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An Electrocoagulation Process Operated at Batch Recirculation Mode for Treatment of Refinery Wastewaters: Optimization via Response Surface Methodology

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Abstract

The performance of an electrocoagulation process operated at a batch recirculation mode for treating petroleum refinery wastewater using aluminium as a sacrificial anode and stainless steel as a cathode was investigated. Effects of operating factors such as the applied voltage (15-30 V), flow rate (50-200 mL/min) and pH (4-10) on the chemical oxygen demand removal were investigated. Using Box-Behnken design (BBD), a mathematical model relating the essential operational parameters to chemical oxygen demand (COD) reduction was constructed. Results showed that chemical oxygen demand (COD) removal efficiency significantly increased with the increase in the applied voltage and with the increase in flow rate till the optimum value. Experimental chemical oxygen demand removal of 87.605% was attained at the optimized conditions (applied voltage=28.2 v, flow rate=200 mL/min, pH=7). Results showed that the successful of Box-Behnken design in determining the optimum condition for removal of chemical oxygen demand (COD).

Keywords: batch recirculation mode, Box-Behnken design, electrocoagulation, refinery wastewater, response surface methodology.

1. Introduction

Large amounts of fresh water are frequently used in industrial processes and subsequently discarded as wastewater. The wastewater must be treated appropriately to minimize or remove contaminants and reach the needed purity level for industrial processes in order to enhance sustainability [1]. Refining processes convert crude oil into petroleum and other useful byproducts. Large amounts of water are consumed during these processes, resulting in a corresponding a huge amount of wastewaters which could be discharged as cooling water, process water, storm water, and sewage [2]**.** The amount of these effluents was increased to be 0.4–1.6 times the volume of treated oil [3]. The wastewater from refineries and petrochemical plants contains more than 20 different types of hazardous pollutants, including phenol, acetone, benzene, petroleum products, and nitrogen compounds. The composition of pollutants in these industrial wastewaters may include suspended particles, biodegradable and refractory organics, hydrocarbons, sulfide, phenols, and nitrogen compounds, despite the fact that the contaminants in the wastewaters greatly depending on the process design [4]. Besides, the composition of refinery wastewater varies greatly depending on the operating procedures as well as the type of oil being refined [5].

To remove hydrocarbons and other organic matter from petroleum refinery wastewater, different manners were used such as chemical coagulation-precipitation[6] , electrochemical processes, such as electro-oxidation, electro-fento and electrocoagulation [7-10] , biological treatment[11,12], activated sludge adsorption[13], a combination of solvent extraction and freeze-thaw [14], photo-degradation [15], and the Fenton and photo-Fenton processes[2].

Chemical coagulation is the process of combining tiny dispersed particles into bigger

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agglomerates that may be removed using other techniques like sedimentation, air floatation, or filtering. A common chemical used in chemical coagulation is alum [$Al_2(SO_4)_3$. $18H_2O$] . Coagulation can also be done in situ by electrolytic oxidation of a suitable anode material, a process known as electrocoagulation [16]. In recent years, the use of electrocoagulation(EC) in the treatment and purification of industrial wastewater has garnered significant interest [17,18]. Electrocoagulation is seen as a potential alternative to chemical coagulation for the treatment of wastewater that is highly polluted. This is because electrocoagulation has a high removal rate and does not involve the addition of any chemicals. In contrast to chemical coagulation, electrocoagulation does not have the same potential for the formation of secondary contaminants because it does not involve the addition of any chemical coagulants .In addition, the production of gas bubbles during the EC process contributes to the floating of pollutants on the surface of the water. As a result, the EC process may eliminate a variety of pollutants from both water and wastewater, including total suspended particles, total organic carbon, oil emulsions, heavy metals, chemical oxygen demand, color and turbidity [19].

The EC process results in the release of Fe^{2+} or Al^{3+} from the sacrificial anode and the production of OH^- at the cathode as a result of electrochemical reactions. Anode-generated coagulants (amounts of Al^{3+} or Fe^{2+} ions released by the anode) and OH^- move into bulk solution and undergo additional spontaneous hydrolysis events to create different monomeric and polymeric species, which change into insoluble oxides/hydroxides/oxyhydroxides . The enormous surface areas of the insoluble (oxy)hydroxides make them excellent adsorbents and trappers of suspended, precipitated, and dissolved pollutants [20]. In an electrochemical cell with aluminum electrodes, the reactions that take place at the surface of electrode and in the bulk solution are presented in Eqs. (1)–(6) but reactions (2), (5) and (6) happen only in wastewaters containing chloride ions [21] .Thus, at the cathode the reaction occurs by formation of OH^- Eq. (3) [22,23] :

At the anode

$$(Al)_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (1)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (2)$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

In the bulk of solution

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)} \qquad (4)$$

$$2Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (5)$$

$$HOCl \rightarrow H^+ + OCl^- \qquad (6)$$

On the electrodes, aluminate ions are generated during hydrolysis or dehydrolysis processes in an aluminum ion solution. At high pH, aluminum dissolves as aluminate as shown in Eq. (7) [1] :

$$2Al(s) + 6H_2O + 2OH^-(aq) \rightarrow 2\left[Al(OH)_4\right]^-(aq) + 3H_2(g) \qquad (7)$$

In the recent years , electrocoagulation (EC) has become widely used as a wastewater treatment technology, with satisfactory chemical oxygen demined removal in a variety of fields, including textiles [24-26], dyes wastewater remediation [27], Compressed natural gas (CNG) lubricant oil waste treatment [28], diesel and bio-diesel wastewaters [29], tannery effluents [30], removal of microplastics [31], and heavy metal bearing effluents [32,33]. Its benefits include ease of use, need small area in occupation, and a high level of automation.

Box-Behnken design (BBD) is a set of statistical methods that approximates a functional connection between a response and a set of influencing variables. It may also be used to optimize multifactor operations by examining the combined influence of various variables on the response. The Box-Behnken experimental design is often used for optimization many treatment operations [34,35].

This study investigates the efficacy of an electrocoagulation method to remediate refinery effluent utilizing a recirculating batch mode. The impacts of factors such as applied voltage, flow rate, and pH on the chemical oxygen demand (COD) removal efficiency were explored using the Box-Behnken design(BBD) by building a mathematical model and producing three dimensional response surface graphs. Finally, the response model was used to optimize affecting factors. The elimination of chemical oxygen demand (COD), turbidity from refinery wastewater at the optimal parameters predicted by the Box-Behnken design was confirmed using experimental findings.

2. Materials and Methods

2.1. Materials and Experimental work

Petroleum refinery effluent sample (80L) was provided by Al- Daura Refinery petroleum refinery plant, southern Baghdad, Iraq. The refinery effluent sample was utilized untreated. It was collected from the feeding tank prior to the biological treatment facility, where it was kept in closed containers at 4ºC until usage. The characteristics of this sample are presented in Table 1. Because raw water's conductivity is so low, it raises the cell potential, which necessitates the addition of supportive electrolytes in order to boost the conductivity. Na_2SO_4 at 0.025 M and NaCl at 0.0625

M were employed as supporting electrolytes, which resulted in a conductivity of 12.16 $mScm^{-1}$, which is within the range necessary to achieve low cell potential [36].

Hydrochloric acid (HCl, 37%, liquid, Sigma-Aldrich) and Sodium hydroxide (NaOH , ≥ 97% , pellets , Sigma – Aldrich) were used to prepare a 1M solution for adjusting the initial pH of the treated wastewater.

Table 1: Characteristics of Al-Dura oil refining wastewater sample.

Property	**Value**
pH (-)	6.8
COD (ppm)	1400
Conductivity (mS/cm)	4.03
Turbidity (NTU)	227
TDS(g/L)	2.07
F^- (ppm)	0.19
Cl^-(ppm)	422.4
Zn-(ppm)	0.08
Cu (ppm)	0.025
Mn(ppm)	0.33
Ni(ppm)	0.5
Pb(ppm)	1
Cd(ppm)	0.1
Cr(ppm)	1

The experiments were conducted by using the laboratory setup as shown in Figure 1. A tubular electrochemical reactor (Fig.1.a and b) made from Perspex glass with 30 mm diameter and 140 mm height. The wastewater was pumped to the cylindrical electrocoagulation cell using peristaltic pump (RUNZE, single stage pump, made in china) with a maximum flow rate of 200 mL/min. The aluminium and stainless steel disk electrodes (30 mm in diameter and 5 mm in thickness) were pierced with 1 mm holes and connected to a DC power source. The effective surface area of each electrode was 7.065cm^2. Each experiment's suitable voltage was supplied by a digital direct current power supply of type (UNI-T, UTP3315PF) with a range (0–30 V, 0–5 A). The system's current and voltage were measured using a multimeter (A-meter and volt-meter). The effluent from the electrocoagulation unit was sent to a settling tank with 1L volume, where the overflow was pumped back to the electrocoagulation cell. At the end of experiment, the electrodes were rinsed with HCl solutions (35 percent) followed by acetone to remove the oxide and passivation layers from the electrodes [37]. HCl solution (0.1 N) and NaOH solution (0.1 N) were used to adjust pH . NaCl and Na_2SO_4 was used as an electrolyte, where NaCl solution was utilized as a supplementary electrolyte because to its many benefits, i.e. chloride ions may considerably lessen the negative effects of other anions such a HCO_3^- and SO_4^{2-} . The presence of carbonate ions would precipitate Ca^{2+} or Mg^{2+} ions, which would produce an insulating layer on the surface of the electrodes. This insulating layer would dramatically raise the ohmic resistance of the electrochemical cell, resulting in a substantial decrease in current efficiency and treatment conversion. To maintain the appropriate operation of EC in water treatment, it is recommended that 20% of the existing anions consist of Cl^- [38]. The ambient temperature for all tests was 25 ±2 °C. After the experiment, samples were filtered using a Whatman glass microfibre filter before being analyzed. Total dissolved solids (TDS), pH, turbidity, and the initial and final chemical oxygen demand concentrations were also measured.

2.2. Methods of analysis

The Lovibond COD VARIO photometer was used for COD analysis with photometric detection (COD Setup, MD 200, UK). To test the chemical oxygen demand (COD), a 2 mL sample of the substrate was thermally oxidized using standard oxidation reagent in a cuvette tube. To achieve thorough oxidation of the substrate, thermo-reactor (RD 125, Lovibond, Germany) was utilized, and chemical oxygen demand (COD) in mg/L was determined. The compact Lovibond® infrared turbidity meter Turbi Check was used for turbidity measuring.

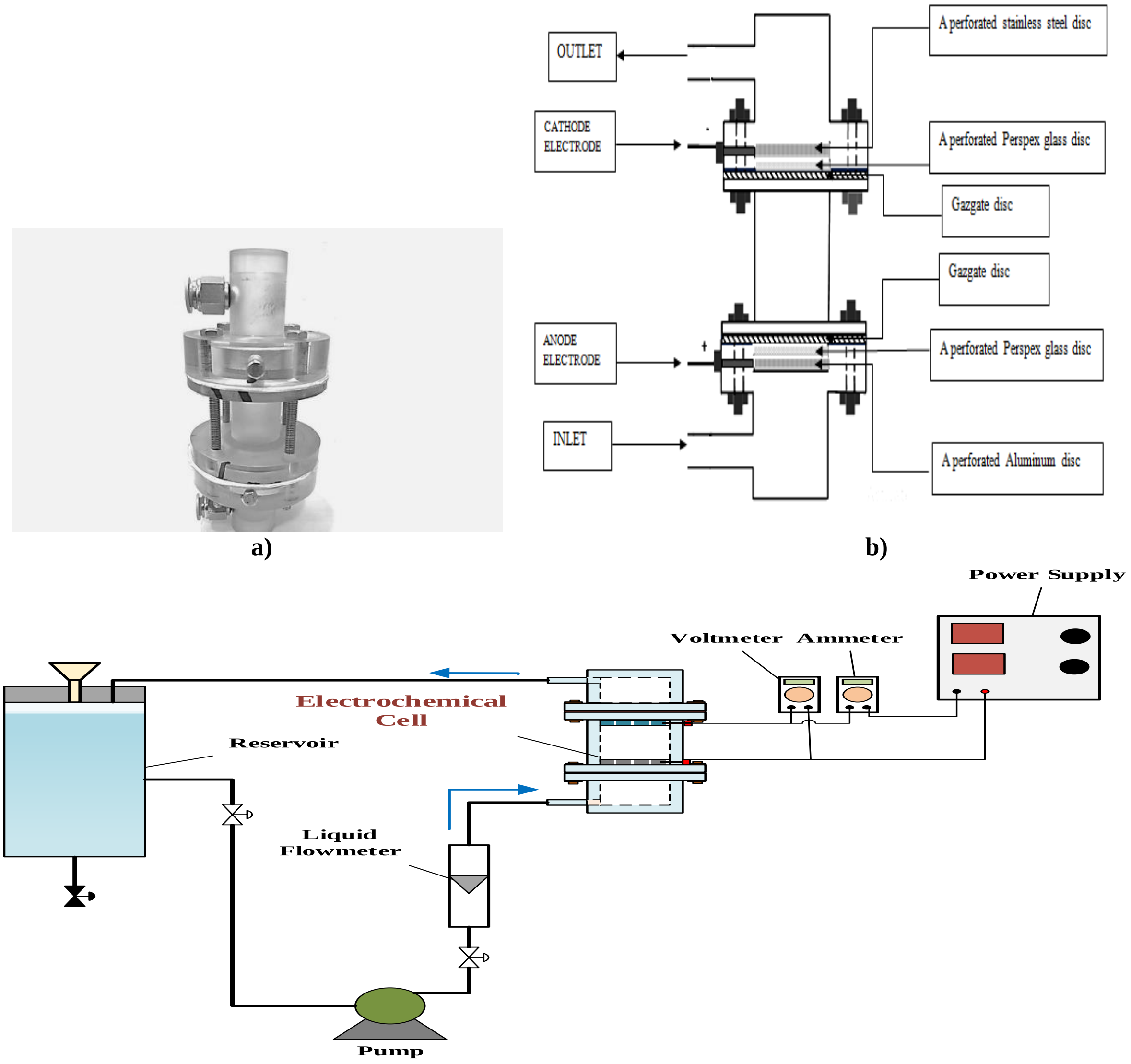
The turbidity and COD removal efficiency were evaluated based on eq. (8), where Ci is the initial concentration (mg L^{-1}) and Cf is the final concentration (mg L^{-1}) [17]:

$$RE\% = \frac{ci-cf}{ci} \times 100 \qquad (8)$$

The quantity of electrical energy that is used up throughout the EC process in order to eliminate one kilogram of COD is referred to as the energy consumption (EC). EC may be determined in terms of kWh/kg by using Equation (9)[39]:

$$EC = \frac{U.I.t\times1000}{(CODi-CODf)V} \qquad (9)$$

Where COD_i and COD_f are the initial and final chemical oxygen demand (mg/L), U is the applied cell voltage (Volt),I is the current (A),t is the electrolysis time (h), ,and V is the effluent volume (L) . A TDS-meter (161002 PurePro Inc.) was used to test the total dissolved solids (TDS), and a pH-meter (HANNA Instruments Co.) was used to determine the pH. Electrical conductivity was measured with (HANNA HI-99301).



a) b)

c)

Figar 1, (a) photograph of the electrocoagulation cell **b)** Schematic diagram of electrocoagulation cell **(c)** Schematic diagram of electrocoagulation system .

2.3. Design of experiments

The experimental design plays a crucial part in the development of the process and may be utilized to solve process problems in order to enhance process performance [40,41]. Response surface methodology (RSM) is a combination of mathematical and statistical tools used to develop models and analyze responses that are impacted by several variables, with the goal of optimizing this response [42]. In this particular investigation, 3-level 3-factor Box–Behnken experimental design was utilized so that the parameters that controlled the elimination of COD could be verified and examined. Applied voltage (X1), flow rate (X2), and pH (X3) were considered as process factors, while the response was RE% of COD. The coded scales of process factors were -1 (low level), 0 (middle or central point) and 1 (high level) [43]. The process parameters, together with their respective levels are presented in Table 2. For the 3-level factorial design, Box–Behnken builds and improves the designs necessary to obtain a viable quadratic model with the relevant statistical features while using just part of the required runs. The following equation can be used to compute the number of runs (N) required to carry out the Box–Behnken design[34,44]:

$$N = 2K(K-1) + cp \qquad (10)$$

Where K is the number of process variables and cp is the number of times the center point is repeated. The total number of trials in this study was 15, based on 3 levels and a 3 factor experimental design, with three replicates in the center of the design to estimate a sum of squares of pure error. Using Minitab 17 software, experimental data from a Box–Behnken design may be evaluated and fitted to a second-order polynomial model, eq. (11)[34,35]:

$$Y=a_o+\sum a_i x_i+\sum a_{ii} x_i^2+\sum a_{ij} x_i x_j \qquad (11)$$

Where Y is the Response Efficiency (RE %), i and j are the index numbers for independent variables, a_o is the intercept term, and x_1, x_2,..., x_k are the coded process variables (independent variables). The first-order (linear) main effect is denoted by a_i, the second-order main effect by a_{ii}, and the interaction effect by a_{ij}. After doing an analysis of variance, the regression coefficient (R^2) was calculated to check the model's validity.

Table 2: Experimental range and levels of the independent variables.

Variables	Levels in Box–Behnken design		
Coded levels	Low(−1)	Middle(0)	High (+1)
X1-Applied voltage(v)	15	22.5	30
X2-flow rate (mL/min)	50	125	200
X3- pH	4	7	10

Table 3: Design matrix in coded and experimental units of the parameters.

Run	Blocks	Process variables (Coded value) x_1	x_2	x_3		Process variables (Real value) Voltage(v) X1	flow rate(mL /min) X2	pH X3
1	1	-1	0	1		15	125	10
2	1	0	0	0		22.5	125	7
3	1	0	-1	-1		22.5	50	4
4	1	0	0	0		22.5	125	7
5	1	-1	1	0		15	200	7
6	1	0	-1	1		22.5	50	10
7	1	-1	-1	0		15	50	7
8	1	1	-1	0		30	50	7
9	1	1	0	1		30	125	10
10	1	1	1	0		30	200	7
11	1	1	0	-1		30	125	4
12	1	0	1	1		22.5	200	10
13	1	0	1	-1		22.5	200	4
14	1	-1	0	-1		15	125	4
15	1	0	0	0		22.5	125	7

3. Results and Discussion

3.1 Statistical analysis

As a first step the time of electrolysis for achieving all the experiments of Box-Behnken design (BBD) was determined by performing an experiment based on the following conditions: applied voltage=30 v ,pH=7, Flow rate=200 mL/min . The results are shown in Table 4.

Table 4: Chemical oxygen demand variation with time

COD(mg/L)	1300	840	492	220	180	150
Time (min.)	0	30	60	80	100	120

It was observed that electrolysis time of 80 min is sufficient to adopted in the experimental design because it gives a COD removal efficiency (RE%)= 83% high than 75%. Using electrolysis time higher than this value may result in obtaining approximated values of COD removal efficiency (RE%) in the experimental design that could be effected on the identification the effect of each parameters and their interactions.

In order to optimize and investigate the combined impacts of the independent factors on the COD removal efficiency, fifteen batch experiments for various process factor combinations were performed. Table 5 illustrates the experimental outcomes for COD removal efficiency (RE %).

Table 5 : Experimental results of Box-Behnken design for chemical oxygen demand removal

Run	Blocks	Process variables (Coded value)				Process variables (Real value)			RE%		Turbidity Removal % (TR%)	Energy consumption (kWh/kg COD)
		x_1	x_2	x_3		voltage(v)	flow rate (mL/min)	pH	Actual	Predict		
1	1	-1	0	1		15	125	10	74	73.61458	96.7	1.978772
2	1	0	0	0		22.5	125	7	83.75	83.08333	98.71	3.921085
3	1	0	-1	-1		22.5	50	4	75	74.875	99.09	3.931521
4	1	0	0	0		22.5	125	7	82.5	83.08333	98.5	3.980496
5	1	-1	1	0		15	200	7	75	75.26042	98.4	2.17399
6	1	0	-1	1		22.5	50	10	78	77.89583	98.57	4.243204
7	1	-1	-1	0		15	50	7	70	70.48958	97.7	1.948567
8	1	1	-1	0		30	50	7	80	79.73958	98	5.659442
9	1	1	0	1		30	125	10	82	82.36458	98.72	8.736403
10	1	1	1	0		30	200	7	87	86.51042	99.35	7.213256
11	1	1	0	-1		30	125	4	81	81.38542	99.2	7.782948
12	1	0	1	1		22.5	200	10	83	83.125	97.02	6.447465
13	1	0	1	-1		22.5	200	4	81.08	81.1875	99.03	4.241056
14	1	-1	0	-1		15	125	4	70	69.63542	97	1.948567
15	1	0	0	0		22.5	125	7	83	83.08333	98	3.956517

It was shown that COD elimination efficiency ranges from 70 to 87 %. Comparing runs 5 and 10, where COD removal increased from 75 to 87 % as the applied voltage increased from 15 to 30 v at pH 7, it is evident that the influence of applied voltage on the efficiency of COD removal was the most significant. At a lower flow rate (50 mL/min), the effect of applied voltage is similar, as demonstrated by the runs 7 and 8 in which COD removal increased from 70 to 80 % when applied voltage climbed from 15 to 30 v . Comparing runs 8 and 10 revealed that the influence of flow rate is less significant than the effect of applied voltage, as COD removal increased from 80% to 87% as flow rate climbed from 50 to 200 mL/min . This contrast demonstrates that the process is governed by electrodes reactions. Nevertheless, an increase in flow rate would improve the performance of electrodes reactions. By using the quadratic model of COD removal efficiency (RE percent) in terms of un-coded(real) units of process parameters, an experimental relationship between COD removal efficiency and process parameters was revealed and formulated using the results of COD removal efficiency analysis performed using Minitab-17 software :

$$RE\% = 4.6 + 3.847\, X1 + 0.0838\, X2 + 5.251 X3 - 0.06759\, (X1)^2 - 0.000228 (X2)^2 - 0.2813\, (X3)^2 + 0.000889\, X1{*}X2 - 0.0333\, X1{*}X3 - 0.00120\, X2{*}X3 \qquad (12)$$

Where RE% is the response, i.e. COD removal efficiency, and X1, X2 and X3 are applied voltage, flow rate and pH , respectively. Whereas the variables X1X2, X1X3 ,X2X3 represent the interaction effect of all the parameters of the model. $(X1)^2$, $(X2)^2$ and $(X3)^2$ represent the measures of the main effect of variables applied voltage, flow rate and pH , respectively.

Individual factors (linear and quadratic) or double interactions impact the COD removal efficiency, as shown in Eq.(12). Positive coefficient values indicated that COD removal effectiveness increased as the relevant variables of these coefficients grew within the investigated range, whilst negative coefficient values indicated the reverse impact. All factors have a favorable influence on COD removal efficiency, as can be observed. Table 4 also includes the predicted values of the COD removal efficiency obtained using Equation (12). Analysis of variance (ANOVA) was used to determine the validity of the Box-Behnken design. ANOVA splits the entire variance in a set of data into individual parts accompanied by particular sources of variation in order to test hypotheses on the model's factors [45]. The Fisher F-test and P-test are used to evaluate the model's acceptability in ANOVA analyses. If the value of Fisher is large, then the regression equation can explain the majority of the variation in the response. P-value is used to determine if F is sufficiently large to determine if the model is statistically significant. (90 %) of the model's variability might be explained when the P-value is less than (0.05) [46]. ANOVA for the response surface model is shown in Table 6. This table evaluates the following terms: contribution percentage (Cr. %), degree of freedom (DF), sum of the square (Seq. SS), adjusted sum of the square (Adj. SS), adjusted mean of the square (Adj. MS), P-value, and F-value. With a P-value of (0.00004) and an F-value of (100.80), it was determined that the regression model is very significant. The model's multiple correlation coefficient was 99.45%, indicating that the regression is statistically significant, and only

0.55 % of the total variations were not validated by the model. In this model, the adjusted multiple correlation coefficient (adj. R^2 =98.47 %) and the predicted multiple correlation coefficient (pred. R^2=94.18%) were quite similar.

ANOVA results indicated that the applied voltage has the greatest effect on the process, with a contribution of 56.92%, followed by flow rate with a contribution of 18.04 % and flow rate with a contribution of 3.33 %. Evidently, the contribution of applied voltage has the greatest impact on COD elimination in the current investigation. The contribution of the linear term to the model is the largest at 78.29 %, followed by the contribution of the square term at 20.20 % and the contribution of the 2-way interaction at 0.96%. The results indicated that interaction effects are considerable, with a total model contribution of (21.16%).

Table 5 Analysis of variance for chemical oxygen demand removal

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	9	367.108	99.45%	367.108	40.790	100.80	0.0004
Linear	3	289.012	78.29%	289.012	96.337	238.07	0.0001
(X1)	1	210.125	56.92%	210.125	210.125	519.27	0.0000
(X2)	1	66.586	18.04%	66.586	66.586	164.55	0.0005
(X3)	1	12.301	3.33%	12.301	12.301	30.40	0.00269
Square	3	74.555	20.20%	74.555	24.852	61.41	0.00023
X1*X1	1	46.502	12.60%	53.364	53.364	131.88	0.00009
X2*X2	1	4.388	1.19%	6.065	6.065	14.99	0.01174
X3*X3	1	23.665	6.41%	23.665	23.665	58.48	0.00061
2-Way Interaction	3	3.542	0.96%	3.542	1.181	2.92	0.13953
X1*X2	1	1.000	0.27%	1.000	1.000	2.47	0.17675
X1*X3	1	2.250	0.61%	2.250	2.250	5.56	0.06491
X2*X3	1	0.292	0.08%	0.292	0.292	0.72	0.43469
Error	5	2.023	0.55%	2.023	0.405		
Lack-of-Fit	3	1.232	0.33%	1.232	0.411	1.04	0.52508
Pure Error	2	0.792	0.21%	0.792	0.396		
Total	14	369.132	100.00%				
Model summary		S	R-sq	R-sq(adj)	PRESS	R-sq(pred)	
		0.636124	99.45%	98.47%	21.4869	94.18%	

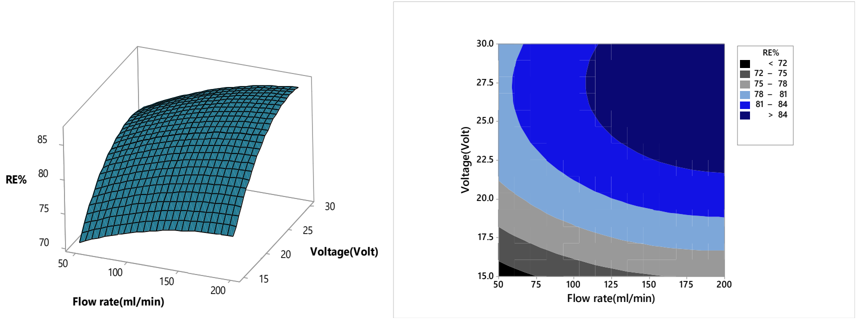
3.2. The influence of process factors on COD removal efficiency

Using response surface methodology (RSM) graphical representations of statistical optimization, the interaction impact of the selected variables and their influence on the response were analyzed. Figures (2-a, b) illustrate the influence of flow rates on COD removal efficiency at varying applied voltage (15-30 v) and constant pH (7). Figure 2-a depicts the response surface plot, whereas Figure 2-b demonstrates the related contour plot. At 15 v, it is evident from the surface plot that the COD removal efficiency drops precipitously when the flow rate decreases from 200 to 50 mL/min. By adjusting the applied voltage from 15 to 22.5 v at pH (7) and flow rate (200 mL/min), it was shown that the COD removal improved from 75% to 84.5%. The rise in voltage increases metal cations and bubble density in the solution, hence facilitating the removal of contaminants [47,48]. COD removal increased marginally from 84.5 % to 87 % when the voltage was raised from 22.5 to 30 v at pH (7) and flow rate (200 mL/min). Due to the fact that extremely high voltage may generate competition between the oxidation of water and aluminum, charge reversal and redispersion of contaminants. This diminished the effectiveness of destabilization and coagulation. In fact, at lower voltages, less aluminum hydroxide is generated, making the removal efficiency unsatisfactory. With a rise in voltage, more aluminum hydroxide is formed, resulting in a greater removal efficiency. After comparing the data, the optimal voltage was determined to be 30 v . According to a research conducted by Fouad [49] on the removal of cottonseed oil from an oil–water emulsion through electrocoagulation, the removal rate rises as the voltage is increased. These results were consistent with the present study's findings. The resulting contour plot reveals that the COD removal efficiency value of ≥84 % lies in a limited region when the applied voltage varied between 22 and 30v and the flow rate varied between 112 and 200 mL/min.

Figures (3-a,b) illustrate the effect of pH on COD removal efficiency for various applied voltages (15-30 v) at a constant flow rate (125 mL/min) and a constant period of 80 minutes . At a voltage of 15 v, the response surface plot (3-a) demonstrates that COD removal efficiency increase exponentially with increasing pH to 7 . COD removal effectiveness decreased with rising pH. By adjusting the pH from 4 to 7 at applied voltage 22.5 v and flow rate (125 mL/min), it was shown that the COD removal improved from 79% to 83 %. .While COD removal decreased marginally from 83 % to 81.8 % when the pH was raised from 7 to 10 at applied voltage 22.5 v and flow rate (125 mL/min). Depending on the chemical characteristics of the solution and the pH, aluminum ions can exist in a variety of forms and phases. Aluminum ions are found in the form $Al(H_2O)_6^{+3}$ at pH values less than 4. In contrast, in a pH range of 5 to 6, aluminum exists in the forms $Al(OH)^{+2}$ and $Al(OH)_2^{+}$. When the pH climbs from 5.5 to 8.8, aluminum changes into the $Al(OH)_3$s form. Aluminum might dissolve as ions again at pH levels greater than 8.8 [50,51]. Based on the effects of pH on Al's chemical form, it is hypothesized that the efficiency of electrocoagulation will rely to some extent on the pH. So that acceptable performance was expected, the removal effectiveness should be reduced at higher pH than the optimal value due to the development of soluble $Al(OH)_4^-$. The matching contour plot (3-b) verifies that the value of the COD removal efficiency ≥82.5 % lies in a limited area where the applied voltage varied between 22 and 30 v and the pH varied between 4.5 and 10.

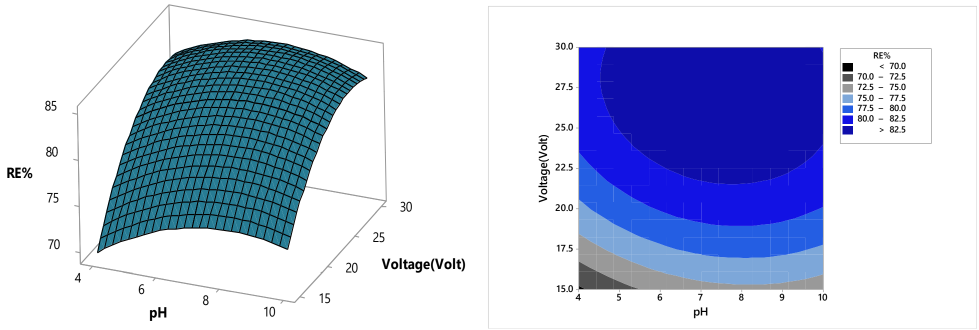
3.3 The optimization and confirmation test

Many criteria were established for improving the system in order to achieve the intended target by maximizing the desirability function (DF) via improving the its weight that changes the aspects of an objective. The variables' target fields contain five options: maximize, objective, minimize, within range, and none the 'maximum' aim for COD electrocoagulation removal was chosen, with a matching 'weight' of 1.0. The independent parameters evaluated in this study were identified within the desired ranges (applied voltage: 15-30 v , flow rate: 50-200 mL/min, pH: 4-10). 70% was taken as the lowest limit of COD removal efficiency, while 87 percent was taken as the higher limit value. Using these boundaries and parameters, the optimization technique was performed ant its results shown in Table 7 with the desirability function of (1). To confirm optimization findings, two further runs were conducted; the results are shown in Table 8. After 80 minutes of electrolysis, a COD removal efficiency of 87 % as a mean value was attained at a pH of 7. This value is within the optimal range determined by optimization analysis with a desire function of (1) (Table 7). Using the Box–Behnken design with a desirability function seems to be effective and efficient for maximizing COD removal in an electrocoagulation process with an aluminum electrode as a sacrificial anode and a stainless steel cathode operated at recirculating batch mode. Based on the finding of the present research, Table 9 compares the parameters of wastewater effluent and treated effluent. It is evident that treated effluent possesses superior qualities. In the present work, COD removal efficiencies of 87.605 %, and turbidity removal efficiencies of 99.44 % were achieved based on the raw effluent properties, confirming the activity of electrocoagulation process with aluminum electrode as a sacrificial anode and stainless steel as a cathode in a recirculation batch mode of Al- Daura petroleum refinery plant wastewater.



a) b)

Figure 2. Response surface plot (a) and contour plot (b) for the impact of applied voltage and flow rate on the COD removal efficiency (RE%)(Hold values: pH 7).



a) b)

Figure 3. Response surface plot (a) and contour plot (b) for the impact of applied voltage and pH on the COD removal efficiency (RE%)(Hold values: flow rate 125 mL/min).

Table 7.: Optimization of process parameters for optimal COD removal performance (RE %).

Response	Goal	Lower	Target	Upper	Weight	Importance
RE%	Maximum	70	Maximum	87	1	1

Solution:
Results
Parameters

Voltage(Volt)	Flow rate (mL/min)	pH	RE% fit	Composite desirability	SE Fit	95% CI	95%PI
28.0303	200	7.273	86.7848	0.9873	1.01	(85.602, 87.967)	(85.602, 87.967)

Table 8: Confirmation of the optimal COD removal performance.

Run	Applied voltage (v)	Flow rate (mL/min)	pH	Current density (mA/cm^2)	COD(ppm)		RE%		Turbidity(NTU)		EC (Kwh/ kg COD)
					Initial	Final	Actual	Average	Initial	Final	
1	28	200	7	31.6	1300	144.69	88.87	87.605	270	1.501	3.599
2	28	200	7	30.7	1300	177.58	86.34		270	2.05	5.398

Table 9: A comparison between the properties of the wastewater after and before the treatment.

Parameter Effluent	**COD (mg/L)**	**Turbidity (NTU)**	**TDS (g/L)**
Raw effluent	1300	270	2.07
Treated effluent	144(88.87%)	1.47(99.44%)	1.77

3.4 Comparison with previous works

The optimum circumstances demonstrated that an Electrocoagulation system in a recirculation batch mode, with aluminum electrode as a sacrificial anode and stainless steel as a cathode, may be used to treat Al-Daura petroleum refinery. Starting with a COD concentration of 1300 mg/L, an electrolysis period of 80 minutes resulted in a COD removal efficiency of 87.605 %. It is necessary to use 3.599 kWh/kg COD in this scenario. Few research have been published on the electrocoagulation technique for the effluent treatment that generated from petroleum refinery.

Table 10 compares the results of current study with earlier studies on the electrocoagulation method for the degradation of petroleum refinery effluent under various circumstances using aluminum as anode.

Table 10: A Comparison of COD removal efficiency for petroleum refinery wastewater treatment by electrocoagulation process based on the present method and literatures at various operating conditions

COD (mg/L)	Current density (mA/cm^2)	Time (min)	COD RE (%)	Ref.
596	13	60	63%	[52]
4050			42%	
562	18	80	90%	[53]
480	12	60	89%	[54]
170000	30 v	150	51.29%	[55]
5064	33	360	59%	[56]
250	12	60	96.9%	[57]
1114	60 A/m^2	30	83.52%	[58]
450	8 mA/cm^2	100	80%	[59]
1300	30 v	80	87.605 %	This work

4. CONCLUSIONS

The present research examined the performance of an electrocoagulation process operated at a batch recirculation mode under many operating factors such as applied voltage, flow rate of recirculation and pH in the treatment of wastewater generated from Al-Dura petroleum refinery using Box-Behnken design as an optimization method. A second-order polynomial equation was used to optimize the operational parameters after the experimental data were fitted to it. A COD removal efficiency of 87.605 % was achieved and an energy usage of 3.599 (KWh/KgCOD) was needed using the optimal operating parameters of voltage 28 v , flow rate 200 mL/min, and pH 7. Anodic and cathodic reactions (reactions on electrode surfaces) are the primary determinants of COD removal in this study, with results showing that applied voltage had the most impact. When the findings demonstrate that the removal rate increases as the voltage rises. Because lower voltages provide lesser quantities of aluminium hydroxide, the removal efficiency is unfavourable. More aluminium hydroxide is formed and the removal efficiency rises when voltage is raised.

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