

Multi-Response Optimization of Electrocoagulation Parameters for the Removal of COD, Phenol, and Colour from Petrochemical Wastewater

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Managing oily wastewater remains a significant challenge due to its complex composition, which usually includes high levels of chemical oxygen demand (COD), phenolic substances, and chromophoric compounds. This study examines the performance of electrocoagulation (EC) using aluminium electrodes to simultaneously remove COD, phenol, and colour from wastewater emanating from an oil refinery. A series of controlled batch experiments was carried out to evaluate how operational variables, such as current density, pH, and electrolysis time, influence treatment efficiency. Under optimized conditions (i.e., pH 6, a current density of 11 mA/cm², and an electrolysis time of 57 minutes), the system achieved removal efficiencies of 92.67% for COD, 92.94% for phenol, and 97.86% for colour. These results highlight the effectiveness of EC as a standalone treatment method. The findings confirm the suitability of aluminium-based EC for treating oily industrial wastewater, providing significant pollutant removal with minimal use of chemical reagents. The study supports further development of EC as a scalable, resource-efficient, and environmentally friendly approach to managing industrial effluents.

1. Introduction

Crude oil has been demonstrated to be a vital natural resource for both economically developed and developing countries. The derivatives of crude oil are used in various sectors of production, including agricultural industries, mechanical and metallurgical industries, and the automobile industry, which are essential for economic growth. Sadly, large amounts of wastewater are being generated by petroleum refineries during the processing of crude oil, oil drilling sites, and petrochemical plants, which pose a serious threat to the ecosystem (Jasim and AlJaberi, 2023). Wastewater emanating from petrochemical industries is characterized by a wide range of constituents, which can be classified as organic (hydrocarbons), inorganic, total suspended solids, chemical oxygen demand (COD), total organic carbon, total dissolved solids, ammonia, cyanide, heavy metals, and phenol, as elucidated by Jasim and AlJaberi (2023). It is imperative to note that wastewater constituents can fluctuate depending on the activities taking place during processing and the chemicals that are used during cleaning in place (Varjani et al., 2020). Furthermore, wastewater emanating from petrochemical industries contain secondary emulsions that are stable in water due to the formation of interfacial films encapsulating the oil droplets, rendering the treatment of these wastewater streams difficult by conventional methods due to the electrostatic repulsion forces (Tir and Moulai-Mostefa, 2008). There are available studies in the literature reporting on the application of response surface methodology using the central composite design and the box-Behnken design for electrocoagulation (EC) process optimisation in the treatment of oily wastewater. However, studies on multi-response optimisation using real wastewater are scant. As such, the scientific contribution of the present study is the optimisation of multi-responses, using pH, current density, and electrolysis time as factors for an EC aluminium-based process of a complex oily wastewater matrix emanating from a petrochemical refinery plant using Design-Expert Version 11.

2. Methodology

2.1 Electrocoagulation (EC) experimental set-up

EC experimental runs were conducted using a 1000 mL beaker, with additional beakers of equal volume reserved for post-treatment analysis. The system employed aluminium blade-type electrodes, each measuring 5 cm in width, 15 cm in height, and 0.1 cm in thickness. A direct current (DC) power source was integrated into the experimental setup (see Figure 1). The beaker, positioned on a digital magnetic stirrer, received power from a variable-voltage supply operating within a 0-30 V range. The aluminium blades, functioning as electrodes, were spaced precisely 1 cm apart using polystyrene spacers positioned at the base, effectively preventing contact between components and the apparatus. The electrodes were configured in a bipolar-parallel orientation.

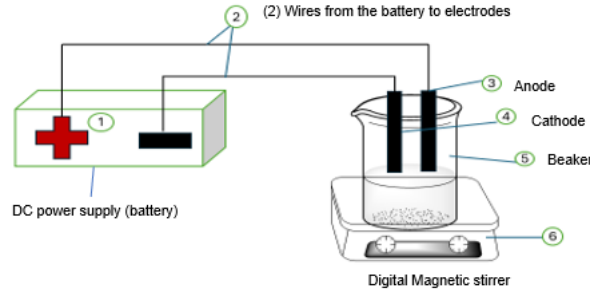


Figure 1: Electrocoagulation experimental set-up.

The EC process employs aluminium electrodes to remove COD, phenol, and colour from oily wastewater through the in-situ generation of Al^{3+} ions that hydrolyse into $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^+$, and amorphous $\text{Al}(\text{OH})_3(\text{s})$, the main flocculant responsible for pollutant removal (Jasim and AlJaberi, 2023). These $\text{Al}(\text{OH})_3$ floc destabilize emulsified oils, adsorb phenolics, and capture colour bodies, while cathodic hydrogen bubbles enhance flotation of hydrophobic contaminants (Jasim and AlJaberi, 2023).

2.2 Numerical Optimization in Design-Expert

To optimise the EC process for the simultaneous removal of COD, phenol, and colour from oily wastewater, a data-driven statistical strategy was employed. Specifically, Design-Expert software (version 11, Stat-Ease Inc., USA) was utilised to implement response surface methodology, which facilitated the development of predictive models, statistical validation, and multi-response optimization. The experimental framework was structured around three key input parameters, namely, pH (A), current density (B) expressed in mA/cm^2 , and electrolysis time (C) expressed in minutes. Each variable was assessed at two coded levels, designated as -1 for the lower bound and +1 for the upper bound, based on the operational ranges established from experimental data, as outlined in Table 1. The study focused on three output responses: the percentage removal efficiencies of COD, phenol, and colour. To capture the nonlinear behaviour of the system, a second-order model was applied to the response data for each target variable, as shown in Equation (1) (Bashir et al., 2015).

Table 1: Experimental design conditions and factor levels.

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High
A	pH	--	Numeric	3.0	10.0	-1 ↔ 3.0	+1 ↔ 10.0
B	Current Density	mA/cm^2	Numeric	3.0	12.0	-1 ↔ 3.0	+1 ↔ 12.0
C	Electrolysis Time	Min.	Numeric	10.0	60.0	-1 ↔ 10.0	+1 ↔ 60.0

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \epsilon \quad (1)$$

Where "Y is the predicted response, X_i and X_j are coded independent variables, β_0 is the intercept, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient, and ϵ is the residual error" (Bashir et al., 2015).

3. Results and Discussion

3.1 Model selection in Design-Expert

The current investigation highlights the pivotal influence of operational parameters, i.e., pH, current density, and electrolysis time, on the effectiveness of EC for the removal of COD, phenol, and colour. To systematically assess and enhance these process variables, Design-Expert software (version 11) was utilised, enabling the construction and refinement of predictive models based on experimental data. Quadratic models were successfully developed for each target response, offering insights into nonlinear interactions across the selected operating ranges. As shown in Tables 2 to 4, the sequential model sum of squares evaluation provided clarity on the hierarchical contribution of different model terms, including linear effects, two-factor interactions (2FI), quadratic responses, and higher-order cubic terms. In each case, the initial comparison between the model mean and total variance revealed substantial base-level variability captured by the response averages (Candiotti et al., 2014). This is demonstrated by the relatively high sum of squares values, i.e., 81992.07 for COD, 90016.27 for phenol, and 76612.27 for colour removal. These figures cement the robustness of the dataset and its suitability for further optimisation (Candiotti et al., 2014). Notably, the incorporation of linear terms proved to be statistically meaningful, with each model yielding p-values below the 0.05 threshold. This supports the hypothesis that linear factors play a significant role in explaining response variation beyond mere averages, as also discussed by Khandegar and Saroha (2013) in their review of EC systems. Consequently, retaining these terms is justified for model accuracy and interpretability. It is worth noting that, aliased models are due to the lack of degrees of freedom.

Table 2: Sequential model sum of squares for % COD removal

Source	Sum of squares	df	Mean square	F-value	p-value	
Mean vs Total	81992.07	1	81992.07			
Linear vs Mean	1574.59	3	524.86	8.93	0.0028	
2FI vs Linear	6.12	3	2.04	0.0255	0.9941	
Quadratic vs 2FI	546.69	3	182.23	9.74	0.0157	Suggested
Cubic vs Quadratic	45.92	4	11.48	0.2411	0.8886	Aliased
Residual	47.61	1	47.61			
Total	84213.00	15	5614.20			

Table 3: Sequential model sum of squares for % phenol removal

Source	Sum of squares	df	Mean square	F-value	p-value	
Mean vs Total	90016.27	1	90016.27			
Linear vs Mean	1632.04	3	544.01	9.85	0.0017	
2FI vs Linear	7.63	3	2.54	0.0339	0.9910	
Quadratic vs 2FI	494.88	3	164.96	7.84	0.0245	Suggested
Cubic vs Quadratic	87.65	4	21.91	1.25	0.5783	Aliased
Residual	17.52	1	17.52			
Total	92256.00	15	6150.40			

Table 4: Sequential model sum of squares for % colour removal

Source	Sum of squares	df	Mean square	F-value	p-value	
Mean vs Total	76612.27	1	76612.27			
Linear vs Mean	1878.93	3	626.31	7.98	0.0042	
2FI vs Linear	9.47	3	3.16	0.0296	0.9926	
Quadratic vs 2FI	752.07	3	250.69	12.38	0.0095	Suggested
Cubic vs Quadratic	85.32	4	21.33	1.34	0.5640	Aliased
Residual	15.95	1	15.95			
Total	79354.00	15	5290.27			

In contrast, the two-factor interaction effects across all three models exhibited minimal statistical relevance, as evidenced by the relatively high p-values exceeding 0.99, coupled with low F-values and sum of squares values. This indicates that such interaction terms do not substantially enhance the model fit and may be excluded to mitigate the risk of overfitting (Montgomery, 2017). Conversely, the inclusion of quadratic terms proved to be statistically significant, with p-values of 0.0157 for COD, 0.0245 for phenol, and 0.0095 for colour, respectively.

These findings imply that the response surfaces exhibit curvature characteristics inadequately captured by linear and interaction effects alone. This supports the necessity of quadratic components in accurately modelling system behaviour (Montgomery, 2017). Accordingly, the Design-Expert platform facilitated the derivation of second-order coded equations as presented in Equations (2) to (4), which express each response as a function of pH (A), current density (B), and electrolysis time (C).

COD (Y_1 , %) quadratic model. Coded variables A, B, and C.

$$Y_1 = 78.51 - 3.21A + 9.43B + 8.99C + 0.4736AB + 0.0631AC + 0.8453BC - 11.85A^2 \quad (2)$$

Phenol (Y_2 , %) quadratic model. Coded variables A, B, and C.

$$Y_2 = 84.76 - 3.29A + 8.39B + 9.66C + 0.0712AB + 0.2552AC + 1.09BC - 11.51A^2 - 4.51 B^2 - 0.2037C^2 \quad (3)$$

Colour (Y_3 , %) quadratic model. Coded variables A, B, and C.

$$Y_3 = 80.29 - 2.79A + 9.74B + 9.96C + 0.2593AB - 0.0206AC + 1.19BC - 14.24A^2 - 5.12B^2 \quad (4)$$

The cubic terms exhibited negligible influence, as evidenced by their high p-values, i.e., 0.8886 for COD, 0.5783 for phenol, and 0.5640 for colour removal, rendering them statistically insignificant and aliased within the model framework. This lack of significance is primarily attributed to constraints in the experimental design, particularly the limited degrees of freedom, which compromise the reliability of cubic estimations (Montgomery, 2017). The residual sum of squares of 47.61 for COD, 17.52 for phenol, and 15.95 for colour reflect the portion of variability not captured by the model, yet these values suggest that the quadratic formulation offers a robust fit with minimal error (James et al., 2023). Analysis of the sequential sum of squares further confirms that the quadratic model provides an optimal trade-off between model complexity and explanatory strength. While both 2FI and cubic terms failed to reach statistical significance, the inclusion of quadratic terms markedly improved the model's predictive performance.

3.2 Model fit statistical test

To assess the reliability and predictive strength of the developed quadratic models targeting the removal of COD, phenol, and colour, a combination of analysis of variance (ANOVA) and model fit diagnostics metrics was applied. As indicated in Tables 5 to 7, each model yielded p-values below the 0.05 threshold, affirming their statistical relevance and suitability for describing the system's behaviour (Montgomery, 2017). The ANOVA results recorded relatively low residual sum of squares, i.e., 143.02 for COD, 105.18 for phenol, and 143.02 for colour, when contrasted with the corresponding model sum of squares values of 2077.91, 2134.56, and 2077.91, respectively. This disparity suggests that the majority of the variation in the response variables is effectively captured by the models, leaving minimal unexplained error (Ateş et al., 2024, Verma and Chaudhari, 2020). Consequently, the quadratic formulations are deemed robust and appropriate for both system optimisation and predictive applications.

Table 5: ANOVA and fit statistics for COD removal model

Source	Sum of squares	df	Mean square	F-value	p-value	
COD model	2077.91	7	296.84	14.53	0.0011	significant
Residual	143.02	7	20.43			
<i>Fit statistics</i>						
Std. Dev	R ²	Adjusted R ²		Predicted R ²		Adequate precision
4.52	0.9356	0.8712		0.8566		12.71009

Table 6: ANOVA and fit statistics for phenol removal model

Source	Sum of squares	df	Mean square	F-value	p-value	
Phenol model	2134.56	9	237.17	11.28	0.0079	significant
Residual	105.18	5	21.04			
<i>Fit statistics</i>						
Std. Dev	R ²	Adjusted R ²		Predicted R ²		Adequate precision
4.59	0.9530	0.8685		0.8780		10.6201

Table 7: ANOVA and fit statistics for colour removal model

Source	Sum of squares	df	Mean square	F-value	p-value	
Colour model	2077.91	7	296.84	14.53	0.0011	significant
Residual	143.02	7	20.43			
<i>Fit statistics</i>						
Std. Dev	R ²	Adjusted R ²	Predicted R ²	Adequate precision		
4.50	0.9631	0.8966	0.8063	12.3494		

From the fit statistics, for all three developed models, the difference between the coefficients of determination, i.e., R², adjusted R², and predicted R², is less than 0.2, suggesting that these statistical parameters are in reasonable agreement. This consistency indicates that the developed quadratic models are statistically sound (Keer et al., 2023). Specifically, the recorded R² values of 0.9356 for COD, 0.9530 for phenol, and 0.9631 for colour suggest that only 6.44% for COD, 4.70% for phenol, and 3.69% for colour of the total variation is not explicitly explained by the developed respective quadratic models. The relatively high adjusted and predicted R² values further reinforce the robustness of the models, signifying minimal deviation and strong predictive accuracy (Yunardi et al., 2011).

3.3 Process optimization

The Design-Expert's numerical optimization module was utilised to determine the optimal operating conditions that enhance treatment performance, as outlined in Table 8. The constraints defined therein support a multi-response optimization framework aimed at identifying conditions that maximise the removal of COD, phenol, and colour, while ensuring operational practicality (Rekhate et al., 2025). By assigning equal weights to the lower and upper bounds of each factor, the model avoids directional bias and maintains neutrality in parameter prioritization. All input variables, namely, pH, current density, and electrolysis time, were assigned a high importance level of 3, signifying their equal relevance in influencing system performance and resource efficiency (Kumar et al., 2019). This uniform weighting also reflects a balanced treatment approach, where no single pollutant is given precedence, thereby reinforcing the multi-objective nature of the optimization strategy. The broad parameter ranges allow the software to explore synergistic interactions that promote high removal efficiencies while minimizing energy consumption. This setup is particularly effective in identifying optimal zones within the response surface where the simultaneous removal of all target pollutants is achieved. Such a configuration supports a robust and integrated treatment solution, reducing the risk of overfitting and enhancing the generalizability of the model.

Table 8: Optimization constraints for the removal of COD, phenol, and colour

Parameter	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
pH	In range	3	10	1	1	3
Current Density	In range	3	12	1	1	3
Electrolysis Time	In range	10	60	1	1	3
COD	Maximize	52	93	1	1	3
Phenol	Maximize	58	97	1	1	3
Colour	Maximize	48	93	1	1	3

The optimal parameters were determined to be a pH of 5.912 (≈ 6), a current density of 10.8973 mA/cm² (≈ 11 mA/cm²), and an electrolysis time of 56.5632 minutes (≈ 57 minutes). Under these conditions, the system predicted optimal removal efficiencies of 94.1409% for COD, 97.2256% for phenol, and 94.0205% for colour. Out of 100 generated solutions, all yielded a desirability of 1 at a 95% confidence level. The desirability function methodology enables simultaneous optimisation of multiple responses by transforming them into a unified composite function, which is then maximised to identify the most balanced solution (Candiotti et al., 2014). This approach assigns a desirability range from 0 (least desirable) to 1 (most desirable), with intermediate values reflecting varying degrees of suitability. A desirability of 1, as observed in this study, indicates that the selected operating conditions offer the most favourable compromise across all target responses. Furthermore, the validation results presented in Table 9 closely align with the predicted values, exhibiting a deviation of no more than $\pm 5\%$. The system recorded an energy consumption of 4.21 kWh/kg COD and 1.75 kWh/kg phenol, which is less than the 4.787 kWh/kg COD reported by Ateş et al. (2024). The findings of the present study at optimal conditions are congruent with other studies reported in the literature (Al-Rubaiey et al., 2022; Ateş et al., 2024). This strong agreement highlights the reliability of the developed models and demonstrates the effectiveness of Design-Expert in optimising complex treatment processes using experimental datasets, as discussed by Erraib and El Ass (2021).

Table 9: Model validation experiments for optimum conditions

	Responses			Ateş et al. (2024)		
	COD (%)	Phenol (%)	Colour (%)	COD (%)	Phenol (%)	Colour (%)
Experimental value	92.6700	92.9364	97.8623	45.5	93.8	95.5
Model predicted value	94.1409	97.2256	94.0205	46.74	94.62	96.04

4. Conclusions

The study demonstrates EC as an effective and adaptable method for treating oily wastewater, particularly in the removal of COD, phenol, and colour. The findings confirm that, when operated under optimised conditions using aluminium electrodes, electrocoagulation can significantly reduce pollutant concentrations. The high removal efficiencies (>90%) observed across all three contaminants cement electrocoagulation's viability as an environmentally conscious solution for managing industrial effluents. Key operational variables, i.e., current density, pH, and electrolysis time were shown to substantially influence the treatment effectiveness of the electrocoagulation process. Optimizing these parameters resulted in significant improvements in contaminant removal, demonstrating the process's flexibility in adapting to specific treatment objectives. Moreover, the EC process demonstrated robustness in treating oily wastewater, which typically poses challenges due to the presence of persistent emulsified organics and complex chemical structures.

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