



Real wastewater Treatment by Electrocoagulation- Electro-oxidation Combined System: Optimization using Taguchi Approach



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Abstract

In this study, the optimum conditions for COD removal from *petroleum refinery* wastewater by using a combined electrocoagulation- electro-oxidation system were attained by Taguchi method. An orthogonal array experimental design (L₁₈) which is of four controllable parameters including NaCl concentration, C.D. (current density), PH, and time (time of electrolysis) was employed. Chemical oxygen demand (COD) removal percentage was considered as the quality characteristics to be enhanced. Also, the value of turbidity and TDS (total dissolved solid) were estimated. The optimum levels of the studied parameters were determined precisely by implementing S/N analysis and analysis of variance (ANOVA). The optimum conditions were found to be NaCl = 2.5 g/l, C.D. = 20 mA/cm², time = 40 min, and pH = 7. Under these optimum conditions, COD removal percentage, turbidity and TDS reach to 90%, 99% and 2.55g/l respectively.

Keywords: electrocoagulation, electro-oxidation, combined, petroleum refinery wastewater, Taguchi design.

1. Introduction

Water pollution has become a severe environmental issue with negative impacts on human health [1]. It contains a wide range of contaminants, including biorefractory organic molecules that are resistant to traditional treatment methods [2]. Petroleum refinery wastewater is complicated and fluctuates a lot, and there are various quantities of emulsified oil, heavy metals, and organic contaminants, in addition to oil and grease (O&G), that can foul or flow past standard municipal wastewater treatment systems, producing environmental problems [3].

Many wastewater treatment techniques have been studied for use in petroleum refineries like, adsorption [4,5], coagulation [6], coupling coagulation–flocculation [7], chemical oxidation [8], biological techniques [9], membranes [10, 11], photocatalytic [12, 13], and electrochemical technology [14, 15].

Electrochemical treatment approaches got a lot of interest in recent years since they can successfully remove various kinds of contaminants. The electron (clean reagent) is the primary reagent in these processes, which incinerates the organics without creating any secondary pollutants [16]. Electrochemical treatments are distinguished by simple apparatus, short maintenance periods, and ease of operation, all of which can help to lower operating costs in large-scale applications [17].

The electrocoagulation process (EC) is one of the major electrochemical technologies because it is a straightforward, efficient, and cost-effective method. EC has the benefit of eliminating the smallest colloidal particles due to their fast motion by the effect of the applied electric field, and EC also has the benefit of creating a comparatively small amount of sludge when compared to the conventional flocculation–coagulation process. Also, the effluent contains less total dissolved solids (TDS) than chemical coagulation. However, because of the electric field that directs them in motion, such charged particles are more likely to be coagulated and destabilized [18, 19].

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The electrolytic oxidation of the sacrificial anodic material produces coagulant species, including hydroxide precipitates. The most sacrificial anodes are Aluminum (Al) and iron (Fe). Consecutively, hydroxyl ions (OH⁻) and some O₂ and H₂ gas bubbles would be generated due to water oxidation and reduction arising at the anode and cathode, respectively. Formation of metallic hydroxides with good adsorption properties would take place due to the interaction between the positive ion (Al³⁺ or Fe²⁺) and the hydroxyl ion (OH⁻) or "sweep flocs" which have high surface areas [19, 20].

These hydroxides can destabilize any dispersed particles existing in the wastewater. The adsorption of dissolved or colloidal contaminants could be attained by these hydroxides that can also aggregate the suspended particles which can be eliminated from electrolytic solution by flotation or sedimentation [21].

Electro-oxidation (EO), which offers adaptability, energy economy, automation, environmental compatibility, and cost effectiveness, has also progressed to the point where it may now be utilized to efficiently destroy hazardous or biorefractory organics [22–24].

Electro oxidation is a term used to describe electrochemical methods used to eliminate dissolved contaminants from water. The contaminant can be oxidized into CO₂ and H₂O by the action of two ways: directly and indirectly. The difference between the two is that direct oxidation is used to remove the pollutant from the electrode's surface by the action of OH• radicals, and indirect anodic oxidation allows oxidants (like H₂O₂, O₃, HClO, and HBrO) to be produced in situ. Chloride salts are present in wastewater and that makes chlorine as one of the most common electrochemical oxidants. In the electrolytic solution, the chloride ions oxidation takes place at the anode to produce hypochlorous acid (HClO) which is an incredibly strong oxidant [24, 25].

Combining the two processes (EC and EO) in the same electrolytic cell to exclude the soluble and insoluble contaminants (such as colloid particles, O&G, COD, BOD, and heavy metals) from wastewater might be interesting [17]. As a result, a hybrid method combining EC and EO processes has been investigated by many studies at the laboratory and pilot scales to remove COD from wastewater [2, 3, 17, 25].

Environmental compatibility, flexibility, energy economy, automation ability, economic effectiveness, and safety are all advantages of the combined EC-EO process [26]. The main goal of this study is to apply a hybrid technique that combines EC and EO in the

same electrolytic cell, and to test its efficiency in handling real wastewater from the Midland Refinery Company located in Baghdad governance in Iraq. This method should be able to remove color from effluents while also clarifying them and eliminate both dissolved and suspended organic contaminants at the same time. Also, one of the goals of this study is to observe the treatment of the real wastewater by EC and EO combined system technique using Taguchi experimental design with L₁₈ orthogonal array to optimize the more controllable factors and investigate them successively. A confirmation experiment was also managed at the optimized conditions.

2. Experimental Work

2.1 Wastewater samples

In this study, the samples were collected from the Midland Refinery Company which is located in Baghdad governance in Iraq. This wastewater is considered one of the most contaminated industrial effluents that have high organic materials content. 60 L of effluent was collected from the feeding tank to the treatment unit and kept in closed polypropylene containers at temperature 4°C till use to avoid the decline in COD during storage following (American Public Health Association) [26, 27]. The characteristics of wastewater were relatively stable with the change of seasons. The main characteristics of wastewater are displayed in Table 1.

2.2 Materials and system

In the electrochemical cell, 1.5 L of real wastewater was handled in each experiment; pH for all experiments was adjusted at the desired value by the addition of (1M) HCl or (5M) NaOH. The initial value of pH of the electrolyte and the final value after treatment were determined by a digital pH meter (HANNA Instrument Inc., HI98107 pHep, Romania).

All chemicals were of the reagent grade. NaCl was supplemented to the waste prior to each experiment at the desired amount (1.5 or 2.5 g/l) as an oxidizing agent and to improve the electrical conductivity and minimize ohmic losses in the EC-EO system and reducing energy consumption. The conductivity of the electrolyte was determined using (HANNA Instrument Inc., HI98304 DiST4, Romania).

The experiments were accomplished at room temperature (25°C ± 2°C) and implemented in duplicate and the average value of COD Re% was taken. COD Removal efficiency can be expressed as

in Equation 1 [28]:

$$COD\ Re\% = \frac{COD_o - COD_f}{COD_o} \times 100 \quad (1)$$

Where: COD_o and COD_f were the initial and final value of COD in ppm respectively.

Table 1: characteristics of waste water and their values

Characteristics	Value
Turbidity (NTU)	315
Total suspension solid TSS (mg/L)	149
Total dissolved solid TDS (mg/L)	1479
PH	7.6
Chlorides Cl. (mg/L)	536
Sulfate (mg/L)	385
Phosphate (mg/L)	0.93
Phenols (mg/L)	20
O&G (mg/L)	60.1
BOD (mg/L)	82
COD (mg/L)	600
Temp	33

The design of the batch monopolar EC and EO reactor used in the current study is shown in Fig. 1. The experiments were carried out in a batch reactor composed of a glass container with [17 cm (width), 13.5 cm (depth), and 17 cm (length)] located on a magnetic stirrer hot plate (Heidolph™ 505-20000-00 , 0-300°C ; 0-1400 rpm) at 250 rpm to attain good mass transfer . One of the anodes electrodes was an aluminum plate (Al) and the other one was a graphite plate, while the cathode electrodes were three stainless steel (St.St.) plates of type 316-AISI. The dimensions of the graphite and aluminum plates were [12.5 cm (width), 13 cm (length), and 0.23 cm (thickness)]. The dimensions of each stainless steel plate were (12.5 X 12.5cm²). The dimensions of each side of the anodes electrodes which were dipped in the wastewater were (4.7 cm width 12.5 cm height for each anode electrode). So, the total effective surface area of anodes is 235 cm².

The electrodes were alternatively fixed in the cell reactor by a Perspex cover [18 cm (width), 18 cm (length), and 1 cm (thickness)] which has five slits for the insertion of electrodes. One hole was drilled to accommodate thermometers, pH probes, and

electrical conductivity probes. Each anode was sandwiched between two cathodes. The distance between any two electrodes was 2 cm.

The positive and negative portions of a DC power supply (JYD APS 3005D, 0-5A; 0-30 V) were coupled to the anode and cathode groups, respectively. The electrodes were mounted vertically on a perforated Perspex plate 2 cm from the bottom of the electrolytic cell.

After each experiment, the electrolytic cell (including the electrodes) was cleaned for at least 10 minutes with a 5 percent (v/v) hydrochloric acid solution, wiped with a sponge, and washed with tap water. The electrochemical treatment was implemented after applying the desired value of current density for a specified time and throughout the experiment, samples were taken at various intervals and examined for a variety of factors.

2.3 Methods of analysis

Each collected sample after any experiment was allowed to settle for a period of one hour. The efficiency in situ EC-EO system was assessed by measuring COD and turbidity in the sample after settling of the suspension at the end of electrolysis. The samples for COD measurement were first filtered and then a sample (2ml) of effluent digested with K₂Cr₂O₇ as an oxidizing agent for 120 minutes at 150 °C in a COD thermos-reactor (RD125, Lovibond). The digested sample was cooled down to room temperature then analyzed in a spectrophotometer (MD200, Lovibond). The amount of turbidity in effluents was measured by using (TB300, Lovibond). The value of turbidity removal percentage can be obtained by Equation 2 as follows:

$$turbidity\ Re\% = \frac{turbidity_{initial} - turbidity_{final}}{turbidity_{initial}} \times 100 \quad (2)$$

To measure the conductivity of heavy metal salts and (TDS), a digital laboratory conductivity meter (CRISON, EC-Meter BASIC 30, Spain) was used. The initial and final value of TDS was measured to attain the value of TDS removal percentage as shown in Equation 3:

$$TDS\ Re\% = \frac{TDS_{initial} - TDS_{final}}{TDS_{initial}} \times 100 \quad (3)$$

2.4 Design of experiments using Taguchi method

Minimizing the completion time of any treatment process and its cost, errors, and variation can be attained by applying the approach of Taguchi due to its simplicity and efficiency. Also, the optimization of the parameters can be achieved with the minimum

number of experiments [29, 30]. The main goal of the present study is to attain the maximum value of COD removal; therefore, the HB (higher is best) S/N ratio analysis was implemented.

Equation 4 performs the S/N ratio with HB characteristic [31]:

$$\frac{S}{N} = -\log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right] \quad (4)$$

Where n is the number of observations, and y is the perceived response of the i th experiment (COD Re %). An evaluation of the influence of the selected parameters can be obtained by ANOVA with 95% confidence level [32]. The experimental results were assessed by MINITAB (version 17) statistical software.

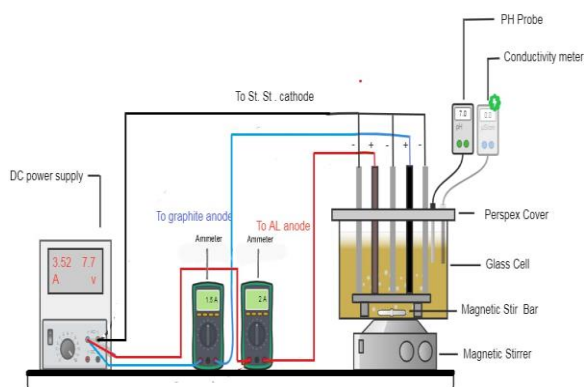


Fig. 1. Schematic diagram of the EC-EO experimental setup

In the current study, four process controllable parameters were investigated; initial NaCl Concentration (coded X1), current density (C.D., mA/cm²) (coded X2), the initial pH of the solution (coded X3), and time (min) (coded X4). The levels of the studied controllable factors are shown in Table 2. According to the Taguchi experiment design, the appropriate orthogonal array that permits investigating the effect of the selected factors and the interaction between them for these mixed levels would be L₁₈ either (3³ × 2¹) array that presented in Table 3. With this array, only 18 tests instead of 243 full experimental runs were conducted for the four controllable factors which mean a pronounced decrease in time and cost.

Table 2, selected experimental parameters and their assigned levels

Parameter	Coded	Level 1	Level 2	Level 3
NaCl (g/l)	X1	1.5	2.5	-
C.D (mA/cm ²)	X2	10	15	20
pH	X3	4	7	10
Time (min)	X4	20	40	60

Table 3, Coded and Real values of L₁₈ orthogonal array

Exp. No.	Coded values				Real values			
	X1	X2	X3	X4	NaCl (g/l)	C.D. (mA/cm ²)	pH	Time (min)
1	1	1	1	1	1.5	10	4	20
2	1	1	2	2	1.5	10	7	40
3	1	1	3	3	1.5	10	10	60
4	1	2	1	1	1.5	15	4	20
5	1	2	2	2	1.5	15	7	40
6	1	2	3	3	1.5	15	10	60
7	1	3	1	2	1.5	20	4	40
8	1	3	2	3	1.5	20	7	60
9	1	3	3	1	1.5	20	10	20
10	2	1	1	3	2.5	10	4	60
11	2	1	2	1	2.5	10	7	20
12	2	1	3	2	2.5	10	10	40
13	2	2	1	2	2.5	15	4	40
14	2	2	2	3	2.5	15	7	60
15	2	2	3	1	2.5	15	10	20
16	2	3	1	3	2.5	20	4	60
17	2	3	2	1	2.5	20	7	20
18	2	3	3	2	2.5	20	10	40

3. Result and discussion

3.1 Multiple regression model and the S/N results

Equation 5 represents the multiple regression equation which shows the relationship between COD Re% and the studied factors which were acquired by MINITAB 17 software. The correlation coefficient (R²) is equal to 99.48%, which specifies an excellent fitting of the model.

$$\begin{aligned} COD Re\% = & [-0.7212 + 0.2803 X1 + \\ & 0.07707 X2 + 0.1351 X3 - 0.003437 X4 - \\ & 0.000698 X2^2 - 0.013567 X3^2 - 0.01214 X1 * \\ & X2 - 0.000195 X2 * X4 + 0.000938 X3 * X4] * \\ & 100 \end{aligned} \quad (5)$$

Fig. 2 shows a comparison between experimental values of COD Re% which is represented in table 4 and the predicted values that are determined based on Equation 5, and it is very evident that the model

predicts very well for COD Re% and Equation 5 can practically reflect the process valuation.

Table 4 represents the experimental and predicted values of the L₁₈ orthogonal array for COD Re%, and the values of S/N ratios that were calculated based on Equation 4 for each experiment. The energy intake for the EC-EO combined process is shown in Table 4 and it was determined for each experiment from Equation 6 [33]:

$$EC = (Uc.I.t)/(V * 1000) \tag{6}$$

Where, EC is in kWh/m³, U_c is the potential (V), I is the current intensity (A), t is the electrolysis time (h), and V is the volume (m³) of treated-water.

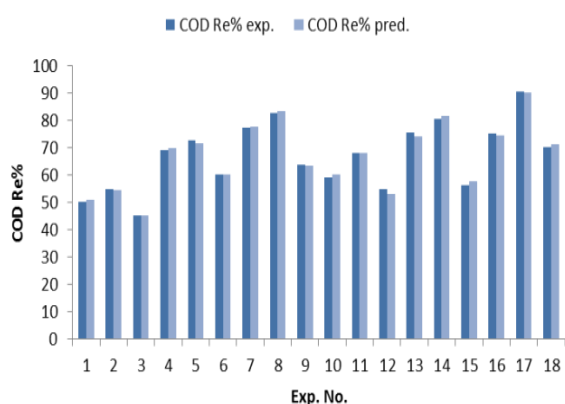


Fig.2. Experimental and predicted COD Re% values

The mean value of COD Re% of each studied parameter at a definite level is represented in Table 5, and it is represented graphically in Fig. 3. The results of the mean response signify that the most vital factors are in the following order: C.D. > pH > NaCl concentration > time.

Table 5, Values of mean of response for data attained from COD Re% removal experiments

Level	NaCl (g/l)	C.D. (mA/cm ²)	pH	Time (min)
1	63.97	55.35	67.81	66.35
2	70.04	69.11	74.82	67.55
3	-	76.57	58.4	67.13
Delta	6.07	21.22	16.43	1.20
Rank	3	1	2	4

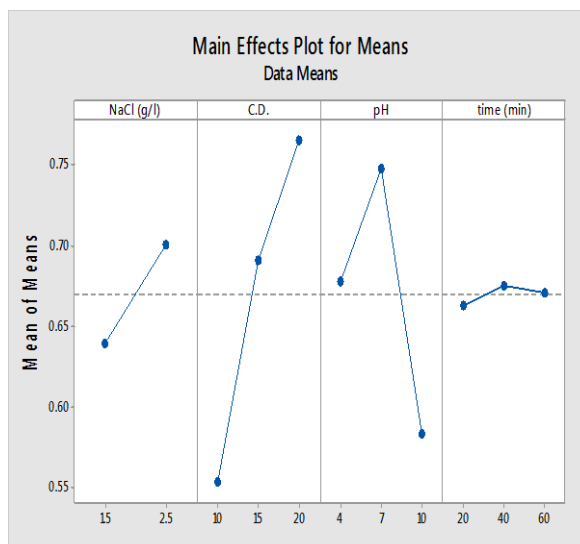


Fig. 3. Main effects plot for means values of COD Re%

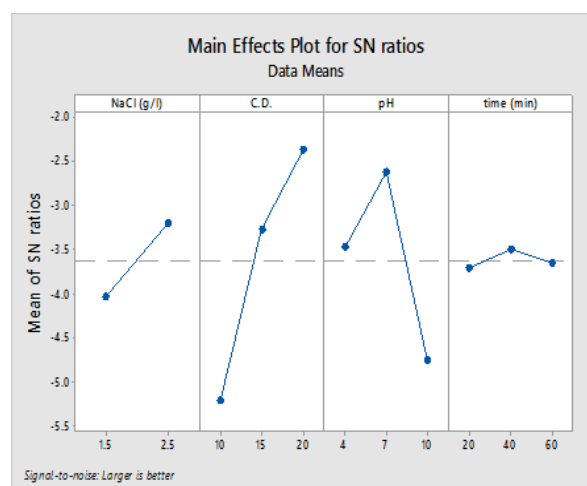


Fig.4. Main effect plots of S/N ratio (Higher is better) for COD Re %

Table 6 represents the estimated values of S/N ratios (HB) and the ranks for each controllable parameter based on Equation 4, and it is represented graphically in Fig. 4. A higher S/N ratio value indicates a higher COD Re%. It is evident from the acquired ranks for each parameter that the order of significance is the same as that obtained with the results of mean response.

Table 6, Response table for S/N ratio (Higher is better)

Level	NaCl (g/l)	C.D. (mA/cm ²)	pH	Time (min)
1	-4.035	-5.210	-3.477	-3.712
2	-3.204	-3.276	-2.628	-3.495
3	-	-2.372	-4.754	-3.651
Delta		0.831	2.838	2.126
Rank		3	1	2

Table 4. The values of experimental and predicted COD Re%, S/N, and energy intake for the EC-EO process

Exp. No.	NaCl (g/l)	C.D. (mA/cm ²)	pH	Time (min)	COD Re%, exp.	COD Re%, pred.	turbidity removal %	EC (kWh/m ³)	S/N ratio
1	1.5	10	4	20	50.23	50.8678	99.52	2.19	-5.9807
2	1.5	10	7	40	54.86	54.6127	99.14	4.6	-5.2151
3	1.5	10	10	60	45.04	45.193	98.98	7.52	-6.9285
4	1.5	15	4	20	69.23	69.6228	99.56	5.41	-3.1941
5	1.5	15	7	40	72.58	71.4177	99.37	10.65	-2.7839
6	1.5	15	10	60	60.26	60.048	99.11	15.75	-4.3992
7	1.5	20	4	40	77.35	77.7178	99.05	17.13	-2.2307
8	1.5	20	7	60	82.46	83.1907	99.60	8.88	-1.6752
9	1.5	20	10	20	63.76	63.241	99.25	7.68	-3.9087
10	2.5	10	4	60	59.15	60.2178	99.37	2.4	-4.5602
11	2.5	10	7	20	68.13	68.1447	98.10	4.49	-3.3337
12	2.5	10	10	40	54.68	53.097	99.68	10.81	-5.2437
13	2.5	15	4	40	75.61	74.2228	99.37	13.87	-2.4281
14	2.5	15	7	60	80.58	81.6457	99.37	4.54	-1.8757
15	2.5	15	10	20	56.40	57.796	99.14	22.25	-4.9746
16	2.5	20	4	60	75.27	74.2978	92.06	7.73	-2.4673
17	2.5	20	7	20	90.35	90.0247	99.22	14.83	-0.8819
18	2.5	20	10	40	70.23	71.077	99.09	2.19	-3.0689

Based on the results of means and S/N ratios, the optimum factors were: NaCl conc. (X1) of 2.5 g/l, C.D. (X2) of 20 mA/cm², pH (X3) of 7, and electrolysis time (X4) of 40 min. At these conditions, a removal efficiency of COD (90 %) with a removal efficiency of TDS of (25.6 %) and removal efficiency of turbidity of (99 %) were achieved while an energy consumption of (15.46 kWh/m³) was required.

3.2 Analysis of Variance (ANOVA)

The influence and relative significance of the studied controllable parameters can be accomplished by ANOVA which represents a statistical method for optimization that provides a superior understanding of how the perceived results are consistent [34, 35].

The estimation of error variance can be attained by ANOVA which reveals whether the observed variation in the response is due to change in level adjustments or experimental standard errors. Also, the impact of each factor on the response can be attained by F-test. If F-test values > 1, this shows that those parameters had variances bigger than error

variance and they have a major influence on the response of the process [29, 34, 36].

P-value is an indication of whether the experiments were accomplished at controlled conditions or not. If the P-value for each factor less is than 0.05 (for a confidence level of 95%) this means that the experiments were conducted at controlled conditions [29]. The results of ANOVA are depicted in Table 7.

The results of ANOVA reveal that C.D. (with contribution % of 54.37) has the major effect on COD Re% followed by pH (with contribution % of 31.87) and NaCl conc. (with contribution % of 6.48), and the less effective parameter on COD Re% was electrolysis time (with a contribution % of 0.17).

Based on the results of the F-value of the present study, all the studied factors have a significant effect on COD Re% except electrolysis time. The same results are confirmed by the results of the P-value.

Table 7, Analysis of Variance (ANOVA) for COD Re%

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
NaCl	1	0.01658	6.48 %	0.01658	0.01658	9.12	0.013
C.D.	2	0.13909	54.37 %	0.13909	0.06954	38.25	0.0
pH	2	0.08154	31.87 %	0.08154	0.04077	22.42	0.0
time	2	0.00044	0.17 %	0.00044	0.00022	0.12	0.886
Error	10	0.01818	7.11 %	0.01818	0.00181	-	-
Total	17	0.25585	100 %	-	-	-	-
Model Summary							
S	R-sq	R-sq(adj)	R-sq(pred)				
0.0426417	92.89%	87.92%	76.97%				

3.3 Effect of Controllable Parameters

a. Effect of NaCl Concentration

The use of NaCl as an oxidizing agent resulted in the greatest elimination rate of color and COD due to its possible contribution in electro-catalytic degradation. Equations 7 and 8 represent the primary chlorine reactions:



It may be seen from the above chemical equation that Cl^- was first oxidized to Cl_2 , and then converted to $HClO'$ (hypochlorous acid/hypochlorite active chlorine species) which burn organic materials into water and CO_2 , but it had been reduced to Cl^- in the meanwhile. So, $(2Cl^-/Cl_2)$ functioned as a reversible redox oxidizer that indirectly oxidized organics during the process. The content of Cl (final) output in water was found to be 25% lower than (initial) intake water, providing significant evidence for the above conclusion [3]. Table 8 represents the values of initial and final conductivity for each conducted experiment. So, the value of Conductivity Removal % can be obtained.

The addition of Na_2SO_4 or NaCl can increase wastewater conductivity, lower cell voltage, and minimize electrical energy consumption [37]. It is clear that the higher the NaCl level, the greater COD Re%. The cell voltage decreases by decreasing solution resistance which resulted from conductivity increasing due to NaCl Addition. Previous research has shown similar results [20]. The role of electrocatalytic degradation of organic components is strengthened, but too much supporting electrolyte results in a significant number of ions adsorbing on the electrode surface, lowering current utilization [3].

Fig. 5 illustrates the contour plot and 3D surface plot for COD Re% vs. C.D. and NaCl concentration. It is clear that the removal percentage increases with current density and NaCl concentration increasing due to $HClO'$ generation increasing.

Table 8, the values of initial and final conductivity, and Conductivity Removal %

Exp. No.	NaCl	C.D.	pH	time	Initial cond. (ms/cm)	Final cond. (ms/cm)	Cond. Re%
1	1.5	10	4	20	8.21	6.96	15
2	1.5	10	7	40	8.43	6.21	26
3	1.5	10	10	60	8.33	6.13	26
4	1.5	15	4	20	8.16	5.89	28
5	1.5	15	7	40	7.75	6.04	22
6	1.5	15	10	60	8.31	6.4	23
7	1.5	20	4	40	7.73	6.26	19
8	1.5	20	7	60	7.7	5.98	22
9	1.5	20	10	20	7.62	6.31	17
10	2.5	10	4	60	10	7.17	28
11	2.5	10	7	20	10.44	7.1	32
12	2.5	10	10	40	10.25	7.18	30
13	2.5	15	4	40	10.33	7.15	31
14	2.5	15	7	60	10.04	7.47	26
15	2.5	15	10	20	10.23	7.3	29
16	2.5	20	4	60	10.05	7.33	27
17	2.5	20	7	20	9.95	7.71	23
18	2.5	20	10	40	10	7.2	28
						average Re%	25.12

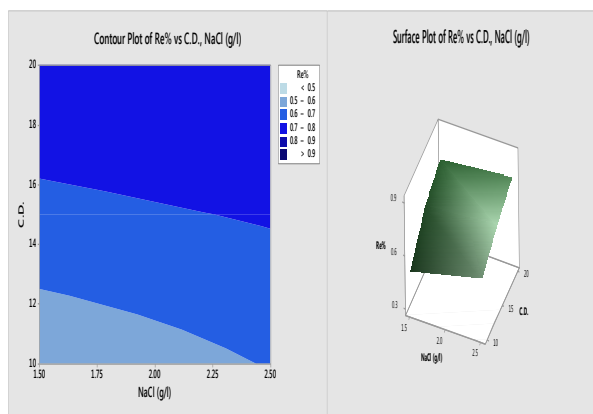


Fig. 5. Contour Plot and 3D surface plot of COD Re% vs. C.D. and NaCl conc.

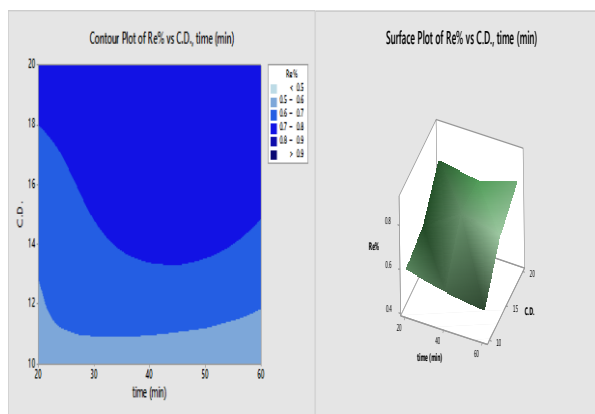


Fig. 6. Contour Plot and 3D surface plot of COD Re% vs. C.D. and Time

b. Effect of time

Reaction time is an important factor for electrolysis. It is important to note that reaction time has an impact on the production rate of active chlorine and Al^{3+} ions and on the operating costs. So, a reaction time value must be chosen for efficient treatment at the lowest possible cost. In this study, a reaction time of 40 minutes is a reasonable compromise because higher values yield only energy consumption. The results were shown in Fig. 6 which illustrates the contour plot and 3D surface plot for COD Re% vs. C.D. and time. So, 40 minutes of treatment is vital to produce a reasonable amount of Al^{3+} ions and active chlorine. As shown in Fig. 6, the highest value of removal rate of COD reached at 40 minutes. The removal rate and turbidity gradually increase over time, eventually reaching more than 90% at 60 min. Because colloidal and suspended particles were the primary sources of turbidity, and residual COD was dependent on tiny organic particles. It was inefficient in removing stable persistent organic molecules for electrocoagulation. So the optimum electrolysis time was selected as 40min.

c. Effect of current density

The most essential factor affecting treatment efficiency is the current density. The experimental procedure was conducted by applying different current densities (10, 15, and 20 mA/cm²). Fig. 5 and Fig. 6 illustrate that the greatest value of COD Re% was obtained at 20 mA/cm². This result is consistent with previous researches, which found that increasing the current density results in higher removal efficiency [20]. High current disadvantages include rapid sacrificial electrode degradation and a high energy cost associated with the voltage necessary to complete the process.

As a result, the optimal current must take into consideration the cost of energy spent as well as the quantity of residual turbidity and TSS. When current density declines, the time it takes to achieve similar efficiencies increases. As a result, choosing an appropriate current density that gives an efficient and cost-effective process is required. In this study, a current density of 20 mA/cm² is a reasonable choice.

d. Effect of pH

The initial pH of an electrochemical process is an essential parameter that determines its performance. It has an effect on the stability of the hydroxide species produced [38]. The effect of pH on the efficiency of EC-EO in situ process was investigated in the present study. Depending on the chemical properties of the solution and the pH, aluminum ions can exist in a variety of forms and phases. Aluminum ions are present in the form $\text{Al}(\text{H}_2\text{O})_6^{+3}$ at pH levels below 4, but aluminum ions are existing in the forms of $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2$ at pH values between 5 and 6. Aluminum changes to the $\text{Al}(\text{OH})_3$ form as the pH rises to higher levels (5.5 to 8.8). Aluminum dissolution as ions may occur at pH levels greater than 8.8 [20]. Fig. 7 illustrates the contour plot and 3D surface plot for COD Re% vs. C.D. and pH. It is clear from Fig. 7 that the initial pH value has a considerable influence on COD Re%. Increasing or decreasing the pH value beyond 7 resulted in a decrease in removal effectiveness. The maximum efficiency of COD removal was obtained at a pH value of 7. Previous researches have shown similar observations [39–41]. The increase in pH during the EC-EO process was associated with increases in hydroxide ion concentrations (OH^-) in solution caused by water reduction at the cathode [25]. The large surface areas of Al flocks assisted in the high

adsorption of soluble chemicals (organic) and colloidal particles [37].

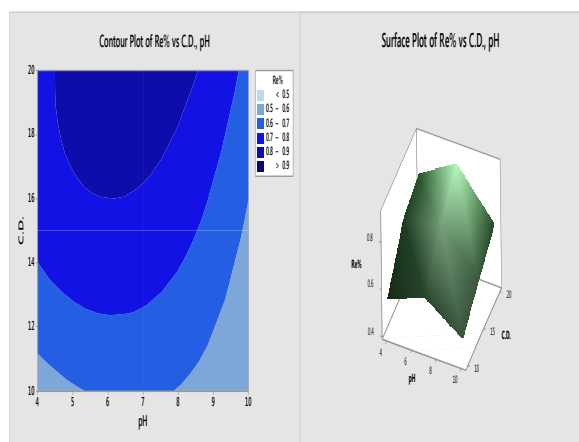


Fig. 7. Contour Plot and 3D surface plot of COD Re% vs. C.D. and pH

4. Conclusions

EC is a rapid technique that effectively removes colloidal and suspended particles, and also charged species. But, it is unsuccessful at removing stable persistent organic compounds. EO is especially successful in oxidising organic substances, but it takes a long time in the application. Combining the two techniques results an efficient process that mineralizes the organic components completely in an acceptable time. Taguchi approach was applied to optimize EC-EO in situ operating factors. It was clear from the results of S/N and ANOVA that the significance of operating parameters followed the order: C.D. > pH > NaCl concentration > time, with contribution percentage of 54.37%, 31.87%, 6.48%, and 0.17% respectively. C.D., pH, and NaCl have a noticeable impact on COD Re% while electrolysis time has a very low effect in comparison with them. Removal efficiency of COD (90 %) with a removal efficiency of TDS (25.6 %) and removal efficiency of turbidity (99 %) were achieved at the optimum conditions.

The studied system showed that it was efficient in real wastewater treatment and applicable.

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