficiencies depend on the amount of metal ions produced on the anode surface. Color and COD removal were followed by samples taken from the EC at 5-minute intervals. The first-order reaction kinetics with a higher slope for the color were well fitted, resulting in faster color removal than that of COD for both electrodes (Fig. 5).

The first-order color removal kinetic constants were determined as $7.29 \times 10^{-2} \text{ min}^{-1}$ and $8.76 \times 10^{-2} \text{ min}^{-1}$ for Al and Fe electrodes, respectively. Similarly, Dalvand et al. [68] reported that the decolorization rate kinetic constant for Reactive Red 198 was $14.2 \times 10^{-2} \text{ min}^{-1}$. Whereas, the first order COD removal rate constants were determined as $5.53 \times 10^{-2} \text{ min}^{-1}$ and $5.74 \times 10^{-2} \text{ min}^{-1}$ for Al and Fe electrodes, respectively. When the kinetic rate constants are compared, color is removed more quickly than COD for both electrodes.

CONCLUSION

Laboratory scale electrocoagulation process optimized by RSM using Fe and Al electrodes was used to investigate COD and color removal from simulated reactive dyebath wastewater. The proposed models, both Fe and Al electrodes, fitted very well to the experimental data. For Fe electrodes, color and COD removal were 92.0% and 80.9%, respectively at optimum conditions. The removal efficiencies for Al electrodes dropped approximately 6% for color and

4% for COD removal. Operating cost was mainly affected by high alkalinity of RDW, which was found as 1.56 €/m³ for Fe and 1.84 €/m³ for Al electrodes. A 70% of the operating cost covers pH adjustment for the electrodes since operation conditions requires low pHs for both electrodes. Based on our kinetic studies, the color removal rate was higher than COD for both electrodes.

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REFERENCES

1. E. Alkaya and G. N. Demirel, *J. Clean. Prod.*, **65**, 595 (2014).
2. O. T. Can, M. Kobya, E. Demirbas and M. Bayramoglu, *Chemosphere*, **62**, 181 (2006).
3. S. K. A. Solmaz, A. Birgul, G. E. Ustun and T. Yonar, *Color. Technol.*, **122**, 102 (2006).
4. G. A. Borges, L. P. Silva, J. A. Penido, L. R. de Lemos, A. B. Mageste and G. D. Rodrigues, *J. Environ. Manage.*, **183**, 196 (2016).
5. S. Coruh and S. Elevli, *Global. Nest. J.*, **17**, 93 (2015).
6. A. Faki, M. Turan, O. Ozdemir and A. Z. Turan, *Ind. Eng. Chem. Res.*, **47**, 6999 (2008).
7. I. Kabdasli, B. Vardar, I. Arslan-Alaton and O. Tunay, *Chem. Eng. J.*, **148**, 89 (2009).
8. I. Arslan-Alaton and I. Alaton, *Ecotox. Environ. Safe*, **68**, 98 (2007).
9. H. Kocyigit and A. Ugurlu, *Global. Nest. J.*, **17**, 210 (2015).
10. P. I. M. Firmino, M. E. R. Da Silva, F. S. B. Mota and A. B. dos Santos, *Braz. J. Chem. Eng.*, **28**, 617 (2011).
11. H. O. Park, S. Oh, R. Bade and W. S. Shin, *Korean J. Chem. Eng.*, **27**, 893 (2010).
12. W. Chu, *Water. Res.*, **35**, 3147 (2001).
13. B. S. Ramavandi and S. Farjadfard, *Korean J. Chem. Eng.*, **31**, 81 (2014).
14. M. Kobya, E. Demirbas, O. T. Can and M. Bayramoglu, *J. Hazard. Mater.*, **132**, 183 (2006).
15. M. M. Hossain, M. I. Mahmud, M. S. Parvez and H. M. Cho, *Environ. Eng. Res.*, **18**, 157 (2013).
16. A. Cerqueira, C. Russo and M. R. C. Marques, *Braz. J. Chem. Eng.*, **26**, 659 (2009).
17. E. Sahinkaya, A. Sahin, A. Yurtsever and M. Kitis, *J. Environ. Manage.*, **222**, 420 (2018).
18. I. Koyuncu, D. Topacik and E. Yuksel, *Sep. Purif. Technol.*, **36**, 77 (2004).
19. A. S. Ozcan, B. Erdem and A. Ozcan, *J. Colloid Interface Sci.*, **280**, 44 (2004).
20. Z. Aksu and S. Tezer, *Process Biochem.*, **40**, 1347 (2005).
21. L. Szyrkowicz, C. Juzzolino and S. N. Kaul, *Water. Res.*, **35**, 2129 (2001).
22. A. Bedolla-Guzman, R. Ferial-Reyes, S. Gutierrez-Granados and J. M. Peralta-Hernández, *Environ. Sci. Pollut. R.*, **24**, 12506 (2017).
23. M. Tichonovas, E. Krugly, D. Jankunaite, V. Racys and D. Martuzevicius, *Environ. Sci. Pollut. R.*, **24**, 17584 (2017).
24. I. Arslan-Alaton, M. Kobya, A. Akyol and M. Bayramoglu, *Color. Technol.*, **125**, 234 (2009).
25. M. Ugurlu, A. Gurses, C. Dogar and M. Yalcin, *J. Environ. Manage.*, **87**, 420 (2008).
26. H. Inan, A. Dimiglo, H. Simsek and M. Karpuzcu, *Sep. Purif. Technol.*, **36**, 23 (2004).
27. U. Tezcan-Un, A. Kandemir, N. Erginel and S. E. Ocal, *J. Environ. Manage.*, **146**, 245 (2014).
28. O. Apaydin, U. Kurt and M. T. Gonullu, *Global Nest J.*, **11**, 546 (2009).
29. M. Bayramoglu, M. Kobya, M. Eyvaz and E. Senturk, *Sep. Purif. Technol.*, **51**, 404 (2006).
30. F. Akbal and S. Camci, *Desalination*, **269**, 214 (2011).
31. U. Tezcan-Un, S. E. Onpeker and E. Ozel, *J. Environ. Manage.*, **200**, 196 (2017).
32. P. K. Holt, G. W. Barton, M. Wark and C. A. Mitchell, *Colloids Surf. A Physicochem. Eng. Asp.*, **211**, 233 (2002).
33. M. Kobya and E. Demirbas, *J. Water Process Eng.*, **8**, 64 (2000).
34. Y. O. A. Fouad, A. H. Konsowa, H. A. Farag and G. H. Sedahmed, *Chem. Eng. J.*, **145**, 436 (2009).
35. M. A. Ubale and V. D. Salkar, *Korean J. Chem. Eng.*, **34**, 1044 (2017).
36. M. Asselin, P. Drogui, H. Benmoussa and J. F. Blais, *Chemosphere*, **72**, 1727 (2008).
37. V. Khatibikamal, A. Torabian, F. Janpoor and G. Hoshyaripour, *J. Hazard. Mater.*, **179**, 276 (2010).
38. T. Coskun, F. Ilhan, N. M. Demir, E. Debik and U. Kurt, *Environ. Technol.*, **33**, 801 (2012).
39. M. Kobya, O. T. Can and M. Bayramoglu, *J. Hazard. Mater.*, **100**, 163 (2003).
40. U. Kurt, M. T. Gonulluoglu, F. Ilhan and K. Varinca, *Environ. Eng. Sci.*, **25**, 153 (2008).
41. P. I. Omwene, M. Kobya and O. T. Can, *Ecol. Eng.*, **123**, 65 (2018).
42. P. Cañizares, F. Martínez, C. Jiménez, J. Lobato and M. A. Rodrigo, *Sep. Sci. Technol.*, **42**, 2157(2007).
43. A. S. Kopalal, Y. S. Yildiz, B. Keskinler and N. Demircioglu, *Sep. Sci. Technol.*, **59**, 175 (2008).
44. K. Thella, B. Verma, V. C. Srivastava and K. K. Srivastava, *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.*, **43**, 554 (2008).
45. F. Ilhan, U. Kurt, O. Apaydin and M. T. Gonullu, *J. Hazard. Mater.*, **154**, 381 (2008).
46. U. Tezcan-Un, S. Ugur, A. S. Kopalal and U. B. Ogutveren, *Sep. Purif. Technol.*, **52**, 136 (2006).
47. J. Vidal, L. Villegas, J. M. Peralta-Hernández and R. S. Gonzalez, *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.*, **51**, 289 (2016).
48. B. Y. Tak, B. S. Tak, Y. J. Kim, Y. J. Park, Y. H. Yoon and G. H. Min, *J. Ind. Eng. Chem.*, **28**, 307 (2015).
49. M. Moradi, F. Ghanbari, M. Manshouri and K. A. Angali, *Korean J. Chem. Eng.*, **33**, 539 (2016).
50. A. Aygun, S. Dogan, M. E. Argun and H. Ates, *Environ. Eng. Res.*, **24**, 24 (2019).
51. G. E. Ustun, S. K. Akal-Solmaz and H. S. Azak, *Clean-Soil Air Water*, **43**, 1344 (2015).
52. S. Y. Guvenc, H. S. Erkan, G. Varank, M. S. Bilgili and G. O. Engin, *Water Sci. Technol.*, **76**, 2015 (2017).
53. I. Atalon, I. A. Balcioglu and D. Bahnemann, *Water Res.*, **36**, 1143 (2002).

54. A. Aygun, Ph.D. Thesis, Selcuk University (2012).
55. M. Kobya, E. Gengec, M. T. Sensoy and E. Demirbas, *Color. Technol.*, **130**, 226 (2014).
56. B. K. Korbahti, *J. Hazard. Mater.*, **145**, 277 (2007).
57. S. Bansal, J. P. Kushwaha and V. K. Sangal, *Water. Environ. Res.*, **85**, 2294 (2013).
58. M. Kobya, E. Demirbas, M. Bayramoglu and T. Sensoy, *Water Air Soil Pollut.*, **215**, 399 (2011).
59. A. Akyol, *Desalination*, **285**, 91 (2012).
60. S. Virolainen, D. Ibane and E. Paatero, *Hydrometallurgy*, **107**, 56 (2011).
61. E. Gengec, M. Kobya, E. Demirbas, A. Akyol and K. Oktor, *Water Sci. Technol.*, **65**, 2183 (2012).
62. S. Ghafari, H. A. Aziz, M. H. Isa and A. A. Zinatizadeh, *J. Hazard. Mater.*, **163**, 650 (2009).
63. T. Olmez, *J. Hazard. Mater.*, **162**, 1371 (2009).
64. A. Aygun, S. Dogan and M. E. Argun, *Braz. J. Chem. Eng.*, **35**, 965 (2018).
65. M. Bayramoglu, M. Eyvaz and M. Kobya, *Chem. Eng. J.*, **128**, 155 (2007).
66. A. R. Amani-Ghadim, S. Aber, H. Olad and H. Ashassi-Sorkhabi, *Chem. Eng. Process.*, **64**, 68 (2013).
67. S. Swati and H. Simsek, *Chemosphere*, **221**, 630 (2019).
68. A. Dalvand, M. Gholami, A. Joneidi and N. M. Mahmoodi, *Clean-Soil Air Water*, **39**, 665 (2011).