Available online at http://ijcpe.uobaghdad.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.23 No.1 (March 2022) 31 – 41
EISSN: 2618-0707, PISSN: 1997-4884

# Study the Optimization of Petroleum Refinery Wastewater Treatment by Successive Electrocoagulation and Electro-oxidation Systems

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## Abstract

In this study, successive electrocoagulation (EC) and electro-oxidation (EO) processes were used to minimize some of the major pollutants in real wastewater, such as organics (detected by chemical oxygen demand (COD)), and turbidity. The wastewater utilized in the present study was collected from the Midland Refinery Company in Baghdad-Iraq. The performance of the successive batch EC-EO processes was studied by utilizing Graphite and Aluminum (Al) as monopolar anode electrodes and stainless steel (st.st.) as the cathode. The Taguchi experimental design approach was used to attain the best experimental conditions for COD reduction as a major response. Starting from chemical oxygen demand COD of (600 ppm), the effects of current density (C.D.) (10- 20 mA/cm$^2$), pH (4- 10), time (2– 4 h), and NaCl concentration (1.5- 2.5 g/l) on the efficiency of COD reduction were examined. The results indicated that COD reduction increased with increasing C.D., NaCl conc., and electrolysis time and increased exponentially at pH (4). The best conditions for the treatment of this wastewater were: C.D. (20 mA/cm$^2$), pH (4), time (4 h), and NaCl conc. (2.5 g/l). At these conditions, approximately 98.12 % of COD reduction was achieved with electrical energy consumption (ENC) of about 62.04 kWh/m$^3$. The result of analysis of variance (ANOVA) revealed that the C.D. and pH have a higher influence on the performance of organics removal, while the time and NaCl conc. have a minor impact on COD Re%.

*Keywords:* *Petroleum, refinery wastewater, Electrocoagulation, Electro-oxidation, Successive, Taguchi method*

*Received on 19/02/2022, Accepted on 08/03/2022, published on 30/03/2022*

https://doi.org/10.31699/IJCPE.2022.1.5

## 1- Introduction

Water is required for the life on planet earth as a basic element. Today, the aquatic environment is severely contaminated and the natural watercourses have been severely destroyed [1]. Petroleum oil is a significant component of the world's energy supply, and huge quantities of wastewater are produced throughout the oil refining process, with significant organic pollutants, severe toxicity, and poor biodegradability [2]. Petroleum wastewater is considered as a substantial polluting source, generally characterized by the high chemical oxygen demand (COD) and salinity and there are various quantities of emulsified oil, heavy metals, and organic contaminants, in addition to oil and grease (O&G) **[**3**]**.

Several techniques were employed for the treatment of refinery wastewater such as adsorption [4], ion-exchange [5], biosorption [6], membrane filtration [7], coagulation-flocculation [8], electro-oxidation [9], and electrocoagulation [10].

In comparison to the conventional methods mentioned previously, electrochemical technology makes a significant contribution in protecting the environment by introducing effluent treatment and reducing waste and harmful chemicals [11].

Due to its unique qualities, such as flexibility, energy economy, automation, and cost effectiveness, electrochemical treatment has received more attention in recent years [12]. One of the major electrochemical technologies is EC which possesses several advantages such as easy operation, short treatment time and no chemical requirement. EC has been lauded as a straightforward, efficient, and cost-effective method [13, 14].

In this process, the metal (M) is oxidized to its cation ($M^{n+}$) when an external power source is delivered to it as potential. Simultaneously, $H_2$ and the hydroxyl ion ($OH^-$) are produced via the reduction process of $H_2O$. The generated metal ions would rapidly hydrolyze to polymeric metal hydroxide that operated as coagulation agents. Tiny hydrogen bubbles form at the cathode and oxygen forms at the anode. Due to the presence of these bubbles, the emulsified oil droplets get free of the water molecules that they were previously linked to, and they float to the surface where they can be seen [14, 15, 16]. The following reactions occur during the process at the anode when an aluminum anode is used [17, 18]:

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

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$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (2)$$

$$x\,Al^{+3} + y\,OH^- \rightarrow Al_x + (OH)_y^{z+} \quad (3)$$

While, the cathodic reactions for aluminum can be summarized as follows [17, 18]:

$$2H_2O + 2e^- \rightarrow H_{2\,(g)} + 2OH^- \quad (4)$$

Because of its simplicity and durability in construction and operation, electrochemical oxidation has received considerable scientific attention. Organic contaminants can be destroyed in the EO method by either direct or indirect oxidation. In direct anodic oxidation, contaminants are adsorbed on the surface of the electrode and subsequently removed via the anodic electron transfer reaction that takes place in this oxidation process. While in the indirect EO process, strong oxidants such as hypochlorite/chlorine, hydrogen peroxide, and ozone are electrochemically generated. The contaminants are subsequently destroyed from the bulk solution via an oxidation process involving the generated oxidants [19, 20, 21]. Main reactions in EO process at the anode, cathode, and in bulk solution in case of NaCl addition may be shown as follows [22]:

At anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (5)$$

At cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (6)$$

At bulk solution:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \leftrightarrow OCl^- + Cl^- + 2H^+ \quad (7)$$

The primary objective of the present study is to evaluate the feasibility of using EC and EO methods in handling real wastewater from the Midland Refinery Company in Baghdad- Iraq. The study typically focuses on investigating and optimizing the effects of main parameters (C.D., time, pH, and NaCl conc.) on the efficiency of EC and EO processes successively by Taguchi experimental design with $L_{18}$ orthogonal array.

## 2- Experimental Work

### 2.1. Chemicals and Apparatus

Wastewater samples in the current study were collected from the feeding tank to the treatment unit from the Midland Refinery Company in Baghdad-Iraq. The main characteristics of this wastewater were attained from the Laboratories Division (Midland Refinery Company) at Water Pollution Control Unit Laboratory; which were as follows: (COD= 600 ppm, total dissolved solids (TDS)=1479 ppm, Turbidity= 315 NTU, Chlorides (Cl)= 536 ppm, pH= 7.6).

Hydrochloric acid (HCl, 37%, liquid, Sigma-Aldrich) and sodium hydroxide (NaOH, ≥ 97%, pellets, Sigma-Aldrich) were used to prepare a 1 M solution for adjusting the initial pH of the treated wastewater; and 1.5 or 2.5 g/l of sodium chloride (NaCl powder, 99.5 % by weight, Fisher Chemicals (USA)) was added to the electrolytic solution which was utilized as the supporting electrolyte.

### 2.2. Electrolytic Cell

The electrolytic cell was comprised of a laboratory DC digital power supply (type JYD APS, model: 3005D) with outlet voltage of 0-30 V and output current of 0-5 A, and the current that was supplied to each anode was measured with the use of two (Pro's kit, MT-1233C) multimeter connected to anodic lines. Also, a Digital pH meter (HANNA Instrument Inc., Model HI98107 pHep, Romania) was utilized to measure the pH of the solution during the experiments.

The batch electrochemical reactor was a glass container with [17 cm (width), 13.5 cm (depth), and 17 cm (length)] and the electrolyte volume was 2 L. In EC process, the anode electrodes were two Al plates and the cathode electrodes were three st. st. plates of type 316-AISI. While in the EO process, the anode electrodes were two graphite plates and the cathode electrodes were the same three st. st. plates of type 316-AISI. Each anode was sandwiched between two cathodes. The distance between any two electrodes was 2 cm. The total dimensions of the graphite and Al plates were [12.5 cm (width), 13 cm (length), and 0.23 cm (thickness)]. The dimensions of each st. st. plate were (12.5 cm X 12.5 cm). The effective surface area of anodes is 235 $cm^2$ (4.7 cm width 12.5 cm height for each anode electrode), which were dipped in the electrolyte.

The electrolytic reactor was placed on a magnetic stirrer hot plate (Heidolph™ 505-20000-00, 0-300°C; 0-1400 rpm) for obtaining a homogeneous solution at a rotation speed of 350 rpm.

Before each experiment all the electrodes must be reactivated, Al electrodes were rinsed with a 5 percent (v/v) HCl solution for at least 10 minutes and st. st. electrodes were rinsed with $HNO_3$ solution (1M) in an ultrasound cleaner and then washed carefully with distilled water.

The positive and negative portions of a DC power supply were connected to the anode (Al in EC process, graphite in EO process) and cathodes (st.st.) respectively, and a multimeter was connected in series with the anode. Many primarily experiments were conducted to assess the range of studied factors and to have an overview of the expected mechanism. So, based on the observations from these experiments the time for the EC process was taken like an hour and the remaining time for the EO process. In the first hour in any run in the set of EC-EO experiments, Al electrodes were utilized as anodes in the EC process then they were replaced by graphite electrodes and the EO process employed for the remaining time. In each experiment, the applied current and associated voltages were recorded for each anode by a multimeter.

The samples were collected and then filtered with Whatman filter paper and analyzed to conclude the performance of treatment (COD, pH measurement, turbidity measurement, and Conductivity analysis).

Experiments were carried out at a temperature of (30± 1°C), and each experiment was duplicated the average value of COD was taken and set as the final result.

### 2.3. Characterization and Measurements

The performance of the successive EC-EO process was examined by reduction efficiency of many characteristics, and the main characteristic in the present study was the COD that was measured by thermos-reactor (RD125, Lovibond). Two ml of initial and treated effluent for each experiment was taken and then added to vial containing an oxidizing agent and they were gently mixed. The vial was placed in the reactor and heated to a temperature of 150 °C for 120 minutes. The digested sample was cooled down to room temperature and then analyzed in a spectrophotometer (MD200, Lovibond Germany Photometers with photometric detection) to measure the COD concentration in mg/l. COD Reduction efficiency can be expressed as in Eq. (8) [23]:

$$COD\ Re\% = \frac{COD_o - COD_f}{COD_o} \times 100 \qquad (8)$$

An optoelectronic meter (TurbiDirect Lovibond, TB 300 IR, Germany) was used to measure turbidity in each sample of treated effluent. This digital meter uses a synthetic light source that gives a known-intensity light to the sample. Sample preparation for turbidity measurements is as simple as shaking the sample vial thoroughly before running the test. The value of turbidity reduction percentage can be obtained by Eq. (9) [24].

$$turbidity\ Re\% = \frac{turbidity_o - turbidity_f}{turbidity_o} \times 100 \qquad (9)$$

A digital laboratory Cond. meter (CRISON (EC-Meter BASIC 30), Spain) was used to measure the Conductivity (Cond.) of heavy metal salts.

Where: o and f were the initial and final values of each analysis respectively.
The values of energy consumed for each experiment was determined by Eq. (10) [25]:

$$ENC = (Uc.I.t)/(V*1000) \qquad (10)$$

### 2.4 Design of experiments by Taguchi Method

The simplicity and efficiency of the Taguchi approach are the main causes to utilize it for reducing time, cost, errors, and variation of any process. Besides, the optimization of the factors can be accomplished with the smallest number of experiments [26, 27].

Signal to noise (S/N) is a quantitative measurement utilized by Taguchi's approach to find the optimal reduction conditions. Also, it is utilized to evaluate variance around a response's mean value due to experimental noise, so an optimal response with lower variation may be achieved. Mean (output characteristic) and standard deviation (output characteristic) are the terminology used to describe acceptable and undesirable values for the output response, respectively [28, 29, and 30]. An increase in the S/N ratio is often associated with an increase in noise. Therefore, the best level of process parameters is the one with the largest S/N ratio [30, 31]. The main objective in the present study is to achieve the maximum value of COD reduction; thus, the HB (higher is best) S/N ratio analysis was applied. Eq. (11) performs the S/N ratio with HB characteristic [32]:

$$\frac{S}{N} = -\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \qquad (11)$$

The experimental results were assessed by MINITAB statistical software (version 17).

The levels of the four chosen factors which were studied in the present study are shown in Table **1**. The suitable orthogonal array according to Taguchi approach would be $L_{18}$ either ($3^3 \times 2^1$) that presented in Table **2**.

Table 1. 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 (h) | X4 | 2 | 3 | 4 |

Table 2. Coded and Real values of $L_{18}$ orthogonal array

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

## 3- Results and Discussion

### 3.1. Multiple regression model and the S/N results

The multiple regression equation (Eq. (12)) which was acquired by MINITAB 17 software is shown as follows which represents the relationship between COD Re% and the studied factors. The value of the correlation coefficient ($R^2$) of this equation is equal to 98.05 % which states an excellent fitting of the model.

COD Re = [0.067 +0.1771 X1+0.0742 X2-0.02930 X3-0.0203 X4-0.001563 X2^2-0.00898 X1*X2-0.00333 X2*X4]*100 (12)

**Table 3** represents the values of experimental COD Re% and the predicted ones that were determined based on Eq. (12). Also, this table shows the values of S/N ratios that were calculated based on Eq. (11) and the values of energy consumed that were determined by Eq. (10).

It is clear from Table 3 that the successive EC-EO processes were very efficient in the reduction of turbidity, where high reduction percentages ranging between 97.14-99.68% were attained.

Table 3. The values of experimental and predicted COD Re%, turbidity Re%, S/N, and energy intake

| Exp. No. | NaCl (g/l) | C.D. (mA/cm$^2$) | pH | Time (h) | COD Re%, exp. | COD Re%, pred. | turbidity Re % | ENC (kWh/m$^3$) | *S/N* ratio |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.5 | 10 | 4 | 2 | 66.86 | 69.25 | 99.21 | 10.11 | -3.4968 |
| 2 | 1.5 | 10 | 7 | 3 | 61.95 | 61.76 | 98.83 | 15.51 | -4.1594 |
| 3 | 1.5 | 10 | 10 | 4 | 55.04 | 54.27 | 98.92 | 20.21 | -5.1868 |
| 4 | 1.5 | 15 | 4 | 2 | 84.58 | 83.40 | 99.49 | 21.50 | -1.4549 |
| 5 | 1.5 | 15 | 7 | 3 | 80.92 | 77.58 | 99.68 | 32.25 | -1.8386 |
| 6 | 1.5 | 15 | 10 | 4 | 70.03 | 71.75 | 98.32 | 45.12 | -3.0948 |
| 7 | 1.5 | 20 | 4 | 3 | 93.40 | 94.38 | 99.37 | 54.29 | -0.5932 |
| 8 | 1.5 | 20 | 7 | 4 | 89.35 | 90.22 | 99.16 | 75.20 | -0.9781 |
| 9 | 1.5 | 20 | 10 | 2 | 72.56 | 72.17 | 98.62 | 37.13 | -2.7857 |
| 10 | 2.5 | 10 | 4 | 4 | 78.61 | 80.58 | 98.03 | 18.33 | -2.0901 |
| 11 | 2.5 | 10 | 7 | 2 | 71.15 | 69.19 | 97.87 | 9.87 | -2.9559 |
| 12 | 2.5 | 10 | 10 | 3 | 63.07 | 61.70 | 97.14 | 13.04 | -4.0034 |
| 13 | 2.5 | 15 | 4 | 3 | 90.58 | 90.61 | 99.31 | 26.44 | -0.8596 |
| 14 | 2.5 | 15 | 7 | 4 | 85.61 | 84.78 | 98.57 | 36.66 | -1.3492 |
| 15 | 2.5 | 15 | 10 | 2 | 66.40 | 70.06 | 97.87 | 18.33 | -3.5568 |
| 16 | 2.5 | 20 | 4 | 4 | 99.81 | 98.76 | 99.08 | 62.04 | -0.0161 |
| 17 | 2.5 | 20 | 7 | 2 | 81.27 | 80.71 | 99.08 | 29.14 | -1.8011 |
| 18 | 2.5 | 20 | 10 | 3 | 76.27 | 76.55 | 98.92 | 47.24 | -2.3527 |

Fig. **1** shows an evaluation of the experimental and predicted values of COD Re%. It is very obvious that the model predicts very well for COD Re% and Eq. (12) can essentially reveal the process valuation.

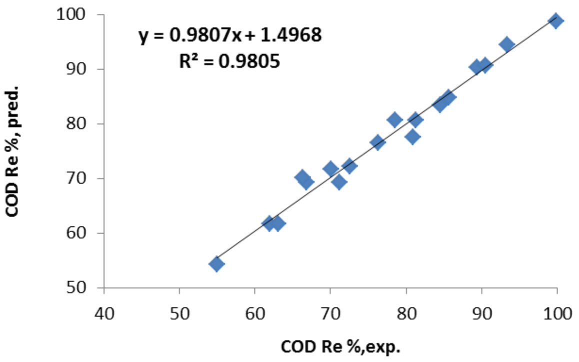

Fig. 1. Experimental and predicted COD Re% values for successive EC-EO processes

Table **4** represents the mean value of COD Re% of each studied parameter at a definite level and it is represented graphically in Fig. **2**. Based on the results of this table, the most governing factors are in the following order: C.D. > pH > time > NaCl concentration.

Table 4. Values of mean of response for data attained from COD Re% reduction experiments

| Level | NaCl (g/l) | C.D. (mA/cm$^2$) | pH | time (h) |
|---|---|---|---|---|
| 1 | 75 | 66.11 | 85.64 | 73.8 |
| 2 | 79.2 | 79.69 | 78.38 | 77.7 |
| 3 | - | 85.44 | 67.23 | 79.74 |
| Delta | 4.23 | 19.33 | 18.41 | 5.94 |
| Rank | 4 | 1 | 2 | 3 |

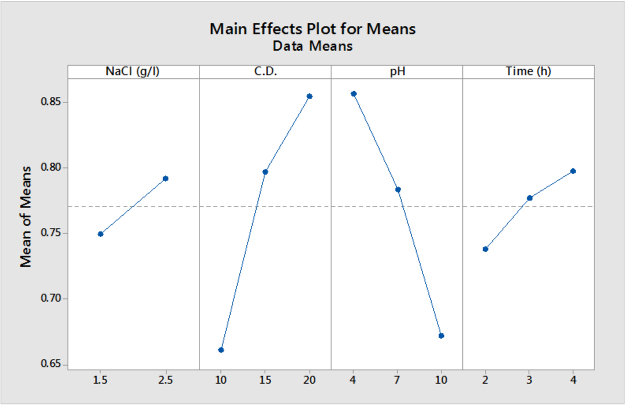

Fig. 2. Main effects plot for means values of COD Re% for successive EC-EO process

The predicted values of S/N ratios (HB) and the ranks for each dominant factor based on Eq. (11) are presented in Table **5**, and it is represented graphically in Fig. **3**. A higher S/N ratio value specifies a higher COD Re%, and the acquired ranks for each parameter show the same order of significance as that obtained with mean response.

Table 5. Response table for S/N ratio (Higher is better)

| Level | NaCl (g/l) | C. D. (mA/cm$^2$) | pH | time (h) |
|---|---|---|---|---|
| 1 | -2.621 | -3.649 | -1.418 | -2.675 |
| 2 | -2.109 | -2.026 | -2.180 | -2.301 |
| 3 | - | -1.421 | -3.497 | -2.119 |
| Delta | 0.511 | 2.228 | 2.078 | 0.556 |
| Rank | 4 | 1 | 2 | 3 |

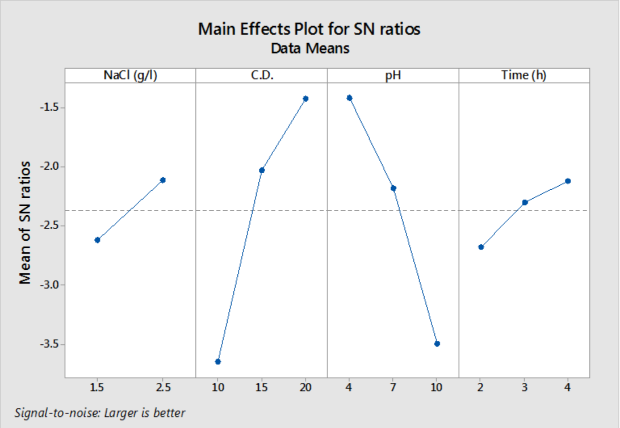

Fig. 3. Main effect plots of S/N ratio (Higher is better) for COD Re%

Based on the results of S/N ratios, the optimum conditions were: NaCl Conc. (X1) of 2.5 g/l, C.D. (X2) of 20 mA/cm$^2$, pH (X3) of 4, and time (X4) of 4 h. At these conditions, two confirmation experiments were accomplished with COD Re% of 97.88% and 98.36% respectively and therefore the higher reduction efficiency of COD was 98.12 %, with energy consumption of about 62.04 kWh/m$^3$.

### 3.2. Analysis of Variance (ANOVA)

ANOVA is a statistical method for optimization that offers a superior understanding of how the perceived results are consistent and the significance of the studied parameters can be attained [33, 34].

The influence of each parameter on the response can be attained by F-test. If F-test values > 1, this means that those parameters have a higher influence [26, 33]. When the P-value of each factor is less than 0.05 (for a confidence level of 95%) this means that the experiments were conducted at controlled conditions [26].

Table **6** shows the results of ANOVA which shows that C.D. (with contribution of 47%) has the major influence on COD Re% followed by pH (with contribution of 41.03%) and time (with a contribution of 4.34%), and the less effective parameter on COD Re% was NaCl conc. (with contribution of 3.21%).

The results of the F and P-value reveal that all factors have a significant effect on COD Re%.

Table 6. Analysis of Variance (ANOVA) for COD Re% for successive EC-EO system

| Source | DF | Seq SS | Contribution % | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|---|---|
| NaCl | 1 | 0.008066 | 3.21% | 0.008066 | 0.008066 | 7.26 | 0.023 |
| C. D. | 2 | 0.118213 | 47.00% | 0.118213 | 0.059106 | 53.21 | 0.000 |
| pH | 2 | 0.103209 | 41.03% | 0.103209 | 0.051605 | 46.45 | 0.000 |
| time | 2 | 0.010921 | 4.34% | 0.010921 | 0.005461 | 4.92 | 0.033 |
| Error | 10 | 0.011109 | 4.42% | 0.011109 | 0.001111 | - | - |
| Total | 17 | 0.251518 | 100.00% | - | - | - | - |
| | | | Model Summary | | | | |
| S | R-sq | R-sq(adj) | R-sq(pred) | | | | |
| 0.0333302 | 95.58% | 92.49% | 85.69% | | | | |

### 3.3. Effect of Controllable Parameters

#### a. Effect of NaCl conc.

Chlorine is often used to enhance the effluent's Cond. during treatment. Chlorine species that are produced at the anode like hypochlorous acid and hypochlorite ions can degrade organic compounds in the indirect EO process. Oxidants are usually stable and move in the bulk solution, where they then indirectly oxidize the waste, which is promoted by the hydrodynamic architecture of the electrochemical cell [35, 36, 37].

Increasing electrolyte conductivity, decreasing cell voltage, decreasing electrolyte resistance, and decreasing ENC can be attained by NaCl addition [38]. So, to eliminate COD and color from wastewater, NaCl can be added as an oxidizing agent in electrochemical systems due to its probable contribution in electro-catalytic degradation.

The content of Cl (final) output in the treated wastewater was found to be 16 % lower than (initial) intake wastewater in successive EC-EO process, providing significant evidence for the above conclusion [39].

Table **7** represents the values of initial and final Cond. for each conducted experiment in the EC-EO successive system. So, the value of Cond. Reduction % can be obtained. Fig. **4** illustrates the 2D and 3D surface plot for COD Re% vs. C.D. and NaCl conc., and it is clear that the reduction percentage increases with C.D. and NaCl conc. increasing due to the increase in the hypochlorous acid generation.

Previous research has shown similar results [40]. 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 [39].

Table 7. The values of initial and final Cond., and Conductivity Reduction %

| Exp. No. | NaCl (g/l) | C.D. (mA/cm$^2$) | pH | time (h) | Initial Cond. (ms/cm) | Final Cond. (ms/cm) | Cond. Re % |
|---|---|---|---|---|---|---|---|
| 1 | 1.5 | 10 | 4 | 2 | 7.04 | 6.37 | 10 |
| 2 | 1.5 | 10 | 7 | 3 | 7.13 | 6.22 | 13 |
| 3 | 1.5 | 10 | 10 | 4 | 7.17 | 6.28 | 12 |
| 4 | 1.5 | 15 | 4 | 2 | 7.29 | 6.04 | 17 |
| 5 | 1.5 | 15 | 7 | 3 | 7.1 | 6.35 | 11 |
| 6 | 1.5 | 15 | 10 | 4 | 7.18 | 6.34 | 12 |
| 7 | 1.5 | 20 | 4 | 3 | 7.22 | 5.35 | 26 |
| 8 | 1.5 | 20 | 7 | 4 | 7.17 | 6.15 | 14 |
| 9 | 1.5 | 20 | 10 | 2 | 7.16 | 5.78 | 19 |
| 10 | 2.5 | 10 | 4 | 4 | 9.12 | 6.12 | 33 |
| 11 | 2.5 | 10 | 7 | 2 | 8.9 | 8.08 | 9 |
| 12 | 2.5 | 10 | 10 | 3 | 8.94 | 8.16 | 9 |
| 13 | 2.5 | 15 | 4 | 3 | 8.96 | 7.12 | 21 |
| 14 | 2.5 | 15 | 7 | 4 | 8.98 | 6.89 | 23 |
| 15 | 2.5 | 15 | 10 | 2 | 8.93 | 8.22 | 8 |
| 16 | 2.5 | 20 | 4 | 4 | 9.05 | 7.38 | 18 |
| 17 | 2.5 | 20 | 7 | 2 | 8.93 | 7.55 | 15 |
| 18 | 2.5 | 20 | 10 | 3 | 8.99 | 8.06 | 10 |
|  |  |  |  |  |  | average cond. Re% | 16% |

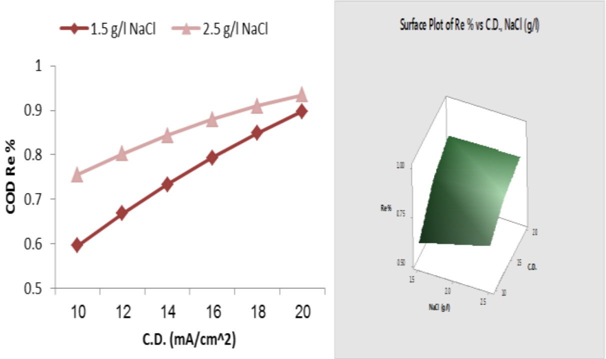

Fig. 4. 2D and 3D surface plot of COD Re% vs. C. D. and NaCl conc.

## b. Effect of Current Density

Current density is considered the most vital element that affects treatment effectiveness in any electrochemical process. As known, it is not surprising that increasing C.D. results in higher pollutants degradation efficiency. In the present study, different current densities (10, 15, and 20 mA /cm2) were conducted to treat wastewater, and it is evident from all illustrated results that the greatest value of COD Re% was obtained at 20 mA /cm2.

In the EO process, current density increasing means an increase in the HOCl generation. While in the EC process it is known that increasing current density leads to a significant amount of generated flocs and a significant growth rate due to more release of aluminum ions by anodic dissolution (according to Faraday's law). So, more generation of aluminum hydroxides necessary to coagulants formation is increased with C.D. increasing [14]. But also it must be taken into consideration that high current density promoted the degradation of sacrificial electrodes with a high energy cost related to the voltage necessary to complete the process [9, 40 .[

## c. Effect of Time

According to Faraday’s law, electrolysis time is an essential factor and it influences the generation rate of active chlorine and Al+3 ions and the operative costs. The treatment of wastewater by EC process was accomplished in all experiments in 1 h and the treatment by EO process was achieved in the remaining time (1- 3h). Fig. 5 depicts the 2D and 3D surface plots for COD Re% vs. C.D. and time.

Fig. **5** indicates that COD reduction efficiency increases rapidly with increasing time at all C.D. values. These findings are consistent with other previous studies [41, 42].

It is known that the EC process is moderately rapid and it is very active in eliminating colloidal and suspended particles but at the same time there are many limitations in removing persistent organics by the EC process. The EO process is very operative in the reduction of COD but demands so much time [43].

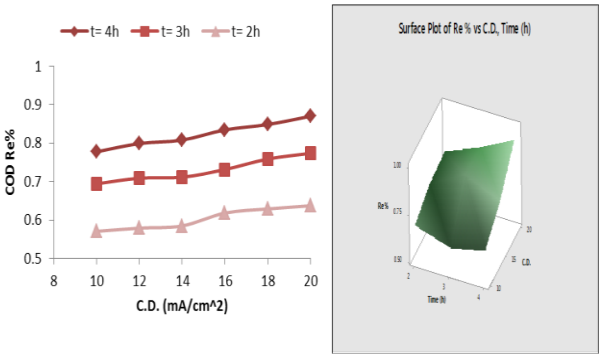

Fig. 5. 2D and 3D surface plot of COD Re% vs. C. D. and Time for successive EC-EO system

d. Effect of pH

**Fig. 6** illustrates the 2D and 3D surface plots for COD Re% vs. C.D. and pH. The highest values of COD reduction percentage are achieved at a pH range of 4–5.5. Different species of Al may be formed when Al is dissolved (electrochemically and chemically) depending on the pH and the presence of other chemical species. In the pH range, 4–9, $Al(OH)^{+2}$, $Al(OH)_2^{+}$, $Al(OH)_3$, $Al_2(OH)_2^{+4}$, and $Al_{13}(OH)_{32}^{+7}$ are produced.

These species have a high positive charge on the surface, which might cause an adsorption electrochemistry neutralization reaction [44]. At high pH values, active chlorine appears as hypochlorite, which is a less effective oxidant toward organic species than hypochlorous acid, which is a highly strong oxidant and the dominant component at low pH values [45].

For all C.D. (10- 20mA/cm$^2$), the reduction efficiency of COD increases exponentially at pH (4), this effect on COD reduction is consistent with some previous studies [41, 46].

This might be explained that an increase in C.D. would result in an increase in the production of hypochlorous acid in acidic solutions and hypochlorite in alkaline solutions, favoring the degradation of organic components via the indirect oxidation process [46].

So, based on these explanations and results of this study; the acidic conditions are preferred for high COD Re% in the successive EC-EO process.

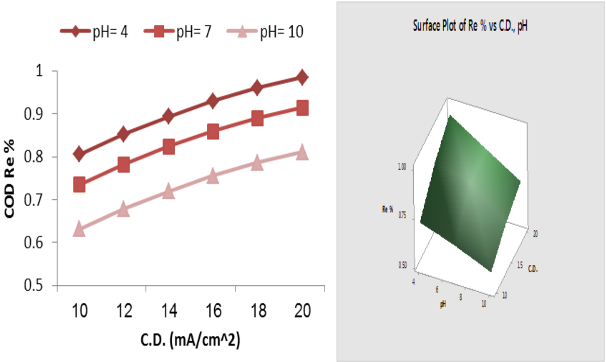

Fig. 6. 2D and 3D surface plot of COD Re% vs. C. D. and pH

3.4. Electrical energy consumption

In electrochemical research and other wastewater treatment technologies, energy consumption is a vital topic. In addition to high reduction efficiency, wastewater treatment systems must also use less energy. In all electrochemical experiments, the energy consumption is inversely related to the solution's electrical conductivity (Cond.) and directly related to the C.D. used. Improvements in electrolyte convection and decreasing the distance between the cathode and anode may reduce power consumption [47, 48]. By plotting the effect of C.D. on the ENC (Eq. (10)) in Fig. **7**, it is clear that the energy consumption values increase with C.D. increasing.

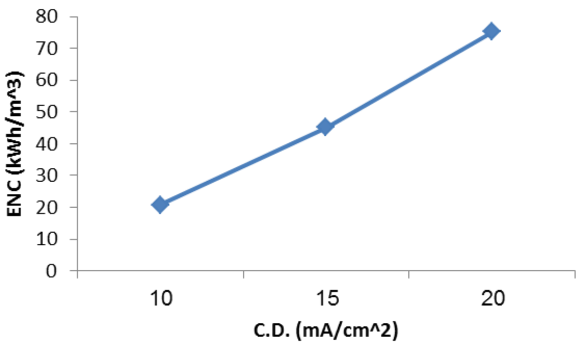

Fig. 7. Electrical energy consumption for successive EC-EO process at different C. D. and time =4 h, vol. = 2 L, NaCl conc. = 2.5 g/l, pH= 4

## 4- Conclusion

The current study showed that the wastewater from the Midland Refinery Company in Baghdad- Iraq was successfully treated using two successive processes EC-EO. The reductions of organic and inorganic contaminants were removed with final concentrations below the standard limits. The impacts of several operating parameters such as C.D., primary pH, NaCl conc., and electrolysis time on COD Re% were examined and optimized by the Taguchi approach.

Increasing the current density and time was result in higher efficiency reduction. The value of time must be chosen for efficient treatment because energy consumption increases with increasing C.D. and time. Increasing NaCl conc. increases wastewater conductivity, lowers cell voltage, and minimizes electrical energy consumption. COD Re% was inversely proportional with pH increasing. The optimum conditions for wastewater treatment by successive EC-EO process were C.D. (20 mA/cm$^2$), pH (4), time (4 h), and NaCl conc. (2.5 g/l). At these conditions, approximately 98.12 % of COD reduction was achieved with energy consumption of about 62.04 kWh/m$^3$. The results of ANOVA revealed that C.D. has the major effect on COD Re% followed by pH, time and the less effective parameter on COD Re% was NaCl conc. Based on the results of the F-value of the present study, all the studied factors have a significant effect on COD Re%.

## Nomenclature

| Nomenclature | Meaning | Units |
|---|---|---|
| AdjMS | Adjusted mean of square | - |
| AdjSS | Adjusted sum of square | - |
| C.D. | Current density | mA/cm$^2$ |
| $COD_0$ | Initial value of chemical oxygen demand | ppm |
| $COD_f$ | Final value of chemical oxygen demand | ppm |
| Cond. | Conductivity | µs/cm |
| DF | Degree of freedom | - |
| ENC | Electrical Energy Consumption | kWh/m$^3$ |
| I | current | A |
| n | number of repetitions | - |
| NaCl conc. | NaCl concentration | g/l |
| *Re* % | Reduction percentage | - |
| *t* | time | h |
| TDS | Total dissolved solids | mg/L |
| Uc | potential | volts |
| V | volume | m$^3$ |
| $y_i$ | performance results of the *i*th experiment | - |

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# دراسة أمثلية معالجة مياه الصرف الصحي المطروحة من المصافي النفطية بوساطة عمليتي الأكسدة و التخثير الكهربائيتين المتتاليتين

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## الخلاصة

في هذه الدراسة ، تم استخدام عمليتي التخثير والأكسدة الكهربائيتين (EC–EO) بصورة متوالية لتقليل بعض الملوثات الرئيسية في مياه الصرف الصحي الحقيقية ، مثل المواد العضوية (معبر عنها بالطلب الكيميائي للأوكسجين (COD)) ، والعكورة. تم جمع مياه الصرف الصحي المستخدمة في هذه الدراسة من شركة مصفى الوسط في بغداد–العراق. تمت دراسة أداء عمليات EC–EO المتتالية باستخدام الكرافيت والألمنيوم (Al) كأقطاب أنود والفولاذ المقاوم للصدأ (.st.st) ككاثود. تم استخدام نهج التصميم التجريبي Taguchi للحصول على أفضل الظروف التجريبية للحد من قيمة COD كاستجابة رئيسية. بدءًا من الحاجة الكيميائية للأوكسجين COD البالغ (600 مغ/لتر)، تأثيرات كثافة التيار (.C.D)(20–10 مللي أمبير/سم$^2$) ، ودرجة الحموضة (4–10)، والزمن (2–4 ساعات)، وتركيز كلوريد الصوديوم (1,5 – 2,5 غم/لتر) تمت دراستها.

أظهرت النتائج أنه قيمة COD Re% تزداد بزيادة كثافة التيار و زمن التحلل الكهربائي و تركيز كلوريد الصوديوم و بأنخفاض قيمة pH. كانت أفضل الظروف لمعالجة هذه المياه العادمة هي: (20 مللي أمبير/سم$^2$) ، ودرجة الحموضة (4)، والزمن (4 ساعات)، و تركيزكلوريد الصوديوم 2,5 غم/لتر). في هذه الظروف ، تم تحقيق ما يقارب من 98,12 ٪ من COD مع استهلاك الطاقة الكهربائية (ENC) بحوالي 62,04 كيلوواط.ساعة /مترمكعب. كشفت نتيجة ANOVA أن .C.D و pH لهما تأثير أعلى على أداء إزالة المواد العضوية ، في حين أن الزمن و .NaCl conc لها تأثير طفيف على COD Re%.

الكلمات الدالة: النفطي, مياه الصرف الصحي من المصافي, التخثيرالكهربائي, الأكسدة الكهربائية, طريقة تاكوشي.