

Application of Response Surface Methodology to Optimize Nitrate Removal from Wastewater by Electrocoagulation

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Abstract— This study concerns with electrochemical process so called electrocoagulation used to treat a high nitrate wastewater whereby sacrificial carbon steel anodes. Response Surface Methodology was applied in the development of statistical analyzing, modeling and interpreting the resulted treatment data of nitrate wastewater by electrocoagulation. In addition, the response, residual, probability, surface and contour plots were achieved. Fractional factorial design has been applied for the simultaneous study of the effects of operation time and the current density on nitrate removal response. The effectiveness of the considered design parameters was well examined to find the optimum experiment condition. Model to perform simulated regression with nitrate removal response gives the best fitted equation of second-order functions of two factor variables that has been obtained to find optimum removal. At initial pH of 8, the optimum condition for predicted maximum nitrate removal of 92.25% were found to be 74.7 min. operation time and 12.7 mA/cm² current density.

Index Terms— Electrocoagulation, Factorial Design, Model, ANOVA, Optimization..

1 INTRODUCTION

Concentration of nitrogen compounds in some industrial wastewaters is tremendously higher than what is in ground water and surface water. Ammonia and nitrate are the most problematic nitrogen compounds in this sort of wastewaters. Ammonia in industrial wastewater is normally converted by nitrification which is achieved by the complete oxidation of ammonia to nitrate. Nitrogen containing compounds create serious problems including eutrophication, destroyed water quality and potential hazards on human and animal health when they enter to water resources [1]. Pollution of water resources by nitrate is occurred due to domestic wastewaters and unconventional consumption of fertilizers in agricultural [2]. Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption. These properties make it difficult to be removed from water. Therefore, treatment for nitrate is typically very complicated and expensive. The conventional methods for nitrate removal from wastewater include ion exchange, biological decomposition, reverse osmosis, electro dialysis and catalytic denitrification [3-5].

Electrocoagulation process has been successfully employed for color, heavy metals and COD removal of industrial wastewaters [6]. Electrocoagulation process has several advantages, involving the ability to deliver a precise coagulant dose via control of the amount of applied electrical current, easy automation, low energy requirements, and the ability to destabilize, aggregate, and separate the pollutants in a single stage [7, 8]. Thus, it has been reported in the literature that nitrates can be removed from wastewater via their adsorption

onto the surfaces of hydroxide precipitates, which are generated from metals and released by the electrodes.

In most electrochemical process, current intensity and electrolysis time are the most important parameters for controlling of the reaction rate [9]. In batch mode, electrocoagulation was investigated for its performance in the removal of nitrate from wastewater using vertical monopolar Al electrodes unit [9, 10]. Moreover, the removal of ammonium, phosphate, nitrite and nitrate from paper mill effluents was investigated by different current intensity, electrodes (Al and Fe) and electrolysis time [11]. Otherwise, continuous flow mode to evaluate some of the factors influencing arsenic and nitrate removals by electrocoagulation was executed for experimental study [12]. Contaminant removal efficiency for voltages range and comparative study was done with distilled and tap water for the two contaminants. Generally, the removal of nitrate from water to an allowable concentration at the pH range 9-11 using electrocoagulation method is possible [13], and full removal of nitrate is also possible but with higher energy consumptions. According to the results of several researches [9, 11, 13], electrocoagulation is an effective process for nitrate removal. However, the reduction of NO₃⁻ to N₂ gas can be occurred with the oxidation of Fe or Al anodes by EC process precipitating Fe(OH)₃ or Al(OH)₃ produced in water, that can reduce and decompose nitrate. Experimentally, the optimum conditions for nitrate removal efficiency were tested in several researches in aqueous solution with Al electrodes and Fe electrodes. In addition the effects of pH, electrical potential difference, nitrate initial concentration, total dissolved solid, kind of electrode, electrode connection methods and number of electrode were also studied [2-13]. Moreover, the simultaneous removal of Cr⁶⁺ and NO₃⁻ from an aqueous solution by EC process using Al as anode was deduced [14]. However, the removal of both Cr⁶⁺ and NO₃⁻ increases with an increase in

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the current intensity and time. In most researches, the maximum removal efficiency of NO_3^- was achieved at high pH values [15].

As an efficient experimentation technique, response surface methodology (RSM) is well known in assessing the effect of parameters on treatment results [16-20]. Consequently, RSM has been successfully applied to different processes for optimization of the experimental design.

In the present study, an experimental data of synthetic nitrate wastewater obtained by electrocoagulation with carbon steel electrodes were applied by response surface methodology (RSM) to accomplish relationship between the removal of nitrate as a response and the operating conditions affecting the EC process (operation time and current density) as factor variables at ambient temperature of 17°C and initial pH of 8. In addition, the methodology was utilized to predict the optimum values for these operating variables in order to obtain the maximum value of nitrate removal.

2 Materials and Methods

2.1 Apparatus and Experimental Procedure

Experiments were carried out in previously mentioned batch electrochemical reactor [15] of 1250 ml capacity with carbon steel electrodes in monopolar parallel (MP-P) connection mode. All experiments were achieved under galvanostatic conditions covering wide range of operating conditions. In all stages of the study, the electrical potential difference was applied and measured by voltmeter and the current densities were fixed to be 2, 4, 6, 8 and 10 mA/cm^2 through rheostat connected with ohmmeter installed on circuit. The galvanostatic conditions were covering a range of operating time of 10, 20, 30, 40, 50, 60 and 70 minutes. However, in each run, 1 liter of aqueous nitrate solution was treated by electrocoagulation process. The synthetic aqueous solution was prepared by sodium nitrate and deionized water in 150 mg/l concentration. In all experiments, sodium chloride was added to solution in 200 mg/l concentration as a support electrolyte due to low electrical conductivity. The pH was adjusted to a value of 8 with 1M NaOH . The EC batch experimental runs were performed at ambient temperature (290 K) in the laboratory.

The calculation of nitrate removal efficiency after electrocoagulation treatment was performed using the following formula:

$$\%NR = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

Where $\%NR$ is NO_3^- removal percent, C_0 and C are concentrations of NO_3^- before and after electrocoagulation.

2.2 Data Analysis

The response surface methodology (RSM) was applied to optimize the most two important operating variables; current density and operation time at initial pH of 8 that have a significant influence on the EC process and also to optimize the process efficiency. As the nitrate is the most undesirable pollutants in water and wastewater [1]; the response of nitrate re-

moval percent was chosen to be a function indicator for the effectiveness of electrocoagulation on wastewater treatment. Selection of the experiment factor levels was carried out based on the effective nitrate removal response. The selected operation time factor levels of 10, 20, 30, 40, 50, 60 and 70 min., interferes sequentially with the effective current density factor levels of 2, 4, 6, 8 and 10 mA/cm^2 , were conducted the experimental set. In this sense, 35 runs of experiment plan to be established for the prediction of response.

2.3 Design of Experiments and Modeling

Response surface methodology is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [16, 18, 20]. When process factors satisfy an important assumption that they are measurable, continuous, and controllable by experiments, with negligible errors [21, 22], the present RSM procedure was carried out as follows:

- 1) A series of 16 experiments were designed of reliable measurement for nitrate removal response.
- 2) Mathematical model of the second-order response surface was developed.
- 3) The optimal experimental factor variables producing the maximum response values were determined.

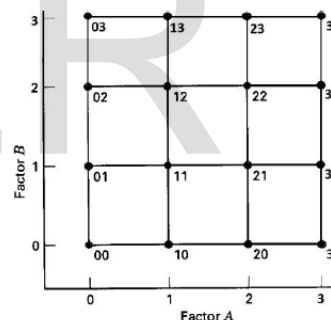


Figure 1. Treatment Combination in 4^2 Design

In a full factorial experiment, responses are measured at all combinations of the experimental factor levels. Factorial designs in which one or more level combinations are excluded are called fractional factorial designs. Fractional factorial designs are useful in factor screening because they reduce down the number of runs to a manageable size; hence a confounding in symmetrical 4^k experiments was taken [19]. The number of experimental runs (N) required for this design is defined as $N = 4^k$, where k is the number of factors. Figure (1) shows the representation of the 4-level factorial design for the optimization of the two variables. A treatment factor A with four levels coded 0, 1, 2, 3 can be represented by two factors F_1 and F_2 each having two levels coded 0, 1. The levels of F_1 and F_2 taken together correspond to the levels of the original factor F. The factors F_1 and F_2 are called pseudo factors. Thus, a 4^k ex-

periment in 4^s blocks of size 4^{k-s} can be represented as a 2^{2k} experiment in 2^{2s} blocks of size $2^{2(k-s)}$.

A quadratic regression model was employed for predicting the optimum conditions. Each response of (Y) can be represented by a mathematical equation that correlates the response surface. The response (Y) can be expressed as polynomial model [16, 20], according to Eq. (2):

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where Y is the predicted response used as a dependent variable, k is the number of independent factors, x_i ($i = 1, 2$) the controlling factors; β_0 the constant coefficient, and β_i , β_{ij} and β_{ii} the coefficients of linear, interaction and quadratic term, respectively and ε is the residual term.

Analysis of variance (ANOVA) was used for graphical analysis of data to obtain the interaction between factors and response. The quality of the fit polynomial model was expressed by the regression coefficients R^2 , and its statistical significance was checked by the Fisher's F-test [16].

Model terms were evaluated by the p-value (probability) with 95% confidence level. The coefficient parameters were estimated using response surface regression analysis employing the software Minitab (version 14); also used to find the residuals, 3-D surface and 2-D contour plots of the response model.

3 Results and discussion

The relationship between the two factor variables and the response for EC process was analyzed using response surface methodology (RSM). The fractional factorial design shown in table-1 allowed the development of mathematical equation, where predicted response Y was assessed as a function of operation time and current density. The optimal factor levels had been defined to fractional factorial design with operation time levels of 10, 30, 50 and 70 minutes and current density levels of 2, 4, 8 and 10 mA/cm². This study involves 35 runs of experiment for response, the design reduces the number of experimental trials; however 16 runs were performed (table-1).

3.1 Statistical Analysis

3.1.1 Scatter plot

The relationship between nitrate removal and the two factor variables is shown in Fig.(3). However, the plot of all operation time- nitrate removal pairs and all current density-nitrate removal pairs as separate groups on the same graph was executed by Figure 2. The plot indicates a gradual increase in nitrate removal with the increases of operation time, while a progressive increase in nitrate removal was achieved as the current density increases.

3.1.2 Normal probability

An extremely useful procedure is to construct a normal probability plot of the residuals. In the analysis of variance, it is usually more effective (and straightforward) to do this with the residuals (the residual is the difference between an

observed value y and its corresponding fitted value \hat{y}), [16]. If the underlying error distribution is normal, this plot will resemble a straight line. In visualizing the straightline, place more emphasis on the central values of the plot than on the extremes.

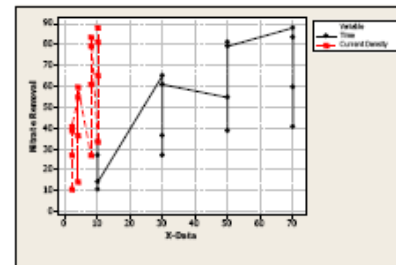


Figure 2. Scatter plot of Nitrate Removal vs. Current density; Time.

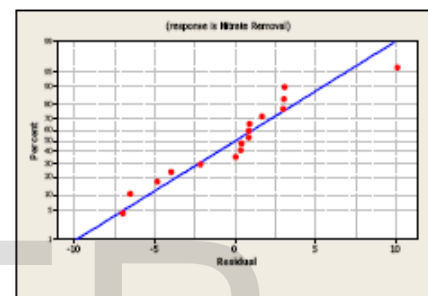


Figure 3. Normal probability of the Residuals

The normal probability plot is shown in Fig.(3). General impression from examining this plot is that the error distribution may be slightly skewed. The probability value (p-value) is less than a predetermined level of significance (α -level) which is the maximum acceptable level of risk for rejecting a true null hypothesis. The nitrate removal residual pattern of normal probability curve has some curvature in the tails as data have fewer than 50 observations.

In graph of Fig.(4) a plot of the residuals versus the order of the data. The row number for each data point is shown on the x-axis. Experiments no. 2, 5, 13 appears to have provided superior residuals. These are t-distribution confidence intervals calculated using the error degrees of freedom and the pooled standard deviation. (square root of the mean square error).

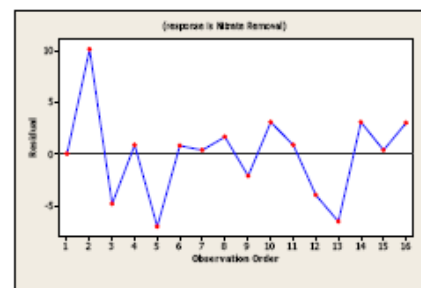


Figure 4. Residuals vs. the Order of Data.

3.1.3 Capability Analysis

A capability analysis (Fig. 5) explains whether the nitrate removal by electrocoagulation is within specification limits and results in acceptable times. The target value of the nitrate removal was taken 49.3% as a mean value between the lower and upper specification limits. The upper specification limit (USL) is 88% and lower specification limit (LSL) is 10.6%. The nitrate removal of electrocoagulation process mean (49.96) falls close to the target (49.3), and both the tails of the distribution fall outside the specification limits.

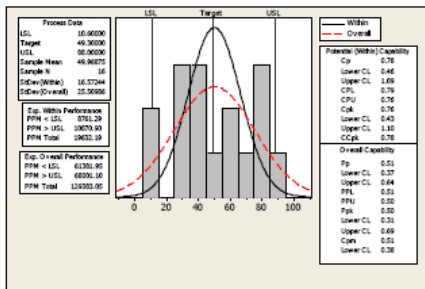


Figure 5. Nitrate Removal Process capability (95% Confidence).

The Cpk index (ratio of the specification tolerance to the natural process variation) indicates whether the nitrate removal will be achieved within the tolerance limits. Here, the Cpk index is only 0.76, indicating that the nitrate removal process is fairly capable, and could be improved by reducing variability and centering the process on the target. Likewise, the PPM total is the number of parts per million characteristic of interest is outside the tolerance limits. This means that approximately 19632 runs out of 1 million runs do not meet the target. Obviously, the analysis indicates that nitrate removal by electrocoagulation process was fairly capable.

3.1.4 Fractional Factorial Design Analyze

The study of the factors affecting the nitrate removal was shown in Fig. (6), the points in the plot are the means of the response variable at the various levels of each factor, with a reference line drawn at the grand mean of the response data. Use the main effects plot for comparing magnitudes of main effects. The main effects of operation time and current density, all have significant effect on nitrate removal. As it can be seen from Fig.(6), mean nitrate removal increases in polynomial manner by increasing operation time ($R^2=0.999$), as well by increasing current density ($R^2=0.997$) within the experimental range considered. The two above mentioned effects can be contributed to enhanced nitrate removal by electrocoagulation.

Fig. (7) shows the interaction effect of operation time and current density on nitrate removal. Interactions plot creates a single interaction plot for two factors. An interactions plot is a plot of means for each level of a factor with the level of a second factor held constant. Interaction is present when the response at a factor level depends upon the levels of other factors. The greater the departure of the lines from the parallel state, the higher the degree of interaction. Consequently, the

interaction of the above mentioned two factors on nitrate removal shows that there are significant interactions between factors on the response as confirm with response equation (Eq.3).

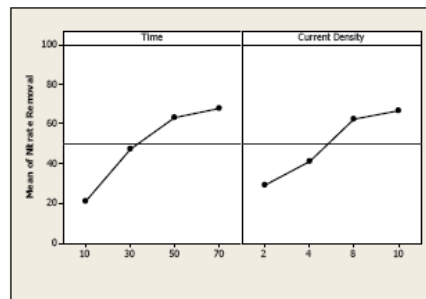


Figure 6. Main Effect for Nitrate Removal

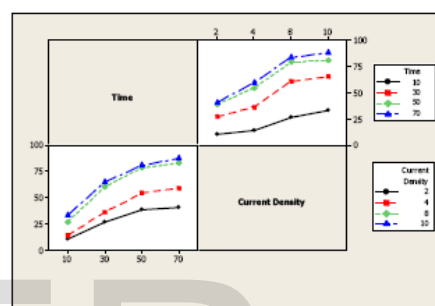


Figure 7. Factors Interaction for Nitrate Removal.

3.2 Model Fitting

Experimental response data were used to conduct a model using response surface methodology (RSM). The response of nitrate removal was correlated with the two factor variables (operation time and current density). To develop a response surface regression model, a general polynomial model (Eq.2) was applied to the experimental observations of the response (nitrate removal percent) and a quadratic regression model was obtained, as shown in Eq. (3):

$$\% \text{ Nitrate Removal} = - 32.5 + 1.77 T + 9.23 C - 0.0147 T^2 - 0.463 C^2 + 0.0337 TC \quad (3)$$

$$R^2 = 0.9920, R^2_{(pred)} = 0.9913, R^2_{(adj)} = 0.9870$$

Where: T; Time factor, C; current density factor and TC; interaction factor.

The value of the factor variables, the experimental data and the predicted data for nitrate removal response for each coded experiment are presented in Table (1). The results obtained were then analyzed by ANOVA to assess the "goodness of fit". The ANOVA analyzed has been tested for full quadratic equations designed values and gives an insight into the linear, quadratic and interaction effects of the factors. The p-value is used as a tool to check the significance of each factor. It was found that the factors with serially major effect on nitrate removal were the linear effect of operation time and current density factors, having p-values of 0.000, respectively, followed by operation time quadratic factor having p-value of 0.000 and current density quadratic factor with p-value of

0.0010. Finally the (operation time × current density) interaction factor p-value of 0.011. Accordingly, the model gives a best fit for linear and quadratic effects with all p-values.

Table (1) Data Matrix and Fractional Factorial Design Results

Run No.	Code No.	Time (min.)	Current Density (mA/cm ²)	Nitrate Removal Percent	
				Exp.	Pred.
1	00	50	4	54.6	55.69
2	01	10	2	10.6	1.05
3	02	10	10	33.3	33.12
4	02	30	10	65.1	63.57
5	10	10	8	26.8	30.66
6	11	50	10	81.2	82.28
7	12	30	2	27.0	26.10
8	13	10	4	14.0	14.62
9	20	30	4	36.3	41.02
10	21	70	10	88.0	89.25
11	22	30	8	60.8	59.76
12	23	50	2	38.8	39.41
13	30	70	2	40.8	40.99
14	31	50	8	79.1	77.12
15	32	70	4	59.5	58.61
16	33	70	8	83.6	82.75

Table(2) illustrates the quadratic model in terms of statistical parameters; standard error, T-test and probability value. Data given in table-2 demonstrates that the model was significant at the 95% confidence level since p-values were less than 0.05. The ANOVA implies that the model was not mainly influenced by operation time and current density in a linear manner, but also influenced by the factors in a different quadratic manner. These analyses were done by means of F-test 'F' and T-test 'T'. However, statistical tests can be used to determine the significance of the regression coefficients of the parameters. In general, the larger the magnitude of T and smaller the value of p, the more significant is the corresponding coefficient term.

Table (2) Estimation of the second-order response surface factors*

Predictor	Nitrate Removal Percent		
	SE	T	P
Constant	6.0050	-5.410	0.000
Time	0.1731	0.240	0.000
Current Density	1.4440	6.390	0.000
Time ²	0.0016	-8.660	0.000
Current Density ²	0.1068	-4.330	0.001
Time × Current Density	0.0107	3.140	0.011

*Note: SE; standard error, T; T-test, P; probability-value

3.3 Validation of Model

The response surface model was developed in this study with predicted value of R^2 higher than 99% for nitrate

removal. Furthermore, an R^2_{adj} close to the R^2 values insures a satisfactory adjustment of the quadratic model to the experimental data. It is usually necessary to check the fitted model to ensure it provides an adequate approximation to the real system. The R^2 coefficient gives the proportion of the total variation in the response predicated by the model, indicating ratio of sum of squares due to regression (SSR) to total sum of squares (SST) [16, 19].

In this study a high regression coefficient (R^2) value was predicted, that gives a reasonable conformity with the adjusted R^2 and ensure a satisfactory agreement of the quadratic model to the experimental data. Graphical method can be used to validate models and also characterizes the nature of residuals of the models. The normal probability plot is generally used to check the normal distribution of the residuals as shown in Figs. (8).

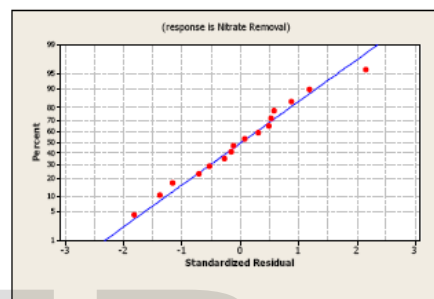


Figure 8. Normal probability of the Residuals

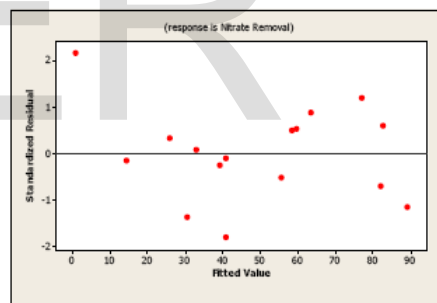


Figure 9. Residuals vs. the Order of Data.

If the underlying error distribution is normal, this plot will resemble a straight line [16]. In visualizing the straightline, place more emphasis on the central values of the plot than on the extremes. The normal probability plot as shown in Fig.(8) shows that the error distribution may be slightly skewed. If the model is correct and if the assumptions are satisfied, the residuals should be structureless; they should be unrelated to any other variable including the predicted response [16, 18, 22]. A simple check is to plot the residuals versus the fitted values \hat{Y} ; these plots should not reveal any obvious pattern. The plot of residuals versus the fitted nitrate removal response is shown in Fig. (9). The pattern indicates more or less than or equal to its value, along a fitted distribution line (the horizontal straightline) and no unusual structure is apparent.

3.4 Analysis of Variance (ANOVA)

Analysis of variance results of quadratic model are presented in Table-3 that indicates the statistical parameters of

regression, residual error and lack of fit and pure error. The p-value of ANOVA table-2, indicates that the relationship between the response and the factors is statistically significant at a level of $\alpha=0.05$ (maximum acceptable level of risk for rejecting a true null hypothesis) [16]. The lack of fit F-test describes the variation in the data around the fitted model. If the model does not fit the data well, the lack of fit will be significant. The high p-value for lack of fit (>0.05) equals 0.084 for nitrate removal shows that the F-statistic was insignificant, implying significant model correlation between the factor variables and process response. Moreover, the ANOVA on this model, as shown in Table-3, demonstrates that the model was highly significant, as evident from the 0.000 p-value in the regression. Accordingly eq.(3) presents high lack of fit F-values of 105.54, implies the significance for the removal of nitrate.

Table (3) Analysis of Variance (ANOVA) of Nitrate Removal

Source	DF	SS	Mean SS	F-value	P-value
Regression	5	369604	73921	234.31	0.000
Residual Error	10	3155	315		
Lack of fit	5	3155	315	105.54	0.084
Total	15	372759			

Note: DF: degree of freedom, SS: the sum of the squares, F-value, Fisher's test, p-value: probability value.

3.5 Optimization Analysis

3.5.1 2D and 3D Plots

The result indicates that all linear and quadratic factors were significant in determining the response value of nitrate removal and also significant in the statistical. The response surface and contour plots are the graphical representation of the regression equation, used to visualize the relationship between the response and experimental levels of each factor.

Fig.(10) shows the 3D response surface plot of nitrate removal model, indicating the response of nitrate removal on z-axis display and the factor variables; current density and operation time on y and x axis's, respectively. The resulted data are represented by irregular surface with slightly increases highest plate zone at right end of plate. This trend was clearly viewed in Fig. (10).

Fig.(11) shows the 2D contour plot of nitrate removal model. In a contour plot, the values for two factor variables are represented on the y-time and x-current density axes, and the value for a response nitrate removal is represented by homogeneous shaded zones, called contours. This plot presents the overall distribution of electrocoagulation process. As shown, increased nitrate removal was observed with increasing operation time and current density values. However, an increase in both factors result an optimum zone for effective nitrate removal within/over a dark shade.

3.5.2 Canonical Analysis

Canonical analysis is used to investigate the overall shape of the curvature and determine the stationary point is a maximal, minimal or saddle point [19]. The eigenvalues and eigenvectors indicate the shape of the response surface. Positive eigenvalues direct an upwards curvature, and

negative eigenvalues direct a downward curvature. Therefore, all positive eigenvalue indicate an estimate stationary is a minimum, and all positive eigenvalue indicate a maximum and mixture of positive and negative eigenvalues indicate a saddlepoint.

A canonical analysis of the model resulted in eigenvalues of λ_{11} and λ_{22} , which were both negative, such as $\lambda_{11} = -0.0141$ and $\lambda_{22} = -0.4636$, indicating that the stationary point was a single point of maximum response. The model predicted a maximum of 92.22% nitrate removal with an operation time of 74.7 min. and current density of 12.7mA/cm².

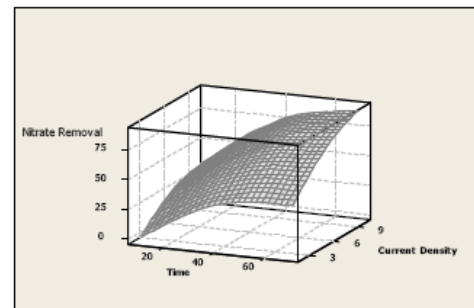


Figure 10. Estimated Removal with Model.

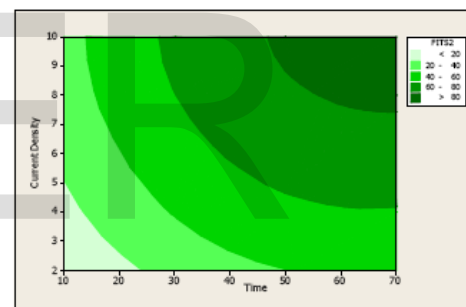


Figure 11. Estimated Removal with Model.

4 Conclusion

A response surface methodology (RSM) has been applied to optimize an experimental data of synthetic nitrate wastewater treatment by electrocoagulation process. A factorial design was performed for adequate and reliable measurements, and mathematical quadratic polynomial model of response surface was developed for nitrate removal. From statistical analyses, it was found that the operation time and current density at initial pH of 8 and ambient temperature of 17°C have significant effects on nitrate removal by electrocoagulation process. The response surface model was developed in this study with value of correlation coefficient R^2 equals 0.992 for nitrate removal. Moreover, the ANOVA on the model demonstrates that the model was highly significant, as evident from the very low probability value of regressions. Furthermore, the model was presented as 3-D response surface and 2-D contour graphs to investigate the optimum zone of nitrate removal, therefore, the regression model explained the removal efficiency was optimized to find maximum level. Accordingly, at initial pH of 8,

the maximum response of 92.22 was predicted for nitrate removal at operation time and current density of 74.7 min. and 12.7mA/cm², respectively.

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