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Optimization of COD Removal from Pharmaceutical Wastewater by Electrocoagulation process using Response Surface Methodology (RSM)

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Abstract

In this research, the feasibility of using an electrocoagulation method as a process for treating of hospital wastewater generated from Al-Dewaniya hospital located at Al-Dewaniya city/Iraq was investigated. Batch experimental runs were conducted using an electrochemical reactor with stainless steel and aluminum as cathode and anode, respectively. The impact of operating variables like current density, pH, and addition of NaCl on the removal of chemical oxygen demand (COD) was investigated. For this purpose, Box-Behnken (BB) design based on the Response Surface Methodology (RSM) was adopted to design and analyze the results. The results revealed that the current density has the major impact on the efficiency of COD removal followed by addition of NaCl while pH has the lower effect on the COD removal under the studied range of pH. The optimized operating parameters were a current density of 25 mA/cm^2, pH of 8.6,and NaCl addition of 2.06 g/l in which COD removal efficiency of 99.45% was achieved with a specific energy consumption of 26.079kWh/kgCOD.

Keywords: Hospital wastewater, Electrocoagulation, COD, Optimization, RSM

1. **Introduction**

Hospitals are public places play an important role for all stages of community via providing health services and their working as centers for health and research education. Hospitals are significant consumers of water and they generate a considerable amount of wastewaters containing various hazardous materials [1]. Hospital wastewaters (HWWs) are those effluents that generated from different activities of hospital such as surgery rooms, radiology rooms, nursery rooms, examination rooms, laundry rooms, laboratories, kitchens and canteens [2]. Recently, HWWs have been identified as a serious issue that may have harmful effects on the human beings and the environment directly or indirectly as well. As a result, every time higher difficulties when treating common illnesses.[3] Therefore, these effluents should be treated on-site to avoid the pollution of different sectors such as the locally sewage system, watercourses and rivers. In case of a proper treatment of HWWs, they could be reused for agricultural purposes [4]. The pollutants in hospital wastewater involve organic compounds at high concentrations, chemical substances such as disinfectants and solvents, and pathogenic microorganisms that resulted disease to the neigh boring societies [1]. Wastewater treatment has become an absolute necessity [5]

The treatment of HWWs is mostly quite complex since each effluent has its own characteristics that may be different from others hence poses specific problems for treatment [6]. Many conventional techniques of HWWs treatment are used such as biological and physiochemical processes [7,8]. Nevertheless, these methods have not the ability to treatment HWWs perfectly because of the composition and nature of these effluents. It was found that the biological treatment process suffered from many problems in the treatment of HWWs due to the adverse effects of the contaminants on the community of organisms used in the biological

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treatment [9]. Therefore, further technologies have been investigated aiming for reducing the concentration of pharmaceutical contaminants. These methods consist of the separation by membrane [10], the technology of advanced oxidation [11], and electrochemical methods such as electrocoagulation as well as electroflotation [8, 12]. In comparison with the conventional treatment techniques, electrocoagulation (EC) has the ability to overcome many drawbacks existing in these conventional methods. A comparative study between EC and chemical coagulation (CC) showed that the CC requires 20 times more mass of reagent for treating wastewater having the same volume, to accomplish the same degree of efficiency [13]. In addition, reduction of acidification of wastewater and its salinity, coagulant with low doses, and the feasibility for automating the treatment system are other advantages observed by EC in comparison with CC [8].

In recent years, more attention has been gained for the electrocoagulation (EC) as an efficient wastewater treatment method due to many features such as its simple operation and design, minimal space required for setup, low cost and energy consumption combined with high removal efficiency, less chemicals requirement, and environment-friendly since it produces little sludge with good settling ability that can be used in hilly areas as less area requiring [14]. The other capability of this process is the removal of contaminants, such as heavy metals. EC method was confirmed as an innovative approach for color and suspended solids removal from various wastewaters [15].

EC is an electrochemical management technique used sacrificial anodes to produce active coagulants. In this process removing of pollutants from the aqueous effluents is based on many mechanisms. Dissolution of Al and producing the adsorbents (hydrated aluminium hydroxides) as an anodic reaction happened simultaneously with the evolution of hydrogen gas as a cathodic reaction which, responsible on absorbent flotation. The formed metal hydroxides have the ability to quickly adsorb organic products due to their large surface. Thus, the formed flocs can be removed by either gas flotation or by the sedimentation. Equations (1, 2, and 3) represent all reactions that occurred at the surface of the anode and cathode as well as in the solution during the electrocoagulation [2, 8]:

Cathode reaction:

$$3H_2O + 3e^- \rightarrow 3/2H_2(g) + 3OH^- \quad (1)$$

Anode reaction:

$$Al \rightarrow Al^{3+} + 3e^- \quad (2)$$

In the solution:

$$Al^{3+}{}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+{}_{(aq)} \quad (3)$$

Two interaction mechanisms (precipitation and adsorption) occurred between contaminants and hydrolysis products during the electrocoagulation process. Adsorption occurs at high pH range (6.5) while flocculation is explained as precipitation at low pH range [16].

The effluent formed from the electrocoagulation can be utilized for irrigation as well as industrial uses [17]. Electrocoagulation process is suitable for a wide variety of wastewater treatment plants such as textile[18], dairy [19], sugar industry [20], laundry wastewater [21], removal of COD from petroleum refinery wastewater[22] and hospital waste waters[2].

Optimization is an essential approach for enhancing the efficiency of any process or system by which results with good and acceptable values could be obtained. Conventionally, optimization method termed as one-variable-at-a-time has been used in which one factor is changed with fixing the others at constant levels. Nowadays, multivariate statistic techniques have been used for optimization using analytical procedures. In the analytical optimization, RSM considers as the most relevant multivariate method used with high efficiency. In comparison with one-variable-a-time approach, RSM generates large quantities of information from a small number of trials and has the ability of estimating the effect of interaction between the response and its variables [23]. Two design methods in RSM are always used namely Box Behnken Design (BBD) and Central Composite Design (CCD). In comparison with CCD, BBD design has less number of experiments for fitting a quadratic model. Besides, each factor was taken only at three levels. No severe combinations of all the factors was found in the BBD design; instead, it works with better prediction accuracy at the factor center. BB is the only design that provides a minimum number of runs and proves to be economical in comparison with the other available designs in the RSM [2].

Application the electrocoagulation process for treating HWWs have been reported by different researches. Kermet-Said et al [8] ooptimized the electrocoagulation process for COD and turbidity removals from waste water generated from pharmaceutical factory at Medea, Algeria using response surface methodology (RSM)). They evaluated effects of three parameters (current density, pH, and time of reaction) using an electrochemical cell composed of pair of aluminum electrodes. Their results showed the ability to remove the COD up to 75.64% and the turbidity up 96.34% with a good fitting of the predicted model at the optimum conditions. Veli et al [14] investigated the application electrocoagulation process for removal total organic carbon (TOC)) from waste water generated from hospital of Kocaeli University, Turkey using response surface methodology (RSM)). They evaluated effects of two parameters (current density and pH) in an electrochemical cell using Al, Fe and SS as anode materials individually. Their results showed that TOC removal efficiencies were >99% for all three electrodes at the optimum conditions.

Recently, Bajpai and Katoch[2]optimized the electrocoagulation process for removal of COD from waste water generated from Hamirpur regional hospital at India using response surface methodology (RSM)). They evaluated effects of three parameters (current, pH, and time of reaction) in an electrochemical cell composed of Iron (Fe) electrodes. Their results showed that the percentage impact of current on COD removal was the maximum in comparison with the other factors. They found the possibility of removing the COD up to 92.81% with a good fitting in relating to the predicted model at the optimum conditions.

The aim of the present work is to estimate the feasibility of application an electrocoagulation process for treating wastewater generated from local Iraqi hospital located at Al-Dewaniya city. The impacts of operating parameters such as current density, pH and NaCl addition on the efficiency of COD removal from hospital wastewater were investigated, and the optimum conditions of these parameters that suitable for higher removal efficiency were determined using RSM.

2.Experimental work

As a case study, 40L hospital wastewater was collected from sewage system of Al-Dewaniya hospital (located at Al-Dewaniya city, Iraq) before mixing with the domestic wastewater of the city. Table 1 shows the properties of the hospital wastewater. This hospital wastewater was kept at 4 °C during the period of the experimental program and the required sample for each experiment (0.7 L) was taken at the time of each experiment.

Table 1.
Properties of wastewater from Al-Dewaniya hospital sewage system

parameter	Value
COD(mg/l)	745
pH	6.5
T.D.S(mg/l)	2410
Cl^-(mg/l)	1.666
SO_4^{-2}(mg/l)	500
Turbidity(NTU)	9.66
Conductivity (mS/cm)	1.92

The conductivity of the examined hospital wastewater was found to equal 1.92ms/cm. This value considers low and leading to an increase in the cell potential, therefore using a supporting electrolyte is recommended to increase the conductivity of solution. By using 0.05 M Na_2SO_4 as a supporting electrolyte , the conductivity was raised to 12.9 $mScm^{-1}$ which is in the limited range for obtaining low cell potential [24].

All experiments were performed in a batch mode by a cylindrical jacketed Perspex electrochemical cell has inside diameter of 100 and length of 200 mm with thickness of 5mm (Figure 1). The cell gives working volume of about 0.7 L. The cover of the electrochemical cell has an outside diameter of 130 mm with thickness of 10mm. Five slits were made in this cover for electrodes fixation in addition to a number of holes for inserting probes of conductivity meter and pH-meter, and for sampling taking out. Three stainless steel (316-AISI) and two aluminium plates with the dimensions of 150mm × 50mm × 10mm were used as cathode and anode electrodes respectively. The gap between the anode and cathode was fixed at 2.5 cm. A magnetic sitter was used to agitate the solution at 300 rpm to ensure homogeneity within the reactor and to minimize break up of flocs [2]. All runs were conduct at a constant temperature of 25 ±2 ºC using water bath circulator (Memmert, type: WNB22, Germany).

pH measurement was achieved by using a digital pH meter (HNNA Instrument Inc.PH211, Romania) while adjusting pH value was accomplished using 0.1 M NaOH or 0.1 M H_2SO_4 solutions. TDS and conductivity were measured using (HM digital Inc. model COM-100, Korea).

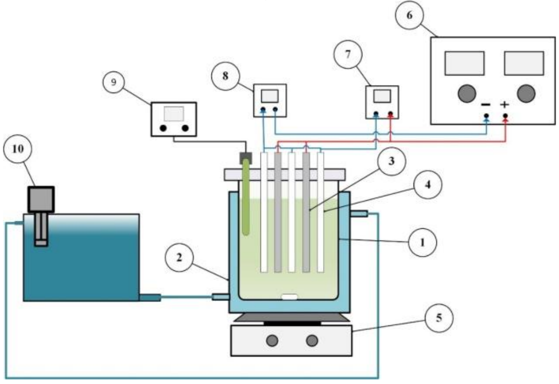


Figure 1. The electrochemical system: 1) cell body, 2) jacket, 3) aluminium anode, 4) stainless steel cathode , 5) magnetic stirrer, 6) power supply, 7) voltmeter 8) Ammeter,9) pH-meter10) water bath circulator.

The DC power supply (UNI-T, UTP3315PF) with a maximum voltage of 30 V and a maximum current of 5 A was used to supply the suitable electrical current. Prior to starting each run, anodes and cathodes were rinsed with ethanol and water to remove impurities. At the end of each run, samples were filtered then examined their COD value for analyzing the process performance. Each experiment was repeated three times then the average value was taken.

To determine the COD , a sample (2ml) of effluent was digested with $K_2Cr_2O_7$ for a period of time 120 min. using COD thermos-reactor (RD125, Lovibond) at a temperature of 150 °C followed by cooling the sample down to room temperature then spectrophotometer (MD200, Lovibond)was used to measure the COD.

The removal efficiency of COD was calculated using Eq. 4, [22]:

$$RE\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (4)$$

where C_f represents the final COD (mg/l) while C_i represents the initial COD (mg/l)

Consumption of aluminium was measured experimentally by weighting of electrodes before and after each experiment then the Al consumption (kgm^{-3}) was calculated using Eq. 5:

Al consumption (kgm^{-3}) = (Initial weight – final weight) / volume of sample (5)

The specific energy consumption (SEC) is the quantity of energy required for digesting a kg of COD. SEC in (kWh/kg) can be obtained using Eq. 6 [25]:

$$SEC = \frac{U.I.t \times 1000}{(COD_i - COD_f)\, V} \qquad (6)$$

Where SEC is the specific energy consumption at kWh/kg COD, U is the voltage of the in Volt, I is the current (A),t is the time of experiment in hour, COD_i and COD_f are the initial and final values of COD (mg/l),and V is the effluent volume in liter.

2.1 *Experimental design*

Fitting of the model of any response and determining the optimum operating conditions for this response can be achieved by using a collection of statistical and mathematical techniques formulated by Minitab-17 Software. In Minitab-17 Software, there are numerous approaches could be used for response optimization, but in this research Box Bhenken design was used to optimize and get the effect of variables such as current density, pH and electrolyte (addition of NaCl) on the removal efficiency of COD by electrocoagulation. The range of operational factors were current density (5-25 mA/cm^2), pH (4 – 10), and addition of NaCl (0-2g/l). The range of chosen values of the operational factors were designed based on reviewing some literatures [1, 2, 8,16]. Table 2 shows the variables were designed as X1, X2, and X3. All variables were set into three levels, namely -1, 0, +1for low, intermediate and high value, respectively. Before starting the experimental runs, a preliminary run was achieved to determine the suitable electrolysis time. The selected operating conditions were current density (25mA/cm^2), pH (7), and NaCl addition (1.5 g/l). Results of COD deceasing with time is shown in Table 3. Based on the results of Table 3, it was found that electrolysis time of 90 min being the suitable for achieving the experimental design to give the significant results of RSM since the removal efficiency of COD is greater than 85%. Using higher time may be not giving a clear picture for the effects of parameters.

Table 2 : Process parameters and their levels for treatment of hospital wastewater.

Process parameters	range in Box–Behnken design		
Coded levels	Low(-1)	Middle(0)	High (+1)
X1- Current density (mA/cm^2)	5	15	25
X2- pH	4	7	10
X3-NaCl (g/l)	0	1	2

Table 3. Selecting the best electrolysis time based on decreasing of COD with time.

Time (min)	0	20	40	60	70	80	90	100	110
COD(mg/l)	758	692	533	346	274	172	100	11	3

Based on Minitab-17 Software using Box Bhenken method, 15 run experiments should be performed in a trial design with three repetitions of the center point. Repetition is useful for evaluating pure errors from sum of squares. Table 4 shows the BBD adopted at present work.

Table 4: Box- Behnken experimental design

Run	Blocks	Coded value			Real value		
		x_1	x_2	x_3	Current density (mA /cm^2) X1	pH X2	NaCl (g/l) X3
1	1	0	0	0	15	7	1.5
2	1	1	-1	0	25	4	1.5
3	1	0	1	1	15	10	3
4	1	0	0	0	15	7	1.5
5	1	-1	-1	0	5	4	1.5
6	1	0	-1	1	15	4	3
7	1	-1	0	-1	5	7	0
8	1	1	0	-1	25	7	0
9	1	0	0	0	15	7	1.5
10	1	0	1	-1	15	10	0
11	1	1	0	1	25	7	3
12	1	0	-1	-1	15	4	0
13	1	1	1	0	25	10	1.5
14	1	-1	0	1	5	7	3
15	1	-1	1	0	5	10	1.5

For the assessment of results, BBD provides correlation in which the data are set in a 2^{nd} order polynomial equation as follows [25]:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (7)$$

Where RE% is termed as Y, i and j refer to patterns index numbers, β_0 is intercept term, $x_1, x_2 \ldots x_k$ are coded form of process variables. β_i refers the first-order(linear) main effect, β_{ii} represents second-order main effect and β_{ij} refers the interaction effect. ANOVA was achieved then the regression coefficient (R^2) was calculated to check the goodness of model fit.

Results and discussion

1.1. Statistical analysis

Fifteen batch runs were performed at different process variable combinations to study the combined effects of the independent factors on the COD removal efficiency. Table 5 displays the experimental results such as COD removal efficiency (RE %), Al consumption, and specific energy consumption (SEC) that obtained at 90 min electrolysis time.

It can be seen that COD removal efficiency is in the range of 80-99.99%. Aluminium consumption is in the range of (0.46-2.416) kg/m^3. The energy consumption is in the range of (2.304-32.813)Kwh/kg COD. The difference among the center points in the design is less than 2% confirming good reproducibility of results. By using Minitab-17 Software. Based on the analysing the results of COD removal efficiency, an quadratic model in term of real units of process variables was obtained which relates COD removal efficiency (RE%) with process variables as shown in Eq.8:

$$RE\% = 61.20 + 1.351\,X1 + 2.722\,X2 + 9.87\,X3 - 0.02042\,(X1)^2 - 0.1200\,(X2)^2 - 1.297\,(X3)^2 - 0.0072\,X1X2 - 0.1005\,X1X3 - 0.233\,X2X3 \qquad (8)$$

Where RE% is the response, and X1, X2, and X3 are current density, pH, and addition of NaCl respectively. Whereas the variables X1X2, X1X3, and X2X3 represent the interaction effect of all model parameters. $(X1)^2$, $(X2)^2$ and $(X3)^2$ represent a measure of the main effect of variables current density, pH, and NaCl addition respectively.

The effects of individual parameters (linear and quadratic) or double interactions on the COD removal efficiency can be shown in Eq.(8) where COD removal efficiency increases with increasing factors whose coefficients have positive values while those factors that their coefficients have negative values decrease the COD removal when they are increased. It is clear that current density, pH and addition of NaCl have a positive effect on the COD removal efficiency, while all the interactions have negative effects. Using equation 8, the predicted values of the COD removal efficiency was estimated and tabulated in Table 5.

Table 5: Experimental results of Box–Behnken design for COD removal.

Run Order	Pt Type	Blocks	X1	X2	X3	RE%		Al consumption Kg/m^3	SEC (Kwh/kg COD)
						Actual	Predicted		
1	0	1	15	7	1.5	95.57	96.46	1.439	12.768
2	2	1	25	4	1.5	96.82	97.18	2.349	30.485
3	2	1	15	10	3	98.00	97.42	1.589	10.425
4	0	1	15	7	1.5	97.08	96.46	1.713	13.105
5	2	1	5	4	1.5	86.95	85.99	0.484	2.532
6	2	1	15	4	3	96.00	96.01	1.536	12.752
7	2	1	5	7	0	80.00	80.37	0.499	2.866
8	2	1	25	7	0	95.07	94.13	2.416	32.813
9	0	1	15	7	1.5	96.74	96.46	1.626	11.259
10	2	1	15	10	0	91.03	91.02	1.367	15.618
11	2	1	25	7	3	99.99	99.62	1.853	29.674
12	2	1	15	4	0	84.83	85.41	1.897	16.779
13	2	1	25	10	1.5	99.30	100.25	2.369	30.310
14	2	1	5	7	3	90.95	91.89	0.463	2.304
15	2	1	5	10	1.5	90.29	89.94	0.853	2.522

Table 6 elucidates ANOVA of response surface model. In this Table, degree of freedom terms as DF, sum of the square terms as SeqSS, contribution for each parameter terms as Contr. %, adjusted sum of the square terms as Adj SS, adjusted mean of the square terms as Adj MS, F-value, and P-value. Fisher F-test and P-test were used to examine the acceptability of the model. Most of the variation in the response can be fit by the regression equation when its Fisher value is large. P-value is used for estimating whether F has large value sufficient to recognize statistical significance of the model. At P-value lower than 5%, then 95% of the variability of the model could be explained [26].

Based on Table 6 , the quadratic model is significant with confidence level equal to 95% and F-value of 42.38. The p-value for COD removal model was calculated as 0.0001, which gives an indication that the developed model is significant. Besides, the Lack of fit is not significant (p-value=0.296 > 0.05) when compared to pure error which reveals that the model is effective, appropriate and significant to explain the contaminants removal by EC process [27,28].

The statistical summary model focuses on the values of three important correlation coefficients namely correlation coefficient (R^2), adjusted correlation coefficient (Adj. R^2) and predicted correlation coefficient (pred. R^2). The correlation coefficient (R^2) should be close to 1 to insure high degree of correlation between observation and prediction value [29]. The sample size as well as number of terms in the models could be corrected based on the value of Adj. R^2, which does not always rise with adding variables. Therefore value of Adj. R^2 should be very close to the corresponding R^2. Besides, the difference between adjusted correlation coefficient (Adj. R^2) and predicted correlation coefficient (pred. R^2) should be less than 0.2 for confirming the good agreement between the experimental and model predicted values [29]. In the present work, values of R^2, Adj. R^2, and pred. R^2 were found to be 0.9871, 0.9638 and 0.830 respectively, which confirms the compatibility of experimental and model predicted values. Besides, the difference between Adj. R^2 and pred. R^2 was 0.1338 confirming the highly significance of the model.

Table 6: Analysis of variance for COD removal of hospital wastewater treatment

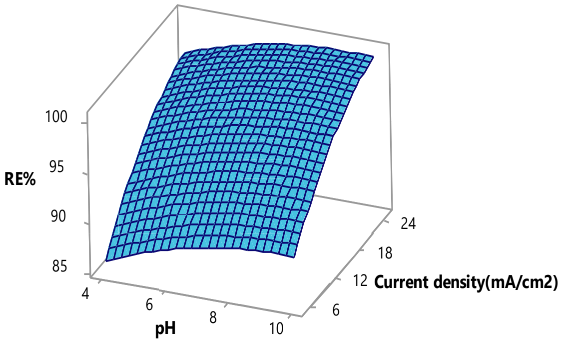
Source.	DOF	Seq. SS	Contr.(%)	Adj. SS	Adj. MS	F-value	P-value
Model.	9	459.563	98.71	459.563	51.063	42.38	0.0001
Linear	3	400.192	85.95	400.192	133.397	110.72	0.0001
(X1)	1	231.071	49.63	231.071	231.071	191.79	0.0001
(X2)	1	24.553	5.27	24.553	24.553	20.38	0.006
(X3)	1	144.568	31.05	144.568	144.568	119.99	0.0001
Square	3	45.683	9.81	45.683	15.228	12.64	0.009
X1*X1	1	11.523	2.47	15.402	15.402	12.78	0.016
X2*X2	1	2.718	0.58	4.306	4.306	3.57	0.117
X3*X3	1	31.443	6.75	31.443	31.443	26.10	0.004
2-Way Inter	3	13.688	2.94	13.688	4.563	3.79	0.093
X1*X2	1	0.187	0.04	0.187	0.187	0.15	0.710
X1*X3	1	9.093	1.95	9.093	9.093	7.55	0.040
X2*X3	1	4.408	0.95	4.408	4.408	3.66	0.114
Error	5	6.024	1.29	6.024	1.205		
Lack of Fit	3	4.769	1.02	4.769	1.590	2.53	0.296
Pure-Error	2	1.255	0.27	1.255	0.627		
Total	14	465.587	100				
Model-summary		S.	R^2	R^2(adj.)	PRESS	R-sg(pred.)	
		1.09763	98.71 %	96.38%	79.1297	83.00%	

As can be seen from Table 6 that among all factors, current density (X1) was the most important factor effect on COD removal with a percentage of contribution (49.63%). The impact of NaCl addition (X3) has the second important with a percentage of contribution (31.05%) which indicates the role of chloride ions on the degradation of organic compound during the electrocoagulation. There is a less impact due to pH factor (X2) on COD removal with percentage of contribution (5.27%) as the range of pH (4 - 10) was taken which exemplifies that maximum pollutant removal efficiency can be obtained in this range of pH [2]. Similar results were observed by different previous works[30,31].

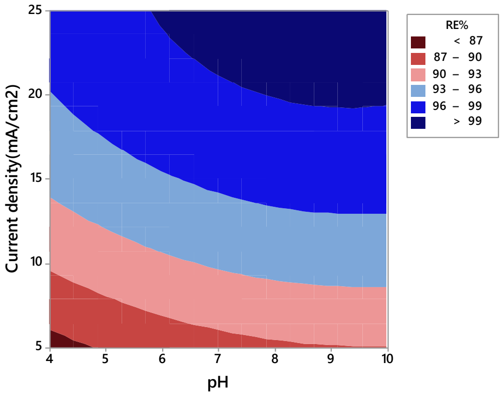
Moreover, the contribution of the interaction effects on the COD removal was found to be 2.94% with the interaction (X1*X3) being significant among the other interactions. The contributions of the quadratic effects on the COD removal was found to be 9.81% with quadratic effect of pH ($X2^2$) is non-significant in compare to current density and addition of NaCl.

3.2 Effect of process variables on the COD removal efficiency

Graphical demonstrations of the statistical optimization based on RSM was used to study effect of process variables and their combination on the COD removal efficiency. Figures (2-a, 2-b) demonstrate the combined effects of current density and solution pH on the COD removal efficiency at constant addition of NaCl. (1.5g/l). Figure 2-a denotes the response surface plot while Figure 2-b displays the equivalent contour plot. From Figure 2-a it was observed that increasing of current density results in increase the COD removal efficiency over the whole pH range (4-10). For example, increasing the current density from 5 to 25mA/cm^2 results in a significant increase in COD removal from 86.95% to 96.8 % at pH=4 (Table 6, Exp.2 and 5). Besides, the increase in COD removal efficiency became relatively the same at pH=10 from 90.29 to 99.3 % (Exp.13 and 15, Table 6). It was observed that current density had the most effect on COD removal efficiency when EC process was performed using aluminum electrode. The reason for these results could be described based on Faraday's law where increasing the current density results in increasing the dissolution rate of Al anode leading to an increase in the production of coagulants ($Al(OH)_3$ particles) at the anode[32]. Additionally, the production rate of hydrogen gas bubbles and their size have an effective role on the eliminating the pollutants by floatation where an increase in current density results in increasing the production rate and decreasing the bubble size [33]. Besides, mass transfer rate as well as floc production increases as the bubbles production at the cathode increases [32]. Similar observations were found by previous studies [15, 34, 35]



(2-a)



(2-b)

Figure 2. The combined effects of current density and solution pH on the COD removal efficiency at constant addition of NaCl (1.5 g/l): (a) 3D surface plot,(b) contour plot .

As can be observed from Fig.2-a,COD removal efficiency increases with increasing the pH. For example, increasing of pH from 4 to 10 at current density 5mA/cm^2 results in increase in COD removal from 86.95% to 90.29 % (Table 6, exp.5 and 15). However, this increasing in COD removal efficiency became relatively less at higher current density. Clearly, the impact of pH on the COD removal efficiency is higher within pH values (4-7) in comparison to 7-10. This behavior can be interrupted as follows: At acidic pH, the decrease in efficiency could be happened as a results of insufficient hydroxyl ions and as well as very low formation of $Al(OH)_3$. Besides, at low pH condition (less than 7) aluminum hydroxide particles are soluble; therefore they are not have the ability to absorb the pollutants. At pH 7, the insoluble $Al(OH)_3$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{32}^{7+}$ are the dominant compounds and have the ability to adsorb the pollutants . At high pH values, $Al(OH)_4^-$ is formed, which is soluble in water resulting in reducing the removal efficiency specifically at pH greater than 10[32,36]. Similar results can be seen in different literatures [32, 37, 38].

Based on contour plot results (Fig.2-b), it is clear that COD removal efficiency ≥95% could be obtained within a limited region in which pH is in the range (7-10) and current density is within 20-25 mA/cm^2.

Figures (3-a, 3-b) demonstrates the combined effects of current density and addition of NaCl on the COD removal efficiency at constant solution pH=7. Figure 3-a denotes the response surface plot while Figure 3-b demonstrates the equivalent contour plot.

From Figure 3-a, it was observed that increasing of current density results in increasing of COD removal efficiency over the whole range of NaCl addition. However, this increasing in COD removal efficiency became relatively less at high concentration of NaCl. As can be seen from Fig.3-a, the removal efficiency of COD increases with increasing NaCl addition. For example, at current density 5mA/cm^2, COD removal efficiency increased from 80% to 90.95%when NaCL was added at 3g/l in comparison with no addition. Literature surveys shown that addition of NaCl potentialy enhanced the EC process efficiency because of the increase in wastewater conductivity that reduces the cell voltage and subsequently the process energy consumption. In addition, the opposing effects of anions such as CO_3^{2-}, HCO_3^- and SO_4^{2-}, can be prevent in the presence of NaCl electrolyte. The presence of such anions results in precipitation of Ca^{2+} or Mg^{2+} cations as an insulating layer on the surface of cathode leading to increase ohmic resistance of the EC cell [39]. Furthermore, addition of NaCl to the electrochemical process will result in the following reactions:

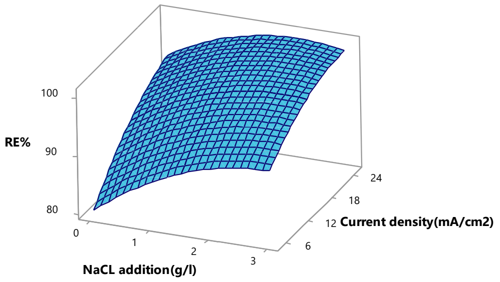
$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (9)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (10)$$

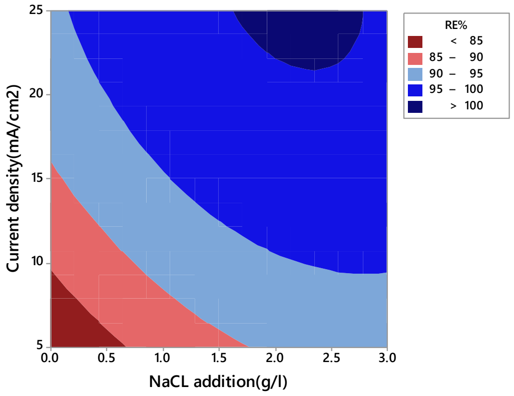
$$HOCl \rightarrow OCl^- + H^+ \quad (11)$$

According to reactions 9 and 10, Cl^- may oxidize to Cl_2, which is a strong oxidizer and may assist in oxidation of the dissolved organic compounds, or may lead to the formation of HOCl, which is a strong oxidizer hence further removal of COD in addition to electrocoagulation [40]. Similar observations were found in similar works [1, 39,41]

Based on contour plot results (Fig.3-b), it is clear that COD removal efficiency ≥95% could be obtained within a limited region in which NaCl addition is in the range (1.8-2.8g/l) and current density is within 22-25 mA/cm^2.



(3-a)



(3-b)

Figure 3. The combined effects of current density and addition of NaCl on the COD removal efficiency at constant solution pH=7(a) 3D surface plot,(b) contour plot .

3.3 The optimization and confirmation test

For optimizing the system using Minitab-17 Software, many criteria should be considered to get desired objective by making the desirability function (D_F) maximum as possible as via adjusting the weight or importance. Five options should be considered as a target namely maximize, objective, minimize, within the range, and none. The aim of optimization is to get higher removal efficiency of COD therefore removal of COD was selected as the 'maximum' with corresponding 'weight'1.0. The parameters studied in this research were identified within the range of the designed levels (Table 2). The lower and upper values of COD removal efficiency were allocated at 80% and 99.99% respectively. Optimization has been achieved using response optimizer of Minitab-17 Software based on these constrains and settings. Results of optimization are illustrated in Table 7 with the desirability function of (1).

Two experiments were conducted using the optimized parameters for confirming the optimization results. The results are shown in Table 8. After 90 min of the electrolysis, 99.45% COD removal efficiency (average value) was accomplished which is in compactible with the range of the optimum value obtaining from optimization results (Table 7). Therefore, Box–Behnken design combined with desirability function can be applied as successful and effective method for optimizing COD removal using EC process. Further experiments was conducted in which pH value of 7 was considered maintaining other parameters at their optimal values and its results tabulated in Table 8. Results showed that the possibility of using pH=7 with good COD removal efficiency (97.4%) but with a slightly increase in the energy consumption.

A comparison between the characteristics of treated effluent based on the present work with the characteristics of effluent without treatment is shown in Table 9. It was clear that treated effluent has enhanced characteristics with a COD removal efficiency of 99.3%.

The optimum conditions showed that the electrocoagulation process can be applied successfully for treatment of Al-Dewaniya hospital wastewater using aluminum electrodes. By starting from an initial COD (745 ppm), COD removal efficiency of 99.3% could be accomplished at 90 min electrolysis time. In this case, specific energy consumption not more than 26.079 kWh/kg COD should be provided. In Table 10, a comparison between the results of present work with the others related to hospital wastewater degradation by electrocoagulation process using Aluminum electrode under various conditions have been achieved. Based on this Table, the efficiency of the EC process is suitable for treating hospital wastewater and requests only 90 min to remove approximately all the COD starting from COD of 745 mg/l with a suitable energy consumption related to previous works.

Table 7: Optimum of process parameters for maximum COD removal efficiency (RE%).

Response	Aim	Lower%	Target%	Upper%	Weight	Important
RE (%)	Maximum	80	99.99	99.99	1	1

Solution: Parameters			Results				
Current density (mA/cm^2)	pH	NaCl addition (g/l)	RE (%) Fit	D_f	SE. Fit	95% CI	95% PI
25	8.60	2.061	100.716	1.0	0.753	(98.780,102.651)	(97.294, 104.137)

Table 8: The optimum COD removal efficiency confirmation

NO.	Current density, mA/cm^2	pH	NaCl. (g/l)	U (volt)	COD, (ppm)		RE %		EC. Kwh/kg COD
					In	out	Actual	Average	
1	25	8.6	2.06	6.4	745	5	99.3	99.45	26.079
2	25	8.6	2.06	6.4	740	2.5	99.6		
3	25	7	2.06	6.0	769	20	97.4		29.11

Table 9: Comparison between the wastewater effluent and the treated effluent

Parameter Effluent	COD (ppm)	pH	Turbidity (NTU)	EC (mS/cm)	Cl^- (g/l)	SO_4^{-2} (g/l)
Raw effluent	745	7.9	9.66	1.92	1.666	0.5
Treated effluent	5	8.6	2.36	14.6	1.568	2.9

Table 10: Comparison of hospital wastewater treatments by electrocoagulation process using various type of electrodes under several conditions

Type of wastewater	Characterization of wastewater	Optimum conditions	Efficiency	Reference
Textile	pH: 11.6, COD: 800mg/L, Color: 401 mg/L, Turbidity: 105 NTU,	C.D.= 8 $mAcm^{-2}$ pH= 7.1 T: 15 min	Color%=86% 82% turbidity COD= 59%	38
Hospital	COD: 4200 mg/L, pH:8.9,Turbidity: 180NTU, TSS:13.32 g/l	C.D= 99.81 A/m^2 , NaCl = 1.5 g/l, pH = 6.0 T = 120 min	Color%=97.83% COD%=58.35% SEC=27.12kWh/kg COD	37
Hospital	pH: 7, COD: 528 mg/L, Turbidity: 269 NTU, Cefazolin: 42.3 pbb,	T: 30 min voltage 15 V	94% cefazolin, 94%turbidity, COD= 85%	32
Hospital	COD: 377.5 mg/L, Turbidity:26NTU, pH=7.81	current: 2.64A and electrolysis time: 41.31 mins pH:7.41,	COD= 92.81%	2
Hospital	COD: 107.157mg /l NaCl: 0.38 M	T=٣٤,٢٦min، voltage 12 V,	COD%= 65.04%.	1
Hospital	COD:745 ppm, Turbidity:9.66NTU pH=7.9	Initial pH: 8.6, C.D: 25 mA/cm^2, NaCl Addition: 2.06 g/l. T=90 min	COD%=99.45% SEC=26.079kWh/kgCOD)	Present work

4. Conclusions

In the current study, EC process was applied to decrease the COD content in the hospital wastewater generated from Al-Dewaniya hospital (located at Al-Dewaniya city, Iraq) using aluminum electrodes. A Box-Behnken (BB) design was effectively applied for designing the experiments and analyzing the results. This study clearly demonstrated that application of Box-Behnken (BB) design based on RSM to optimize the operating factors and maximize COD removal is the most suitable approach. The obtained correlation coefficient R^2 was found equal to 0.9871 for COD removal, indicating that the actual data fit quite well with the predicted data by applying the quadratic model. According to the results, current density has the main effect on the electrocoagulation process because of higher aluminum hydroxide formation in the solution by using aluminum electrode at higher current density values. The optimum COD removal efficiency (99.45%) was found at initial pH of 8.6, current density of 25 mA/cm^2, and NaCl addition of 2.06 g/l. The corresponding energy consumption was found equal to 26.079kWh/kgCOD.

5. Conflicts of interest

There are no conflicts to declare.

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